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Thermodynamic properties of iron hydride

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Abstract

X-Ray diffraction studies of the iron sample subjected to high hydrogen pressure inside a diamond anvil cell have been carried out in order to determine the equilibrium conditions of formation and decomposition of the iron hydride. Due to hysteresis, commonly observed in transition metal hydrides, the pressure of decomposition of the corresponding hydride describes the equilibrium as decomposition is considered to be a stress-free process. X-Ray diffraction studies have revealed the structural phase transition from the b.c.c. structure of iron metal to the d.h.c.p. of hydride at 3.5 GPa, while the decomposition process has been observed at a hydrogen pressure of about 2.2 GPa. Both processes are accompanied by a volume change of the host lattice of 2.8 Å^3 as compared to the volume of hexagonal iron, extrapolated from high pressure. Free enthalpy of formation of iron hydride was calculated as equal to 23.5 kJ/mol of hydride. Assuming the entropy of formation of 52.25 J/mol/K, enthalpy of iron hydride is positive and equals to 7.9 kJ/mol of FeH. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Application of the diamond anvil cell (DAC) to the investigations of the metal–hydrogen systems has extended the limit of hydrogen pressure by almost two orders of magnitude [1]. This technique enabled the possibility of the synthesis of new hydrides and also the determination of the thermodynamic properties of these compounds because hydrogen activity is well defined in the DAC contrary to the techniques requiring application of organic solvents as pressure transmitting media [2]. Due to the phenomenon of hysteresis, only the decomposition pressure of the hydride phase provides us with the information about the real equilibrium. Although this issue is controversial, raising discussion in the literature [3,4], we firmly believe that the model proposed by Baranowski [4] represents the most realistic approach. Thus determination of the pressure of decomposition is the essential feature for calculation of the thermodynamic properties of these compounds.

The iron–hydrogen system is particularly interesting due to its technological importance. It is also of geological interest because of the high cosmic abundance of iron and hydrogen in the space. Although iron hydride cannot be synthesized at ambient pressure, experimental evidence for the hydride formation at high pressure and temperature has been already reported [1,2]. Spectacular optical and X-ray observations of the iron hydride formation in the DAC have been published [1]. Unfortunately up to now the experimental data concerning conditions for the iron hydride decomposition have been unavailable for ambient temperature. The purpose of this paper is to determine the equilibrium conditions for the formation and decomposition of the iron hydride by high pressure X-ray diffraction studies of the metallic iron subjected to high hydrogen pressure in a diamond anvil cell. Calculations of the thermodynamic function of formation of iron hydride will be given along with the discussion on the possibility of a new hydride synthesis.

2. Experimental

The high pressure technique for loading the DAC with gaseous hydrogen has been described elsewhere [5]. The iron samples compacted from a powder into layers of a few μm thick have been loaded into the stainless steel gasket with a drilled hole of 0.2 mm diameter. A ruby chip for pressure determination accompanied the iron sample in the gasket hole using the pressure scale proposed by Mao et al. [6].

Energy dispersive X-ray diffraction (EDXD) has been used for taking diffraction patterns as the function of hydrogen pressure. A Bragg angle θ equal to 5.19° was

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determined by diffraction from gold and silver foils placed between diamonds in the DAC instead of the sample. The data were recorded with a HPGe solid state detector and multichannel analyzer (4k). The polychromatic X-ray beam from the conventional tungsten target tube has been collimated down to 0.1 mm in order to avoid diffraction from the gasket material. The starting pressure of hydrogen was around 0.5 GPa to assure a relatively large molar ratio of hydrogen to iron since the hydrogen gas plays a double role as a chemically active component and pressure transmitting medium. The experiments were carried out at room temperature.

3. Results and discussion

X-Ray diffraction patterns taken at a hydrogen pressure of 2.2 GPa (below the pressure of iron hydride formation) show only b.c.c. iron structure. The upper spectrum corresponds to a hydrogen pressure of 4 GPa (above the pressure formation of the iron hydride), indexed according to Ref. [7]. Both spectra are presented in Fig. 1. The first diffraction lines from the d.h.c.p. iron hydride were observed at a pressure of 3.5 GPa and that pressure was considered to be the pressure of formation. The rate of transformation from the b.c.c. structure of iron to the hexagonal of iron hydride at room temperature is rather low. This is the reason for the presence of the {211} diffraction line of the b.c.c iron structure above the pressure of formation, although the collection time for obtaining diffraction spectra of about 24 h was applied in these studies. In fact, it took almost a week to complete the transformation at this pressure from the first observation of hexagonal structure appearance in the spectra. The observation of persistence of iron metal up to 15 GPa, reported by Badding et al. [1] had a probably similar origin. Also exposure to a hydrogen pressure of about 9 GPa at a temperature as high as $T=350°\text{C}$ during 24 h does not produce a single phase of iron hydride as reported by Antonov et al. [7].

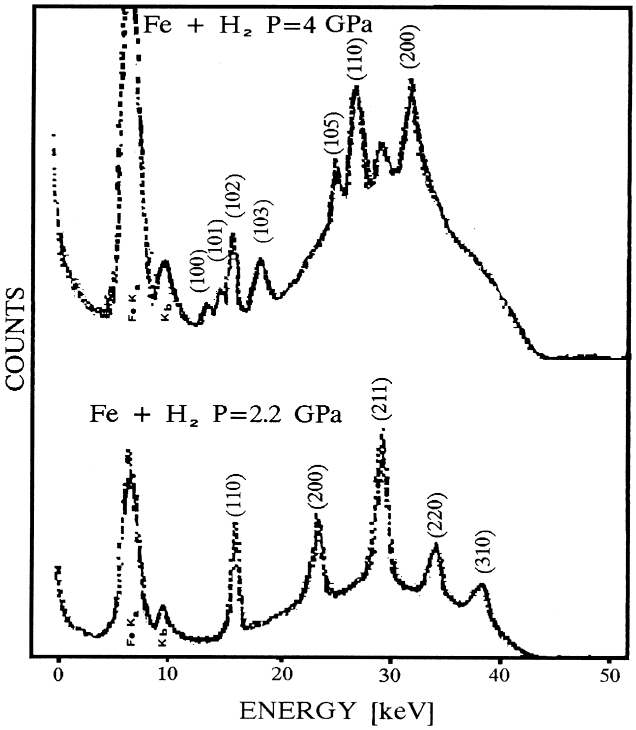

Fig. 1. Energy dispersive X-ray diffraction patterns for the b.c.c. iron phase (lower) and for d.h.c.p. iron hydride (upper) taken at hydrogen pressures of 2.2 and 4.0 GPa, respectively. $Ed_{hkl}=34.42$ [keV Å].

When the pressure is carefully decreased after transformation is completed, the structure of the b.c.c. iron metal is observed again along with hydride lines at a pressure of about 2.2 GPa. According to Antonov et al. [7], the iron hydride has the double close packing hexagonal structure with a lattice volume of about 55.6 Å^3, measured at low temperature. The lattice constants $a=2.69$ Å and $c=8.79$ Å calculated from the upper spectrum presented in Fig. 1 are in good agreement with previously reported data [1,7].

In the case where pressure is below 2.0 GPa only b.c.c. lines are detected on the spectrum.

Assuming that for almost all transition metal hydrides the increase in cell volume due to incorporation of one hydrogen atom is approximately 2.9 Å^3 [8], one can calculate the hydrogen content from X-ray diffraction data. Unfortunately, during the iron hydride formation the structure transformation from b.c.c. iron to d.h.c.p. of hydride takes place, so direct comparison of volume changes due to different volume sites for hydrogen in these structures is rather doubtful. Instead, as the reference metal lattice we used the volume of hexagonal iron extrapolated to zero pressure using the equation of state determined by Badding et al. [1]. That way the composition of the hydride can be calculated as H/Fe=0.95 atomic ratio.

Although the volume change of the solid phase due to hydride formation is slightly different for different metals, the method for calculating the hydrogen concentration using 'universal volume change' is the only method to determine its quantity in the DAC due to the extremely low mass used in this technique.

It must be also pointed out that determination of hydrogen content in the sample subjected to high hydrogen pressure by volumetric measurements of hydrogen released from metallic sample after quenching to low temperature from high pressure is not an easy problem due to the instability of such a sample. On the other hand, thermal decomposition, particularly when carried out at high temperature, could result in an increase of hydrogen as the product of water reduction (which is always present in the process) by active metals.

The determination of decomposition pressure along with lattice changed due to the hydride formation and decomposition provides us with the data required for the calculation of the free enthalpy of formation of the iron hydride as proposed by Baranowski and Bocheñska [9] for nickel hydride.

For the reaction:

$$\mathrm{Fe} + 1/2\mathrm{H_2} \leftrightarrow \mathrm{FeH} \tag{1}$$

free enthalpy of formation of iron hydride can be expressed in the following relation:

$$\mu_{\mathrm{FeH}} = \mu_{\mathrm{Fe(FeH)},p_{\mathrm{eq}}} + \frac{1}{2}\cdot\mu_{\mathrm{H_2(FeH)},p_{\mathrm{eq}}} \tag{2}$$

where $\mu_{\mathrm{Fe(FeH)},p_{\mathrm{eq}}}$ and $\mu_{\mathrm{H_2(FeH)},p_{\mathrm{eq}}}$ correspond to the chemical potential of iron in iron hydride and hydrogen in iron hydride, respectively. Chemical potential of hydrogen in equilibrium with iron hydride can be expressed in term of fugacity as:

$$\mu = \mu(p_0,T) + 1/2RT \ln f \tag{3}$$

Fugacity at the equilibrium pressure of hydrogen over solid iron hydrides equals 4×10^9 [10,11] so the chemical potential calculated from Eq. (3) equals 54.5 kJ per mol of hydrogen.

The first term in Eq. (2) has been calculated using Gibbs–Duhem's formula:

$$\mu_{\mathrm{Fe(FeH)},p_{\mathrm{eq}}} = -\frac{1}{4}\cdot RT\int_{x=0}^{x=1} x\,\mathrm{dln}\,f + \int_{1}^{p_{\mathrm{eq}}} V_{\mathrm{Fe}}\mathrm{d}p \tag{4}$$

where x denotes the atomic ratio H/Fe, f is the fugacity of hydrogen and V is the molar volume of iron metal.

The first term in Eq. (3) is due to the formation of solid solution of hydrogen in iron and can be neglected. Taking 6.74 ccm as the molar volume of pure iron, the chemical potential of iron in the iron hydride can be calculated as equal to 15.1 kJ/mol of Fe and so the free enthalpy of formation of iron hydride at formation pressure equal to 42.3 kJ/mol of hydride.

Returning to the standard conditions the following relation has been applied:

$$\Delta G^0 = \Delta G_{\mathrm{FeH},p_{\mathrm{eq}}} + \int_{p_{\mathrm{eq}}}^{1} V_{\mathrm{FeH}}\mathrm{d}p \tag{5}$$

where V, equal to 8.4 ccm, denotes the molar volume of iron hydride.

The standard thermodynamic potential of iron hydride formation equals:

$$\Delta G^0_{\mathrm{FeH}} = 23.5\ \mathrm{kJ/mol_{FeH}}$$

Up to now only a few metal–hydrogen systems have been thermodynamically characterized, especially those formed at high pressure. As compared to the standard free energy of formation of the nickel [9] and chromium hydrides [12], the value for the iron hydride is much higher, but it is smaller than the value for rhodium hydride [13]. It is worth noting that the value of entropy hydride formation for various face centered-cubic transition metals and alloys is almost the same and equals about 52.25 J/K per mole of hydride. Assuming the same value for the iron hydride, the enthalpy of formation of iron hydride can be estimated using the relation:

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

as equal to 6.8 kJ/mol of FeH. At the moment this is the only way to estimate the enthalpy of formation for the iron hydride because it is rather difficult to imagine the direct calorimetry measurements within the diamond anvil cell. This means that the formation of iron hydride should be endothermic, similarly to the rhodium hydride as discussed earlier [13]. As the consequence of the positive enthalpy of formation of rhodium hydride, one can expect a lowering of the equilibrium pressure with the increase of temperature, according to van't Hoff's relation in the form:

$$\frac{1}{2}\cdot\frac{\mathrm{dln}\,f_{\mathrm{eq}}}{\mathrm{d}1/T} \approx \frac{\Delta H^0}{R} \tag{7}$$

However the fugacity of hydrogen shows strong temperature dependence with negative slope [11,12] so fugacity at higher temperature is smaller than at lower temperature for the same pressure. Assuming the enthalpy for the formation process as equals to 6.8 kJ per mol of hydride one can calculate the pressure the formation of iron hydride at 250°C as equal to about 4 GPa as compared to about 5 GPa reported by Ponyatovsky et al. [2].

From Eq. (6), assuming universal value of entropy formation as 52.25 J/K per mole of hydride and neglecting the compressibility of solid phases, one can calculate the pressure of hydrogen above which hydride formation is accompanied by a positive heat of reaction. This value was estimated in vicinity of about 1 GPa. It means that the fugacity of hydrogen required for hydride formation should be lowered by increasing the temperature. But as mentioned before, corresponding hydrogen pressure will also increase at higher temperatures for endothermic hydrides but with lesser slope as compared to the hydrides with exothermic character. This conclusion may have great importance regarding the synthesis of the new hydrides under high pressure conditions. Therefore, the proper combination of both high temperature and high pressure of hydrogen must be compromised as these features are acting in opposite direction on the chemical potential of hydrogen gas. Although increasing the temperature causes decrease of hydrogen fugacity it is required to maintain hydrogen in the gaseous phase otherwise the rate of hydrogen uptake could be significantly diminished. Additionally, the higher temperature should increase atoms oscillations in metallic lattice facilitating hydrogen uptake and metal atoms rearrangements particularly in the case of the structure transformation during the hydride phase formation.

Semiempirical models for the equilibrium pressure of hydrogen given to date [14,15], predict that within the capability of modern diamond anvil cells a number of hydrides (to date unknown) could be synthesized.

4. Summary

By using the X-ray diffraction studies of an iron sample subjected to high hydrogen pressure inside a diamond anvil cell the equilibrium conditions of formation and decomposition of iron hydride (for the first time) have been determined at room temperature. Free enthalpy of formation of iron hydride was calculated as equal to 23.5 kJ per mole of hydride assuming that pressure of decomposition describes the equilibrium as this reaction is considered to be a stress-free process. X-Ray diffraction studies have revealed the structural phase transition from the b.c.c. structure of iron metal to d.h.c.p. of hydride at 3.5 GPa while the decomposition process has been observed at pressure of hydrogen of about 2.2 GPa. Lattice parameters of the d.h.c.p. iron hydride calculated from the EDXD method are in good agreement with the data found in the literature [1,7]. Regarding relatively large errors in pressure and temperature estimations reported by Antonov et al. [7], extrapolation of their data to room temperature gives comparable results.

Assuming the entropy of formation as 52.25 J/mol/degree, enthalpy of iron hydride is positive and equals 7.9 kJ/mol of FeH. Consequences in regard to the new hydride formation were also discussed.

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