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論　文

Pd–Ag–Rh 三元系合金における磁化率と水素吸収量の相関

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Relation between the magnetic susceptibility and the amount of absorbed hydrogen for the Pd–Ag–Rh ternary alloy

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Abstract

The magnetic susceptibility and equilibrium pressure of a Pd─Ag─Rh ternary alloy and hydrogen system were simultaneously measured, and the relationship between the magnetic susceptibility and the amount of absorbed hydrogen was investigated. The magnetic susceptibility linearly decreased to a value approaching zero with increasing hydrogen content. A high hydrogen content with a magnetic susceptibility close to zero is consistent with a hydride phase. This behavior is similar to that of Pd─Ag or Pd─Rh binary alloys and hydrogen systems, suggesting that the amount of hydrogen absorbed by the Pd─Ag─Rh ternary alloy is correlated with its electronic band structure, as in the case of the Pd-binary alloys.

1. Introduction

Palladium metal is well-known as a hydrogen storage material, and various

applications related to hydrogen usage have been developed including hydrogen sensing and hydrogen purification systems. Pd-based binary alloys that contain a second transition metal have been designed to adjust the hydrogen absorption properties, and systematic studies on Pd-based binary alloys and hydrogen systems have been performed to obtain the relation between the properties and the alloying elements [1].

The amount of hydrogen absorption in metallic Pd depends on its electronic structure; the number of unoccupied d-states is correlated with the amount of absorbed hydrogen [2]. Each absorbed hydrogen atom provides an electron to Pd, thereby occupying the unoccupied d-states of Pd. When the unoccupied d-states of Pd are completely filled with electrons by the absorption of hydrogen, Pd hydride is formed, which cannot undergo further hydrogen absorption.

Alloying Pd with a transition metal is an effective way to control the number of unoccupied d-states in Pd; the amount of absorbed hydrogen is reduced with the supply of electrons from the transition metal to Pd. To determine the relation between the amount of absorbed hydrogen and the unoccupied d-states in a Pd alloy, Pd–Ag, and Pd–Rh were systematically investigated [3]. Because alloying Pd with Ag or Rh corresponds to addition or removal of electrons from Pd, respectively, the number of unoccupied d-states of Pd can be controlled without deformation of the electronic band structure of Pd. Magnetic susceptibility measurements of a Pd alloy with various hydrogen contents can be used to study its electronic structure. The magnetic susceptibility of a Pauli paramagnet is proportional to the density of states at the Fermi level [4]. If the electronic band structure of a Pd alloy is regarded as the same as that of Pd metal, the change in the unoccupied d-states via alloying and the degree of filling of these d-states by hydrogen absorption can be estimated from magnetic susceptibility measurements. We previously investigated the magnetic susceptibility of Pd–Ag and Pd–Rh binary alloys with various hydrogen contents and found that the

amount of absorbed hydrogen was correlated with the amount of doping electron by alloying, namely the amount of substituting elements [3].

The hydrogen absorption properties of Pd-based ternary alloys have not been extensively studied; therefore a lack of the information about the effect of a third element on the hydrogen absorption properties still exists. In the present study, we measured the magnetic susceptibility and the hydrogen absorption isotherm of a Pd–Ag–Rh alloy with various hydrogen contents to verify that the model applied to Pd-based binary alloys can be extended to analyze Pd-based ternary alloys.

2. Experimental

The $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ ternary alloy was used as prepared in previous study [5]. Predetermined amounts of Pd, Ag, and Rh metals were weighed out; then, the mixture was melted in an arc melting furnace [5]. The obtained ingot was grounded into powder using a file, and a part of the powder was subjected to X-ray diffraction (XRD) analysis. Then 1 g of powder was introduced into a quartz cell connected to the pressure–composition isotherm measurement system. The quartz cell was evacuated down to 1.0×10^{-4} Pa; future, the powder alloy was heated at 523 K for 2 h. The magnetic susceptibility of the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ powder was measured via the induced method, which was described in detail in previous papers [3,6].

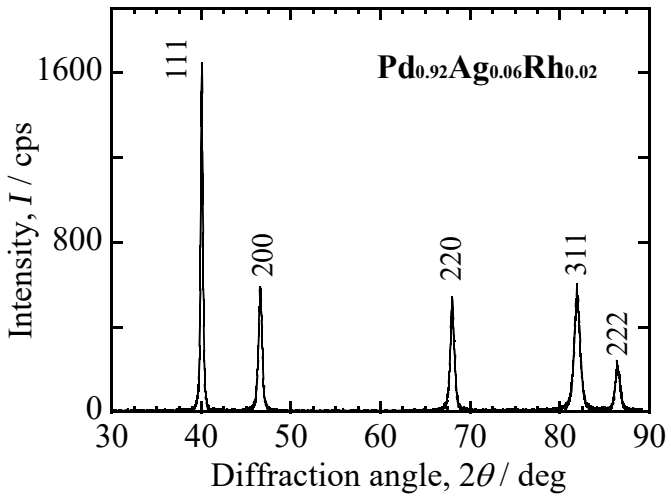

Figure 1 Powder X-ray diffraction pattern of $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ ternary alloy.

3. Results

Figure 1 shows the XRD

pattern of the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ alloy. The XRD data was indexed using a face-centered cubic structure and no unknown diffraction lines were observed. The lattice constant of the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ alloy was calculated to be 0.3900 nm. If the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ ternary alloy was regarded as a binary alloy of $Pd_{0.92}Ag_{0.08}$ and $Pd_{0.92}Rh_{0.08}$, the lattice constant of $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ expected from Vegard's law would have been 0.3898 nm, which was consistent with the measured value. These results indicated that a homogeneous $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ ternary alloy with a face-centered cubic structure was obtained.

Figure 2 shows the dependence of both the magnetic susceptibility and equilibrium pressure on the hydrogen content of $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ (denoted as [H]/[Pd–Ag–Rh]). The equilibrium pressure sharply increased with increasing [H]/[Pd–Ag–Rh] from zero to 0.04. This range corresponded to that of the dissolved hydrogen region. The equilibrium pressure

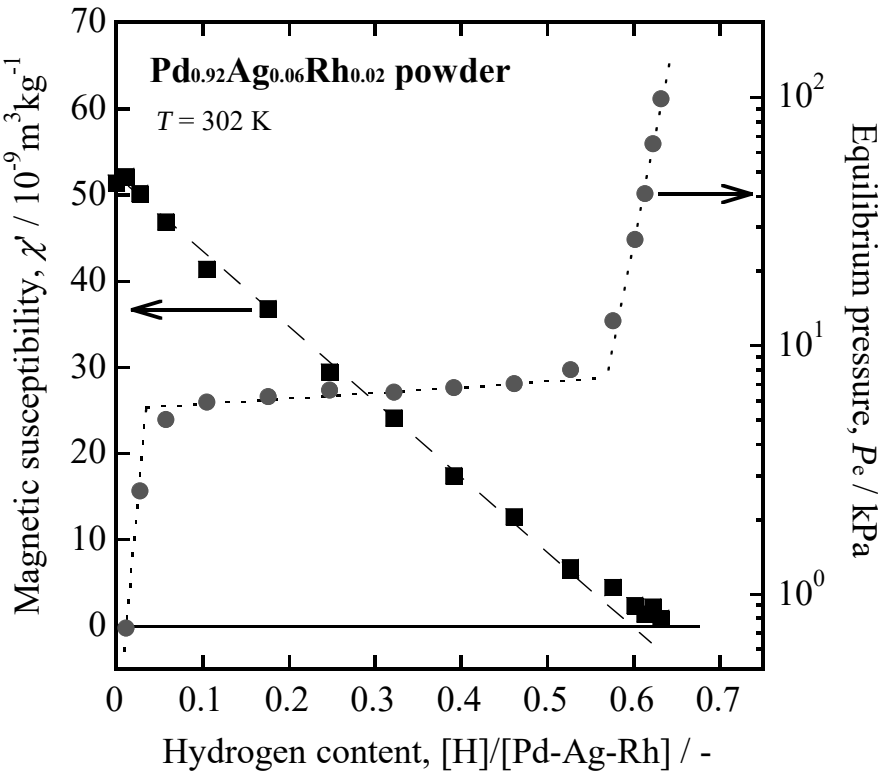

Figure 2 The dependence of both a magnetic susceptibility and an equilibrium pressure on hydrogen content in the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ ternary alloy. The evaluation of the phase boundary from magnetic susceptibility and equilibrium pressure was performed using the dashed and dotted lines.

was maintained between 6 to7 kPa within 0.1 < [H]/[Pd–Ag–Rh] < 0.5, which is generally called a plateau. Because the equilibrium pressure sharply increased above this value, the hydride phase appeared at [H]/[Pd–Ag–Rh] > 0.6. This behavior was qualitatively the same as that of Pd-based binary alloys and Pd metal [3,6,7].

The magnetic susceptibility of $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ was 51 × 10^{-9} m^3/kg. This value is slightly smaller than that of Pd metal. With increasing [H]/[Pd–Ag–Rh], the magnetic susceptibility linearly decreased to the small positive value of 2 × 10^{-9} m^3/kg at [H]/[Pd–Ag–Rh] > 0.6. The dependence of the magnetic susceptibility on [H]/[Pd–Ag–Rh] was similar to that found for Pd-based binary alloys and Pd metal [3,6,7].

4. Discussion

Since Pd–Ag and Pd–Rh alloys were found to show paramagnetic behavior [3], and the magnetic susceptibility of Pd–Ag–Rh was very small in comparison with that of other Pd-based ferromagnetic binary alloys such as Pd–Co and Pd–Ni [8,9], the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ alloy is considered to be a paramagnet at room temperature. In addition, we proved in a previous study [3] that the rigid band model could be applied to Pd–Ag and Pd–Rh systems; the electronic band structure of Pd metal was not affect by the substituting Ag or Rh, and the density of states at the Fermi level for Pd-binary alloys was related only to the change in the number of electrons by alloying. Considering that the Ag and Rh content of the Pd ternary alloy used in this study was low, the rigid band model could be applied to the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ and hydrogen system. In this section, the magnetic susceptibility of the Pd ternary alloy will be analyzed based on the rigid band model.

The principal values obtained from Fig.1 and 2 are summarized in Table 1. The values for Pd metal and Pd-binary alloys are also included for comparison. As cn be extracted from the data, the magnetic susceptibility of $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ without hydrogen is consistent

Table 1. The principal values obtained from Fig.1 and Fig.2. The values for related materials are also summarized in comparison.

	[H]/[Pd–Ag–Rh] at β_{min}		χ' without hydrogen	Plateau pressure	Lattice constant	Ref.
	from P_e	from χ'	/10^{-9}m^{3}kg^{-1}	/kPa	/nm	
$Pd_{0.92}Ag_{0.08}$	0.52	0.49	42.2	0.639	0.3903	[1]
$Pd_{0.96}Ag_{0.04}$	0.57	0.55	50.6	1.04	0.3896	[1]
Pd	0.62	0.63	64.3	2.45	0.3890	[1]
$Pd_{0.96}Rh_{0.04}$	0.67	0.65	73.9	10.3	0.3886	[1]
$Pd_{0.92}Rh_{0.08}$	0.70	0.71 [1)]	71.1	27.4	0.3883	[1]
$Pd_{0.92}Ag_{0.06}Rh_{0.02}$	0.57	0.60 [1)]	51.3	6.29	0.3900	This work

1) the value was obtained by the extrapolation of the magnetic susceptibility at the plateau region.

with that of the $Pd_{0.96}Ag_{0.04}$ alloy. Because the magnetic susceptibility of a Pauli paramagnet is proportional to the density of states at the Fermi level [4], this result suggests that the density of states at the Fermi level in $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ is similar to that in $Pd_{0.96}Ag_{0.04}$, and that the number of electrons in both specimens are practically the same.

In the Pd–Ag or Pd–Rh and hydrogen systems, the change in the number of electrons induced by Ag or Rh substitution resulted in the change of the terminal of the plateau because the amount of unoccupied d-states in the absence of hydrogen was related to the minimum hydrogen content at the hydride phase (β_{min}) [3]. The β_{min} for $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ was estimated from the equilibrium pressure; the hydrogen content at the terminal of the plateau was determined at the point where the plateau intersected the extrapolated line of the hydride phase. The obtained value was the same as that for $Pd_{0.96}Ag_{0.04}$, suggesting that the β_{min} for the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ ternary alloy had the same implications as in the Pd-based binary alloy.

According to our previous study, the magnetic susceptibility of the Pd alloy reached zero at β_{min}, and it kept a small negative value within the hydride phase [3]. Because the

magnetic susceptibility of $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ showed a positive value within the measured [H]/[Pd–Ag–Rh] range, the β_{min} was estimated from the intersection of the extrapolation to zero of the magnetic susceptibility at the plateau region. The estimated value thus obtained was [H]/[Pd–Ag–Rh] = 0.60, which was consistent with the β_{min} estimated from the terminal of the plateau. Consequently, the amount of absorbed hydrogen for the Pd ternary alloy was also correlated with its electronic band structure. It is worth noting that the magnetic susceptibility of the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ hydride ([H]/[Pd–Ag–Rh] > 0.60) was kept a small positive value, which was indicative of the existence of a small amount of ferromagnetic impurities in the Pd ternary alloy. When the magnetic susceptibility data decreased to 2×10^{-9} m^3/kg, the estimated β_{min} became 0.58, which approached the value obtained from the equilibrium pressure. We tried to estimate the amount of magnetic impurities. As can be extracted from reference [10], the magnetic moments of the constituent atoms in a $Pd_{0.97}Fe_{0.03}$ alloy were determined to be $3.0\mu_B$ for Fe and $0.15\mu_B$ for Pd. The Fe content in the Pd matrix was estimated to be 0.2at% from the enhancement of the magnetization of Pd by a factor of 1.04 induced by the Fe atoms as magnetic impurities. Accordingly, the amount of ferromagnetic impurities could be estimated to be rather small, and the change in the electronic band structure induced by such impurities can be considered negligible in this study.

In the previous study on Pd–Ag and Pd–Rh alloys, the equilibrium pressure at the plateau systematically changed depending on the number of conduction electrons [3]. In the $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ and hydrogen system, however, the equilibrium pressure at the plateau did not follow the same trend [3]. Future investigation on the Pd–Ag–Rh alloy with various element compositions and different hydrogen contents is required to gain a better understanding on this discrepancy.

5. Conclusions

The magnetic susceptibility of a $Pd_{0.92}Ag_{0.06}Rh_{0.02}$ ternary alloy and hydrogen system with various hydrogen contents was measured. It was found that the magnetic susceptibility linearly decreased with increasing the hydrogen content and approached zero at the hydride phase. The hydrogen content at the terminal of the plateau was consistent with that obtained at the point of zero magnetic susceptibility, suggesting that the β_{min} of the Pd–Ag–Rh ternary alloy could be estimated from its magnetic susceptibility measurement, as in the case of the Pd–Ag and Pd–Rh binary alloys.

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