

Hydrogen Caused Ordering in PdAg Alloy*

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Summary

Hydrides of PdAg alloy synthesized at high hydrogen pressures have been studied by neutron diffraction. At temperatures of about 470K saturation with hydrogen causes ordering of the metal atoms. At higher temperatures of about 640K no ordering occurs. The results have been explained by the theory taking into account an influence of interstitial atoms on the ordering temperature of binary alloys. It is expected that hydrogenation and subsequent dehydrogenation could be a perspective technique for manufacturing ordered alloys in the cases when the ordering cannot be made by the usual means.

Introduction

Recently the authors /1/ have conjectured that PdAg alloy becomes ordered when saturating with hydrogen. The supposition was based on the appearance of a tetragonal distortion of the f.c.c. lattice and a decrease in the electrical resistance. However, no superlattice reflections in the X-ray patterns were observed because the X-ray scattering amplitudes for Pd and Ag are almost identical. In the present

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work we have studied PdAgH_x alloys by neutron diffraction to verify this conjecture.

Experimental Results and Discussion

The samples (Table 1) were subjected to hydrogen pressures of 2.0-2.8 GPa and temperatures of 370-640K /1/. After that treatment, the reaction chamber was cooled down to 180K and then was unloaded. The samples obtained (with weights about 100 mg) were kept in liquid nitrogen. To eliminate any texture effects they were ground. Neutron experiments were carried out at 100K using a multidetector diffractometer DISK /2/. The hydrogen contents were determined after the experiments by measuring the volumes of the gas evolved on thermal decomposition of the samples at 770K and then

Sample	Hydrogen content, x	Preparation conditions			Structure	
		T(K)	P(GPa)	t(h)	Cell parameters (Å)	Space group, atom positions
<u>PdAgH_x</u>	0.94	370	2.8	24	f.c.c. a=4.066	Fm3m: Me(4a) H(4b)
	0.64	640	2.0	15	f.c.c. a=4.048	- " -
	0.90	470	2.8	30	tetragon. a=2.810 c=4.255	P4/mmm: Me(1a,1d) H(1b)
<hr/>						
<u>¹⁰⁸Pd¹⁰⁷AgH_x</u>						
	0.70	370	2.8	30	f.c.c. a=4.057	Fm3m: PdAg(4a) H(4b)
	0.94	470	2.8	24	tetragon. a=2.819 c=4.250	P4/mmm: Pd(1d) Ag(1a) H(1b)

TABLE 1. Structure of PdAgH_x alloys.

were improved by means of the diffraction data.

All the peaks in the neutron diffraction patterns of the samples treated at 370K and 640K are indexed in the f.c.c. cell with the parameters (Table 1) consistent with the X-ray data /1/. The calculations of the peak intensities have established that the H-atoms occupy octahedral interstices, and the ratios of H/Me are close to those determined on thermal decomposition of the samples. These samples, having the NaCl-type defective structure, are disordered f.c.c. interstitial solid solutions. In the neutron diffraction pattern of the sample treated at 470K, superlattice reflections are present and the structural peaks are split. All the Bragg's peaks are indexed in the primitive tetragonal cell (Table 1) with $a \approx a_0/\sqrt{2}$, $c \approx a_0$, where a_0 is the parameter of the f.c.c. cell. The calculations have established that H-atoms are ordered in octahedral interstices so that a layer superstructure of H-atoms forms along the c-axis. We were unable to establish an ordering of the metal atoms because the neutron coherent scattering amplitudes for Pd and Ag are almost identical.

To determine the arrangement of Pd and Ag-atoms in the alloys we used isotopic samples made of ^{108}Pd (94.6%) and ^{107}Ag (98.9%) where there is a much larger difference of the neutron amplitudes. Beforehand we had determined the unknown amplitudes for the metallic palladium isotopes, $b/10^{-12}\text{cm}$: 0.66 for ^{104}Pd , 0.73 for ^{105}Pd , 0.68 for ^{106}Pd , 0.5 for ^{108}Pd , 0.69 for ^{110}Pd (for ^{107}Ag $b=0.83$).

For the f.c.c. isotopic sample (Fig.1a) the disordered NaCl-type defective structure has been confirmed.

In the tetragonal isotopic alloy (Fig.1b), in addition to the hydrogen superstructure, the layer superstructure of Pd and Ag-atoms (CuAu-type) has been found, in which the Pd-atoms are the nearest neighbours of the H-atoms (Table 1). The structure of the ordered PdAgH alloy consists of the layers -Ag-PdH-Ag-PdH-. To ensure that the ordering of the metal atoms is caused by hydrogen, we have carried out

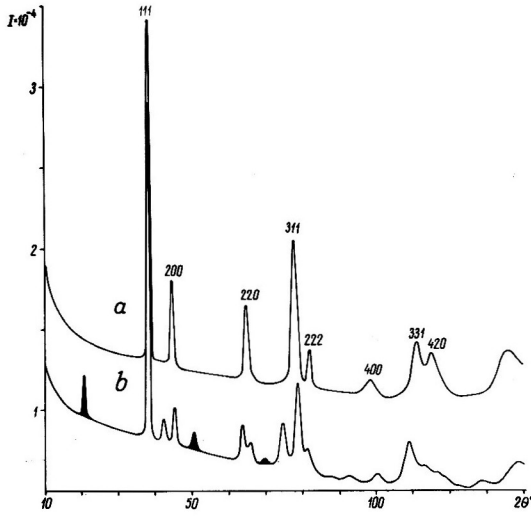


Fig.1. Neutron diffraction patterns for cubic (a) and tetragonal (b) $^{108}\text{Pd}^{107}\text{AgH}_x$ (see Table 1), $\lambda=1.533 \text{ \AA}$. Superlattice peaks are blackened.

control experiments at the same temperatures and pressures but with substitution of argon for hydrogen. In all cases the disordered f.c.c. structure only has been found. As was shown in the theoretical work /3/ using the short-range interaction approximation, occupation of octahedral interstices in b.c.c. binary alloys leads to an increase in the ordering temperature for the metal atoms irrespective of the sort of interstitial atoms. One can show that this conclusion is valid for all the Bravais lattices when accounting for the long-range interaction. Thus, the results obtained here can be explained as follows. In PdAgH_x alloys, hydrogen causes an ordering of the metal atoms if the samples are hydrogenated at 470K; the ordering does not occur at lower temperatures due to the low diffusive mobility of the metal atoms, and does not occur at higher

hydrogenation temperatures, because these then exceed the ordering temperature. This conforms to the data on the temperature and concentration dependences of the electrical resistance /1/. The PdAg alloy remains ordered if the ordered PdAgH_x alloy is dehydrogenated below the ordering temperature. Thus, hydrogenation and subsequent dehydrogenation can be a perspective technique for manufacturing ordered alloys if the ordering cannot be made by the usual means.

References

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