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Synthesis and properties of AB_5-type hydrides at elevated pressures

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Abstract

A new installation for high pressure investigations of hydrogen interaction with alloys is presented. The installation is designed for measurements of PC-isotherms at pressures up to 3000 bar in the temperature range −30 to 100 °C. The latest results of such measurements for typical representatives of AB_5-type alloys are presented and discussed. For YNi_5 and YCo_5 PC-isotherms at temperatures −20 to 80 °C were measured. The maximum absorption capacity corresponded to compositions $YNi_5H_{5.4}$ and $YCo_5H_{3.6}$.

Keywords: Metal hydrides; Gas–solid reactions; Thermodynamic properties; High pressure

1. Introduction

Intermetallic compounds $LaNi_5$ and $LaCo_5$ absorb hydrogen at high pressure up to the predicted theoretical maximum. However, there are serious contradictions in data for absorption capacity of near analogue YNi_5. At comparatively low pressure (up to 100 atm) it does not react with gaseous hydrogen [1–3]. Application of high pressure up to 1550 atm allowed Takeshita et al. [4] to synthesize $YNi_5H_{3.5}$ hydride. Still PC-isotherms indicate that possibly the reaction with hydrogen was not completed in full. Different results for YNi_5–H_2 were obtained by Anderson et al. [5]. YCo_5 is known to absorb hydrogen at low pressure [2,3], but there is no data for behaviour of this compound at elevated pressure. This work presents the results of high pressure investigation of YNi_5 and YCo_5 interaction with hydrogen.

2. Experimental

Alloys were prepared by arc melting from initial metals in argon atmosphere. Phase composition and lattice parameters of starting alloys and their hydrides were determined by X-ray diffraction (Cu Kα). In order to stabilise obtained hydrides for X-ray experiments they were cooled to liquid nitrogen temperature in the sample holder and then opened to air for 1 h.

Interaction with hydrogen was studied in a new high pressure installation for temperature range of −20 to +80 °C. Schematic drawing of the high pressure installation is shown in Fig. 1. The installation consists of the section of preliminary hydrogen purification and the HP-section itself. Preliminary purification section consists of hydrogen source vessel and two hydrogen storage and purification vessels, one filled with $LaNi_5$, second with $Ti,Zr(V,Mn)_2$. This combination was chosen in order to prevent as much as possible the HP-generator system with VH_2 from possible contamination by impurities in hydrogen, which could significantly poison the vanadium hydride surface, decrease its absorption capacity and consequently decrease the maximum high pressure value.

The HP-section consists of HP-generator with VH_2, sample holder, buffer vessel, two pressure transducers with upper pressure limits 250 and 3000 bar. Both sample holder and HP-generator can be heated to high temperature with muffle furnaces. The experimental temperature around the sample holder can also be maintained with thermostat operating in the temperature range −30 to 60 °C.

The data from pressure transducers and from thermocouples attached to sample holder and HP-generator is collected by computer-powered control system.

For all constituent parts of the device the relevant value of volume were determined in order to perform correct calculations of amounts of absorbed/desorbed hydrogen. The values were obtained in two ways—calculating the volume basing on blueprint dimensions, and volumetric determination by water infill. This value for sample holder was found to be 8.929 ml. Additionally, the volume of initial alloy or relevant hydride was taken into account when calculating the total volume of the sample holder. Standard sample mass for experiment was 15–20 g.

For calculation of amount of hydrogen we have chosen the modified van-der-Vaals equation, proposed by Hemmes et al. [6]:

$$\left(\frac{P + a(P)}{V^{\alpha}}\right)(V - b(P)) = RT \quad (1)$$

where a and b are the pressure dependent coefficients ($P > 1$ bar); P is the pressure (bar); T the temperature (K); V the volume (cm^3); R is the universal gas constant (82.06 cm^3 bar/mol K).

Eq. (1) is valid for temperatures from 100 to 1000 K and pressures from 1 to 10^6 atm. In this range the maximum value of error is 0.5%.

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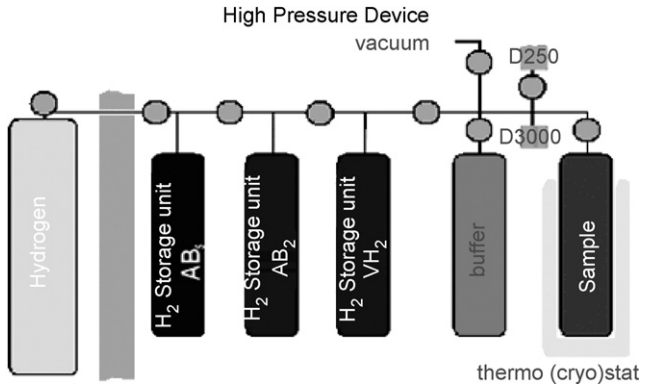

Fig. 1. Schematic drawing of the device.

3. Results and discussion

YNi_5 and YCo_5 were found to crystallize in hexagonal $CaCu_5$-type with lattice parameters in good agreement with literature data (Table 1). Slight traces of yttrium oxide were always present in the diffraction patterns.

Noticeable interaction of YN_5 with hydrogen started at pressure higher than 500 atm. The equilibrium pressures for absorption and desorption at room temperature in the middle of the plateau were found to be 674 and 170 atm correspondingly. The hydride composition at 1887 atm at room temperature was determined to be YNi_5H_5 and at −20 °C, $YNi_5H_{5.4}$. Fig. 2 shows the PC-isotherms for YNi_5–H_2 system. They exhibit strong deviations from both results of [4,5]. In case of [4] there were two plateaus at 300 and 1000 atm and the maximum hydride composition corresponded to $YNi_5H_{3.5}$, while in [5] the desorption plateau pressure was 12 atm and hydride composition, $YNi_5H_{4.4}$.

These distinctions in PC-isotherms maybe explained by extremely slow rate of hydrogen absorption and especially desorption. In our case the equilibrium in desorption steps was established only in 2–4 h (Fig. 3). Authors of [1,4,7] marked the difference in hydrogen sorption properties of YNi_5 compared to other representatives of this type of intermetallic compounds. From their point of view low-temperature heat-capacity, electronic structure and surface oxidation do not explain this difference while the compressibility of YNi_5 being the lowest among AB_5-type alloys could possibly be the reason for this peculiarity [4]. We may also add that the unit cell volume

Table 1
Lattice parameters for YNi_5 and YCo_5

a (Å)	c (Å)	V (Å^3)	Reference
YNi_5			
4.869 ± 0.003	3.972 ± 0.001	81.9	This work
4.892	3.960	82.07	[4]
4.888	3.963	82.0	[5]
YCo_5			
4.937 ± 0.002	3.986 ± 0.002	84.1	This work
4.952	3.975	84.42	[5]
4.920	3.977	83.37	[3]

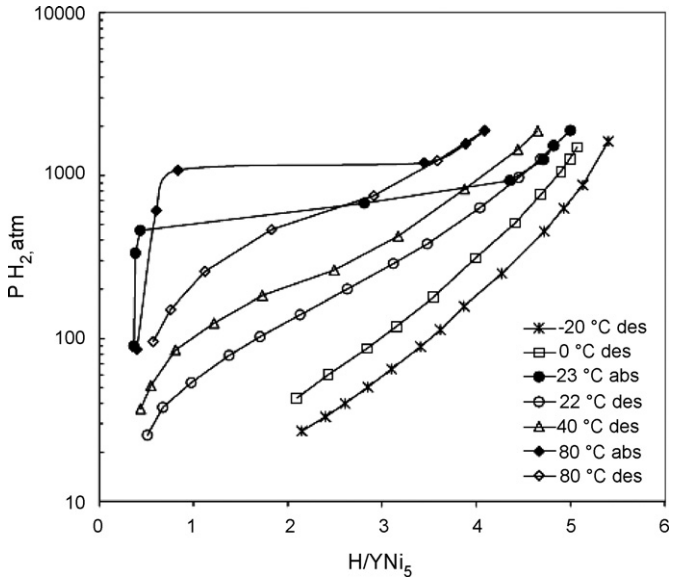

Fig. 2. PC-isotherms for YNi_5–H_2 system.

of YNi_5 is the also the smallest of all AB_5 hydride forming compounds.

The interaction of hydrogen with YCo_5 starts at pressure below 50 atm. The equilibrium absorption and desorption pressure at room temperatures is about 53 and 24 atm, correspondingly. The rate of reaction is incomparably higher than that of YNi_5. Hydrogen content at 2579 atm corresponds to composition $YCo_5H_{3.6}$. The PC-isotherms are shown in Fig. 4. Obtained results are in good correlation with previous data [3,4]. At pressures higher than 150 atm one can see only some additional solubility of hydrogen in β-hydride.

The enthalpies and entropies of reaction of both compounds determined from vant-Hoff equation were found to be 21.9 ± 1.7 kJ/mol H_2 and 115.8 ± 6.3 J/K mol H_2 for YNi_5–H_2 (at $H/YNi_5 = 2.5$) and 30.3 ± 1.0 kJ/mol H_2 and 130.0 ± 3.6 J/K mol H_2 for YCo_5–H_2 (middle of the plateau). Enthalpy for cobalt compound is in good agreement

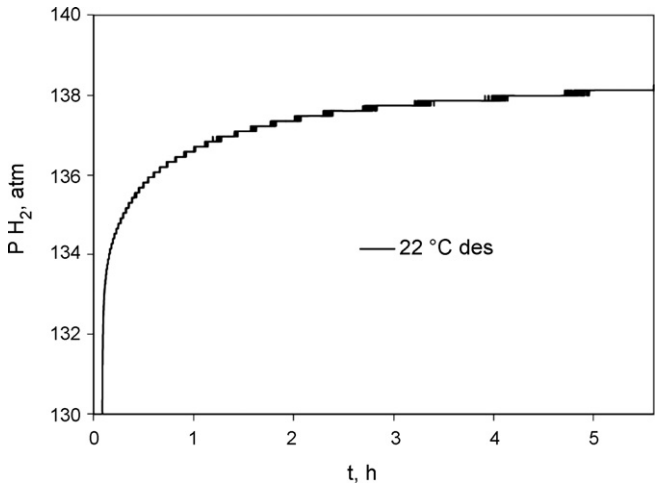

Fig. 3. Rate of equilibrium establishment in a typical desorption step for YNi_5–H_2.

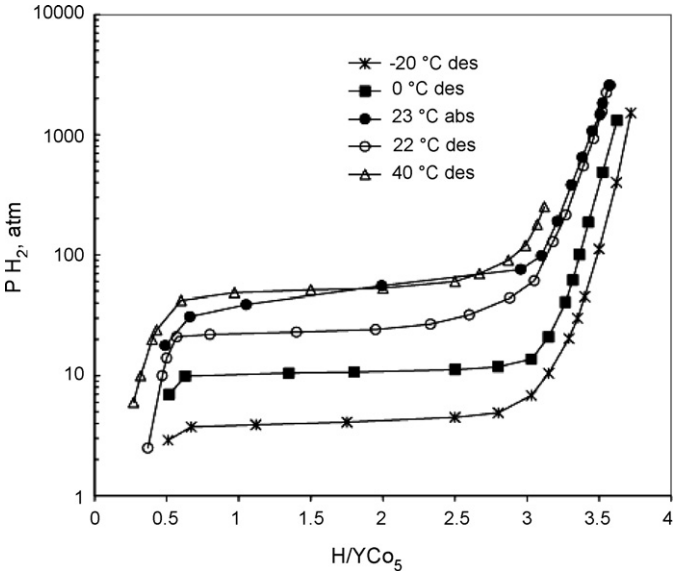

Fig. 4. PC-isotherms for YCo_5–H_2 system.

Table 2
Cell parameters for YNi_5H_5 and $YCo_5H_{3.6}$

a (Å)	c (Å)	V (Å^3)
YNi_5H_5		
5.147	4.198	96.3
$YCo_5H_{3.6}$		
5.231	4.257	100.9

with previous results 32.2 kJ/mol H_2 [4] and 28.5 kJ/mol H_2 [5].

X-ray investigation of hydrides showed that hydrogen absorption does not change the initial metal matrix structure while the increase of unit cell volume as about 19% (Table 2).

4. Conclusions

Investigation of hydrogen sorption properties of YNi_5 and YCo_5 at pressure up to 3000 atm showed, that YNi_5 behaviour differs from that reported in [2–5], while the results for YCo_5–H_2 are in good agreement with previous results [3,4]. The time for equilibrium establishment in YNi_5–H_2 system is rather long and could possibly be explained by low lattice compressibility of YNi_5. The thermodynamic parameters for YNi_5–H_2 system and cell parameters for hydrides were determined for the first time.

Acknowledgements

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References

[1] T. Takeshita, K.A. Gschneidner Jr., D.K. Thome, O.D. McMasters, Phys. Rev. B 21 (1980) 5636–5641.
[2] T. Takeshita, W.E. Wallace, R.S. Craig, Inorg. Chem. 13 (1974) 2282–2283.
[3] V.K. Sarynin, V.V. Burnasheva, K.N. Semenenko, Izv. AN SSSR Metall. 4 (1977) 69–70.
[4] T. Takeshita, K.A. Gschneidner Jr., J.F. Lakner, J. Less-Common Met. 78 (1981) 43–47.
[5] J.L. Anderson, T.C. Wallace, A.L. Bowman, C.L. Radosewich, M.L. Courtney. Los Alamos Rep. LA-5320-MS, Informal Report (1973).
[6] H. Hemmes, A. Driessen, R. Griessen, J. Phys. C 19 (1986) 3571–3585.
[7] J.H. Weaver, A. Franciosi, D.J. Peterman, T. Takeshita, K.A. Gschneidner Jr., J. Less-Common Met. 86 (1982) 195–202.