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High pressure studies of cobalt-hydrogen system by X-ray diffraction

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ABSTRACT

Cobalt—hydrogen system was studied in diamond anvil cell at high hydrogen pressure up to 22 GPa at room temperature by X-ray diffraction. Hydride formation from a solid solution of hydrogen in metal was observed at pressure around 4.5 GPa, and the decomposition of the hydride was observed at pressure around 3 GPa. Our studies are complementary to the earlier investigations conducted at higher temperatures, which employed technique that does not allow for the study of decomposition process.

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1. Introduction

In the last few decades metal-hydrogen systems have been extensively studied throughout the world due to their interesting properties and potential applications. The main attention of researchers was drawn to transition metal hydrides and systems that can be used for hydrogen storage.

In spite of a huge amount of experimental data some systems are still awaiting for the deeper and more comprehensive insight into their properties. One of them is cobalt—hydrogen system for the first time investigated at high pressure by group of Ponyatovsky [1,2], and, later, by group of Fukai [3] and Takemura [15]. Their studies, conducted at hydrogen pressures up to 9 GPa, revealed a continuous increase of hydrogen concentration in hcp metal lattice followed by a formation of cubic monohydride phase at pressure around 7 GPa and T = 250 °C. The lattice parameter of the new hydride phase, a = 3.7124(5) Å, was almost identical to that of nickel hydride [4,2]. Although nickel and cobalt are neighbors in the periodic table, they possess different crystal structures – an fcc and hcp respectively.

A neutron diffraction investigation at ambient pressure and 120 K showed [5] that hydrogen atoms in the solid solutions with concentration H/Co \leq 0.26 are randomly distributed over octahedral interstices which are characteristic of all hydrides with close packed metal lattices that are formed by transition metals of groups

* Corresponding author. E-mail address: mtkacz@ichf.edu.pl (M. Tkacz). VI–X. In the solutions with H/Co \geq 0.34, hydrogen atoms form layered superstructures, occupying every third octahedral base layer at H/Co = 0.34 and every second layer for 0.38 \leq H/Co \leq 0.5.

High hydrogen solubility in primary solution is hardly found in the systems where initial metal possesses cubic structure. In the majority of such metals solid hydrogen solution has very narrow concentration region. Good example is the palladium—hydrogen system [6].

Utilization of the diamond anvil cell technique allows for *in situ* studies and extends available pressure range significantly. The other members of group IX of the periodic table were recently found to form hydrides with H/Me > 1: RhH_2 [7] and IrH_3 [8]. So we decided to revise the cobalt–hydrogen system, aiming at the determination of thermodynamic properties and looking for the possibility of the increase of hydrogen content in cobalt at much higher pressure than studied before.

2. Experimental details

We used diamond anvil cell of the modified brilliant type with a culet diameter of about 400 μ m. A 200 μ m hole was spark-drilled in a rhenium gasket of ~50 μ m thickness after indentation of a 250 μ m foil. Samples were made compressing high purity cobalt powder, consisting of 5–10 μ m flakes. Samples were 10–20 μ m thick. Pressure was measured by a ruby fluorescence method [9], using an excitation from 633 nm HeNe laser and a THR1000 spectrometer for spectra recordings.

Hydrogen was loaded into the gasket hole at initial pressure of





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about 0.4 GPa by the technique described earlier [10]. Hydrogen was in significant excess in all experiments.

X-ray powder diffraction was measured by energy-dispersive method with white radiation from tungsten target tube [11] collimated down to about 100 μ m to avoid diffraction from the gasket material. Scattering angle was set as $2\theta \sim 20^{\circ}$, corresponding to $E^*d = 35 \div 40 \text{ keV*}^{\text{Å}}$. Scattering angle was calibrated using the diffraction pattern of hydrogen-free cobalt metal. All experiments were conducted at room temperature.

3. Results and discussion

The selected X-ray spectra are shown in Figs. 1 and 2 for compression and decompression respectively. Lattice volume of cobalt as a function of hydrogen pressure is given in Fig. 3.

Energy dispersive X-ray diffraction showed that at pressure increase the lattice parameters of hcp cobalt are increasing continuously up to about 4 GPa. Above this pressure a formation of a monohydride phase with fcc structure is observed. Further hydrogen pressure increase up to 22 GPa does not produce any peculiarities on the V(P) dependence of the hydride. No evidence of hydrogen content increase over H/Co = 1 was observed. Unlike rhodium, which form dihydride at hydrogen pressures less than 10 GPa [7], cobalt does not form hydrides with H/Co > 1 at such pressures.

During decompression the hydride remains down to about 3 GPa, where a complete transformation to the hcp structure is observed. This means that the reaction of hydrogen and cobalt is reversible with a hysteresis about 1.6 GPa.

A comparison of the equations of state for cobalt in a hydrogen atmosphere and in a 4:1 mixture of methanol and ethanol is shown in Fig. 3. The bulk moduli of Co and CoH are 183(1) GPa and 190(20) GPa respectively and their volumes at ambient pressure are 11.082(4) Å³ per Co atom and 13.2(1) Å³ per Co atom respectively. Within the experimental error the compressibilities of both materials are the same. This behavior is typical for transition metals and their hydrides. The difference in lattice volumes of CoH and Co is 2.1(1) Å³ per H atom, in agreement with the estimation obtained in Ref. [5].

Assuming that equilibrium pressure for hydride formation reaction is close to the decomposition pressure (see Ref. [13] for discussion), we conclude that at room temperature the equilibrium takes place at hydrogen pressure $P_{eq}^H = 3.0(5)$ GPa. This estimate is much lower comparing to 7 GPa, obtained by Ponyatovsky et al.



Fig. 1. Energy dispersive X-ray diffraction patterns for cobalt as a function of hydrogen pressure taken during pressure increase. For clarity only selected spectra are presented here. Scattering angle corresponds to $E^*d = 34.8 \text{ keV}^*$ Å.



Fig. 2. Energy dispersive X-ray diffraction patterns for cobalt as a function of hydrogen pressure taken during pressure decrease. Scattering angle corresponds to $E^*d = 34.9 \text{ keV}^*\text{\AA}$.



Fig. 3. Pressure–volume relationships for the cobalt–hydrogen system and pure cobalt [12]. The solid triangles denote compression data and the empty ones indicate decompression. The left Y axis corresponds to the volume calculated per one metal atom, and the right axis shows molar volumes of cobalt both in pure state and in the hydride phase.

[1,2] at T = 250 °C. However, in these works only formation process was studied, and not the decomposition. We think that the discrepancy is accounted for by a large baric hysteresis, accompanying cobalt hydride formation. There should also be a considerable temperature dependence of equilibrium pressure in temperature range $20^{\circ}C-250^{\circ}C$.

A standard Gibbs free energy for the reaction Co $+1/2H_2 \rightarrow$ CoH at T =298 K was calculated using the following equation:

$$\Delta G_{H}^{0} = \int_{P_{eq}^{H}}^{P_{0}} \Delta V dP$$

= $\int_{P_{eq}^{H}}^{P_{0}} \left(V_{CoH} - V_{Co} - \frac{1}{2} V_{H_{2}} \right) dP \approx -\beta_{H} P_{eq}^{H}$
+ $\frac{1}{2} \int_{P_{o}}^{P_{eq}^{H}} V_{H_{2}} dP \approx 27(2) \ kJ/mol H$

where $\beta_{\rm H} = 2.1 \text{ Å}^3/\text{atom}$ and the molar volume of gaseous hydrogen was calculated using the equation of state from Ref. [14]. We neglected the solubility of hydrogen in hcp cobalt at 3 GPa, which is 10–20 at %.

4. Conclusions

Formation and decomposition conditions of cobalt hydride were determined at room temperature. Cobalt does not form hydrides with H/Co > 1 at hydrogen pressures less than 22 GPa, unlike rhodium, which is right under cobalt in the periodic table.

Our results suggest a considerable temperature dependence of equilibrium cobalt hvdride formation pressure at $20 \circ C < T < 250 \circ C$. We think that the phase diagram of cobalt-hydrogen system should be reconsidered for this temperature range.

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