Thermodynamic and Magnetic Properties of Pd$_{0.93}$Ag$_{0.07}$ Hydride

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Thermodynamic and magnetic properties of the Pd$_{0.93}$Ag$_{0.07}$ hydrides were measured. The isotherms of Pd$_{0.93}$Ag$_{0.07}$ - H and - D systems in the temperature range 373–523 K showed the plateau regions to be within 0.05°C. From an investigation of the thermodynamic isotope effect for the formation and decomposition of hydride, the enthalpy changes, $\Delta H_{f}^{\text{H}}$ or $\Delta H_{f}^{\text{D}}$, for desorption of hydrogen and deuterium were evaluated to be 43.0 kJ/mol$_{\text{H}_2}$ and 36.4 kJ/mol$_{\text{D}_2}$, respectively. It was observed that the magnetization of Pd$_{0.93}$Ag$_{0.07}$H$_x$ at ambient temperature increased with increasing magnetic field. Since the magnetization was not saturated up to 7 T, it can be concluded that the temperature range 373–523 K showed the plateau regions to be within 0.05°C. The magnetic susceptibility of Pd$_{0.93}$Ag$_{0.07}$H$_x$ progressively decreased with increasing hydrogen content and vanished at [H]/[Pd$_{0.93}$Ag$_{0.07}$] = 0.4. The disappearance of the susceptibility coincided with the termination of the plateau region of the isotherms. This fact can be explained by the rigid band model, according to which the vacant part of d-band of Pd$_{0.93}$Ag$_{0.07}$ can accept electrons from absorbed hydrogen atoms. [doi:10.2320/matertrans.MRA2007150]

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1. Introduction

Palladium and its alloys with transition metals have attracted considerable interest in applications for hydrogen purification, isotope separation, material coating, and so on. Especially, palladium rich alloys are promising column materials for a newly developed gas chromatography for hydrogen isotope separation owing to a large isotope effect for hydrogen absorption.$^{1-4}$ The gas chromatographic system working near ambient temperatures can separate each hydrogen isotope from a mixture of hydrogen isotopes without using any replacement gas.

The thermodynamic properties of hydrogen absorbing alloys constitute one important pieces of information for practical developments. From this viewpoint, the formations of hydrides by palladium and its alloys have been extensively studied experimentally as well as theoretically. Griessen and Driessen have shown that the heat of hydride formation can be evaluated from the electronic structures of metals.$^5$ The present authors have also proposed a semi-empirical method to estimate the heat of hydrogen absorption from solid solutions of Pd-TM by accounting Fermi energy of alloys,$^6$ where TM shows for transition metal. However, these estimation methods$^{5,6}$ can only take the electronic structures of pure elements into account, because of the difficulties in calculating electronic structures of alloys. Papaconstantopoulos et al. reports in detail the electronic structure of the palladium-hydrogen system.$^7,8$ According to them, the s-orbital of hydrogen absorbed in palladium lies below the d-band of palladium, and hence the formation of a hydride causes uplifting of the Fermi level and a change in density of states at the Fermi level.

To the author’s knowledge, however, theoretical calculations of electronic structures of Pd-TM alloys and those hydrides have not been investigated in detail, except for Pd-rich solid solutions of Pd-Ag$^{9,10}$ or Pd-Pt.$^{11}$ The information of electronic structures of alloys and its hydrides can be experimentally obtained by photoelectron spectroscopy or other techniques. But palladium and palladium alloy hydrides have equilibrium pressures that are too high at room temperature to allow their analysis in instruments requiring ultra high vacuum conditions. Measurements of the magnetic susceptibility of metal hydrides are useful for obtaining information on the change in the electronic structure with absorbing hydrogen,$^{12,13}$ because the susceptibility of a paramagnetic material is proportional to the density of states at Fermi level.$^{14}$ Such a change in susceptibility with absorbing hydrogen has been reported for palladium by several investigators.$^{8,15,16}$ The measurements can be carried out under a hydrogen atmosphere, although the Fermi level itself can not be determined by the susceptibility measurement.

Among the palladium alloys, the one with silver are attractive from viewpoint of the changes in electronic structure with hydrogen absorption. An absorbed hydrogen atom in palladium donates an electron to the unfilled part of the palladium d-band. On the other hand, a silver atom added to palladium can also give an electron to the palladium d-band, because silver has an excess electron in comparison to palladium.$^{13}$ According to the electronic structure calculations for the Pd-Ag system,$^9,10$ the d-band of silver lies below the d-band of palladium. It is similar to the electronic structure of Pd hydride.$^7,8$ Both alloyed silver and absorbed hydrogen in palladium contribute their electrons to the unfilled part of the d-band in palladium. Sänger and Voitländers$^7$ have reported that Pd hydride and Pd-Ag solid solution give similar behavior with respect to change of magnetic susceptibility at 611 K. The measurements of the

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The present paper describes thermodynamic and magnetic properties of Pd$_{0.93}$Ag$_{0.07}$ hydride. The magnetic susceptibility of Pd-Ag hydride as well as of Pd-Ag itself should provide further information on the relationship between physicochemical properties and electronic structures of metal hydrides.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (Ag/at%)</th>
<th>Weight Before Melting (g)</th>
<th>Weight After Melting (g)</th>
<th>Assay Composition (Ag/at%)</th>
<th>Lattice Parameter (10$^{-10}$ m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{0.93}$Ag$</em>{0.07}$</td>
<td>8.099</td>
<td>15.0011</td>
<td>14.8751</td>
<td>7.12</td>
<td>3.9023</td>
</tr>
</tbody>
</table>

![X-ray diffraction pattern of Pd$_{0.93}$Ag$_{0.07}$ powder.](image)

### 2. Experimental

#### 2.1 Preparation of Pd-Ag alloy

The Pd-Ag alloy was prepared by argon-arc melting. Source metals were purchased from Tanaka Kikinzoku Kougyou K. K. and Koujundo Chemical Lab. Co. Their purities were guaranteed to be Pd > 99.9% and Ag > 99.9%. The source metals were weighed out to make a mixture of 92 at% of palladium and 8 at% of silver as shown in Table 1. The mixture was melted several times in an argon arc melting furnace. The Pd-Ag ingot prepared was homogenized at 1073 K for 10 hours under vacuum. According to X-ray fluorescence measurements using a Philips PW 2300 spectrometer equipped with a UniQuant 3.0 program package, the content of silver in the ingot was 7.1 at%. This indicates that approximately 1 at% of silver evaporated during the preparation. Powder sample required for the measurement of isothermal pressure-composition curves (hereafter denotes as p-c curves) were prepared by filing the ingot. The X-ray diffraction pattern of the Pd-Ag powder using the Cu-K$_\alpha$ line is shown in Fig. 1. The lattice constant of the prepared Pd-Ag was determined to be 3.9023 × 10$^{-10}$ m. It agrees well with the value reported for Pd$_{0.93}$Ag$_{0.07}$, verifying the composition of the Pd$_{0.93}$Ag$_{0.07}$ envisaged material.

#### 2.2 Measurement of pressure-composition curves

The p-c curves for hydrogen absorption and desorption were measured by means of a volumetric method. The device could automatically determine the equilibrium pressure within the pressure range $1 \times 10^3$ to $1 \times 10^6$ Pa. For a measurement 1 g of the Pd$_{0.93}$Ag$_{0.07}$ powder was placed into the sample tube, where the temperature was measured with an alumel-chromel thermocouple fixed to the outer surface of the sample tube. H$_2$ and D$_2$ gases from Nippon Sanso Corporation were guaranteed to have purities better than 99,9999% and 99.6%, respectively. These gases were used without further purification. Prior to an isotherm measurement, the sample in the device was first activated by vacuum heating at 523 K for 2 hours, and then by five consecutive hydrogen absorption and desorption cycles at room temperature to stabilize the sample and to confirm the reproducibility of the measurements. Subsequently, the sample was heated up to 523 K for removing residual hydrogen trapped in the sample.

The p-c curves for absorption and desorption at a given temperature were continuously measured. After these measurements, the sample was heated at 523 K for 2 hours under vacuum to restart the measurements at another temperature. Further details of the measurements can be found in a previous publication.

#### 2.3 Measurement of magnetization

The magnetic properties of Pd$_{0.93}$Ag$_{0.07}$ hydrides were determined under a hydrogen atmosphere in a closed vessel. The vessel was specially designed for magnetization measurements of metal hydrides under a hydrogen atmosphere. The vessel was made of a copper tube and contained glass beads. Details of the vessel have been described in a previous paper. A columnar fragment of Pd$_{0.93}$Ag$_{0.07}$ 0.1 g in weight was introduced into the copper tube and fixed there with glass beads. To activate the Pd$_{0.93}$Ag$_{0.07}$, the vessel was attached to a high vacuum system and evacuated to less than $1 \times 10^{-5}$ Pa. Activation was carried out by heating the sample at 473 K for 2 hours under vacuum. Subsequently the sample was cooled down to ambient temperature and a given amount of hydrogen was introduced into the vessel. After the hydrogen absorption attained equilibrium, the amount of absorbed hydrogen was determined volumetrically and the vessel was pinched at its upper part to isolate it from the vacuum system. By this procedure the sample in the vessel could be kept under the hydrogen atmosphere during magnetization measurements. The magnetization of Pd$_{0.93}$Ag$_{0.07}$H$_x$ was measured by using a Quantum Design MPMS 7 equipped with a SQUID amplifier. The apparatus could generate a strong magnetic field of up to 7 T. The isolated vessel was fixed to the sample holder of the apparatus and the magnetization of the sample was measured at ambient temperature.

### 3. Results and Discussion

#### 3.1 Thermodynamic property

Figures 2 and 3 show p-c curves for protium and deuterium, respectively. The abscissa shows the atomic fraction of the amount of absorbed hydrogen by Pd$_{0.93}$Ag$_{0.07}$. 

![Graph of p-c curves for protium and deuterium.](image)
All the p-c curves of Pd$_{0.93}$Ag$_{0.07}$Q$_x$ have a clear plateau in the concentration range $0.05 < [\text{H or D}] / [\text{Pd}_{0.93}\text{Ag}_{0.07}] < 0.4$ at 373 K, that corresponds to the two phase $\alpha + \beta$ region. The width of plateau becomes smaller with increasing temperature. This feature agrees with previous observations reported for pure palladium. The plateau region of Pd$_{0.93}$Ag$_{0.07}$ at a given temperature, however, was narrower than that of Pd. According to the former reports, the width of the Pd-Ag-hydrogen plateaus decreases with increasing silver content.

The hysteresis of the isotherms; i.e., absorption equilibrium pressures higher than those for desorption, was found to be moderate. For instance, the equilibrium pressures for absorption and desorption for Pd$_{0.93}$Ag$_{0.07}$H$_{0.01}$, at 443 K were found to be 76 and 74 kPa, respectively. It is seen in Figs. 2 and 3 that the equilibrium pressures with the deuterium system are noticeably higher than those with protium at a given temperature. To better understand the hysteresis and isotope effect, some isotherms were plotted as shown in Fig. 4, where the isotherms of protium and deuterium at 413 and 473 K were shown. It is clear from the figure that the hysteresis effect is rather minor. On the other hand, the isotope effect is significantly large. For instance, the ratio of protium desorption pressure in the plateau region to that of deuterium was found to be about 3.7 at 413 K and 3.1 at 473 K (see Fig. 4). The isotope effect for the equilibrium pressure decreased with increasing temperature. This feature was the same as reported for other Pd alloys, but magnitude of the isotope effect for the present alloy was

Fig. 2 Isothermal pressure–composition curves of the Pd$_{0.93}$Ag$_{0.07}$–H system.

Fig. 3 Isothermal pressure–composition curves of the Pd$_{0.93}$Ag$_{0.07}$–D system.

Fig. 4 Comparison between the Pd$_{0.93}$Ag$_{0.07}$–H and –D systems.
for both protium and deuterium. The lines for deuterium lie
shown in Fig. 5. The van’t Hoff plots yielded straight lines
slightly larger than that for palladium. This suggests that
the potential curve for hydrogen in the octahedral site, which
is the site occupied by hydrogen in the present alloy, is
slightly gentler than that of palladium. A gradual potential
curve of the octahedral site generally gives rise to a large
isotope effect on hydrogen absorption. In fact, it has been
reported that the volume of the octahedral site in Pd-Ag
alloys is larger than that in palladium.

The thermodynamic properties of Pd$_{0.93}$Ag$_{0.07}$ hydride and
deuteride were evaluated at a hydrogen concentration of [H
or D]/[Pd$_{0.93}$Ag$_{0.07}$] = 0.2 from van’t Hoff plots such as
shown in Fig. 5. The van’t Hoff plots yielded straight lines
for both protium and deuterium. The lines for deuterium lie
above the respective lines for protium and the difference
between absorption and desorption pressure increases with
decreasing temperature. The enthalpy and entropy changes
obtained are summarized in Table 2 together with data from
the literature. The enthalpy change for Pd$_{0.93}$Ag$_{0.07}$
indicated that this alloy forms hydride, that is more stable
than those of palladium. According to ab initio calculations
by Ke and Kramer, the hydrogen atom in the octahedral
site of Pd$_{0.75}$Ag$_{0.25}$, which consists of six palladium atoms
neighbored by an octahedral site containing two silver atoms,
becomes more stable than that of PdH$_{0.25}$. The energy for
hydrogen absorption per H atom in Pd$_{0.75}$Ag$_{0.25}$H$_{0.25}$ atom
i.e. 61.8 kJ mol$^{-1}$H$_2$ (0.32 eV) is larger than that in PdH$_{0.25}$
i.e. 32.8 kJ mol$^{-1}$H$_2$ (0.17 eV). The calculated energy for
PdH$_{0.25}$ is comparable to the enthalpy of formation of
PdH$_{0.20}$ obtained by p-c curves (see Table 2). If the
calculated energy can be assumed to be proportional to the
silver content, Pd$_{1-x}$Ag$_x$ in the range 0 < x < 0.25, the
energy in Pd$_{0.93}$Ag$_{0.07}$H$_{0.25}$ is evaluated to be 40.9
kJ mol$^{-1}$H$_2$. The evaluated energy is almost the same as
the enthalpy obtained for Pd$_{0.93}$Ag$_{0.07}$H$_{0.2}$. On the other hand, the
entropy changes were comparable to those palladium.

In summary, the differences between the enthalpy change
for protium and for deuterium were 5.4 kJ/mol for the
absorption reaction and 6.6 kJ/mol for the desorption reaction.
These differences were slightly larger than those for palladium. As already mentioned, this suggests that the
potential curve for hydrogen in the octahedral site in Pd$_{0.93}$Ag$_{0.07}$ is less steep than that of palladium as described
above.

### 3.2 Magnetic property

Figure 6 shows the dependence of the magnetization of
Pd$_{0.93}$Ag$_{0.07}$ hydride on application of a magnetic field. The
ordinate represents the magnetization, and the abscissa
the magnetic field. As seen, the magnetization of Pd$_{0.93}$Ag$_{0.07}$
and of its hydride increases linearly with increasing magnetic
field. A saturation of the magnetization was not observed at
magnetic fields below 7 T. It indicates that Pd$_{0.93}$Ag$_{0.07}$ and
its hydride are paramagnetic. On the other hand, the
magnetization decreased with increasing hydrogen content
in the alloy, which is in good agreement with measurement
carried out with palladium and Pd$_{0.92}$Pt$_{0.08}$.16)

### Table 2 Enthalpy and entropy changes in hydride formation and decomposition for Pd$_{0.93}$Ag$_{0.07}$.

<table>
<thead>
<tr>
<th></th>
<th>Absorption</th>
<th>Desorption</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_{\alpha \rightarrow \beta}$/kJ mol$^{-1}$</td>
<td>$\Delta S_{\alpha \rightarrow \beta}$/J K$^{-1}$ mol$^{-1}$</td>
<td>$\Delta H_{\beta \rightarrow \alpha}$/kJ mol$^{-1}$</td>
</tr>
<tr>
<td>PdH$_{0.2}$</td>
<td>-33.1</td>
<td>-82.2</td>
<td>40.2</td>
</tr>
<tr>
<td>PdD$_{0.2}$</td>
<td>-29.8</td>
<td>-83.2</td>
<td>35.1</td>
</tr>
<tr>
<td>PdH</td>
<td>-39.0</td>
<td></td>
<td>35.4</td>
</tr>
<tr>
<td>PdD</td>
<td>-32.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdT</td>
<td>-38.7</td>
<td>-85.4</td>
<td>43.0</td>
</tr>
<tr>
<td>Pd$<em>{0.90}$Ag$</em>{0.10}$H$_{0.2}$</td>
<td>-33.3</td>
<td>-83.3</td>
<td>36.4</td>
</tr>
<tr>
<td>Pd$<em>{0.90}$Ag$</em>{0.10}$D$_{0.2}$</td>
<td></td>
<td></td>
<td>42.4</td>
</tr>
<tr>
<td>Pd$<em>{0.90}$Ag$</em>{0.10}$H</td>
<td></td>
<td></td>
<td>38.9</td>
</tr>
<tr>
<td>Pd$<em>{0.90}$Ag$</em>{0.10}$D</td>
<td></td>
<td></td>
<td>35.8</td>
</tr>
</tbody>
</table>

Fig. 5 Equilibrium pressure of the Pd$_{0.93}$Ag$_{0.07}$ – H and – D systems at [Q
(Q = H or D)/[Pd$_{0.93}$Ag$_{0.07}$] = 0.2 as a function of reciprocal temperature.
alloys, the d-band of silver lies below that of Pd and the d-band of silver addition is supported by the calculation of the electronic structure of Pd-Ag alloys. The susceptibility of Pd with silver addition is supported by the calculation of the density of states at Fermi level of Pd-Ag alloys. With increasing silver content, the density of states at Fermi level decreases. This is in line with the observation that the magnetic susceptibility of Pd<sub>0.93</sub>Ag<sub>0.07</sub> is smaller than that of palladium as shown in Fig. 7. The electrons from hydrogen atoms absorbed also occupy the unfilled part of the d-band. Consequently, the Fermi level is lifted up by the absorption of hydrogen, but the extent of the lift-up should be gradual because of the high density of states of the d-band. It also causes to decrease the density of states at Fermi level, because the Fermi level of palladium lies just above the peak of density of states in the d-band. Therefore the susceptibility decreases with increasing hydrogen content as seen in Fig. 7. On the other hand, the gradual lift-up of the Fermi level means that the chemical potential of hydrogen in the Pd-Ag alloy gradually increases while electrons from absorbed hydrogen atoms occupy the unfilled part of d-band. This change in Fermi level is reflected by the plateau region in the p-c curve. After the d-band is completely filled, electrons from absorbed hydrogen atoms must enter into the unfilled part of sp-band having lower density of states, bringing about a significant elevation of the Fermi level. Thus, the susceptibility is expected to become zero with progressing hydrogen concentration owing to low density of states of sp-band and the raising of the chemical potential of hydrogen atoms in Pd-Ag. In other words, the equilibrium pressure of hydrogen suddenly increases after the d-band is filled as seen in Figs. 2 and 3. Consequently, the relationship between the width of the plateau region and the susceptibility is explained by fraction of the unfilled part of d-band of the Pd-Ag alloy. The decrease in susceptibility rate with the amount of hydrogen absorbing in Pd<sub>0.93</sub>Ag<sub>0.07</sub> was almost the same as for Pd and Pd<sub>0.92</sub>Pt<sub>0.08</sub> (see Fig. 7). If the shape of unfilled part of d-band of Pd<sub>0.93</sub>Ag<sub>0.07</sub> can be assumed similar to that of palladium, the rate of susceptibility reduction of Pd<sub>0.93</sub>Ag<sub>0.07</sub> with hydrogen absorption is expected to be similar to that of Pd. It should be mentioned here that the rate of susceptibility reduction of palladium strongly depends on temperature. This phenomenon suggests that the isotherms of magnetic susceptibility can be applied to determine the terminal points of the plateau region in p-c curves.
4. Conclusions

The p-c curves of Pd$_{0.93}$Ag$_{0.07}$ in the temperature range 373–523 K showed plateau regions from 0.05 < [Q]/[Pd$_{0.93}$Ag$_{0.07}$] < 0.4. The equilibrium pressure of Pd$_{0.93}$Ag$_{0.07}$ at a given temperature was found to be lower than that of Pd. This observation is supported by theoretical calculations of Ke and Kramer.\textsuperscript{27} A marked isotope effect for the absorption of protium and deuterium by Pd$_{0.93}$Ag$_{0.07}$ was clearly observed; the isotope effect was slightly larger than that for Pd. This indicates that the potential curve of octahedral site is less pronounced than that for palladium.

The magnetic susceptibility of Pd$_{0.93}$Ag$_{0.07}$\textsubscript{H$_x$} obtained under a hydrogen atmosphere at ambient temperature confirms the influence of the absorption of hydrogen on the electronic structure. The magnetization of Pd$_{0.93}$Ag$_{0.07}$ and of its hydride increased with increasing magnetic field, indicating that Pd$_{0.93}$Ag$_{0.07}$ and its hydride are paramagnetic. The magnetic susceptibility of Pd$_{0.93}$Ag$_{0.07}$\textsubscript{H$_x$} at 5 T was found to decrease with increasing hydrogen content. The susceptibility reached almost zero at a [H]/[Pd$_{0.93}$Ag$_{0.07}$] ratio of 0.4. It corresponded well with the end of the plateau region. This feature is explained by the rigid band model. According to this model, the unfilled part of d-band corresponds with the density of state at Fermi level decreases with increasing hydrogen content. The Fermi level of Pd$_{0.93}$Ag$_{0.07}$ is lifted up with absorbing hydrogen. Simultaneously, the density of state at Fermi level decreases with lifting up the Fermi level.

REFERENCES