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Thermodynamics of processes of hydrogen sorption by hydrides of intermetallic compounds of CrB structural type

I. E. Nemirovskaya and A. M. Alekseev
State Institute of Nitrogen Industry, 108915 Moscow (U.S.S.R.)

V. V. Lunin
Moscow Lomonosow State University, 119899 Moscow (U.S.S.R.)

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Abstract

The intermetallic compounds (IMCs) HfNi, ZrNi, HfCo and ZrCo are studied by thermoanalytical methods. The thermodynamic characteristics calculated from the van't Hoff equation and obtained by the calorimetric method are compared with literature data. The dependence of the partial molar enthalpy on the IMC hydrogen content has a tendency to decrease with increasing hydrogen content in the α solution region; in the region near the α–$(\alpha+\beta)$ and $(\alpha+\beta)$–β boundaries there is a discontinuity; in the region of two-phase coexistence $\Delta\bar{H}_H$ does not depend on the IMC hydride hydrogen content; during the formation of a new phase (monohydride, β hydride) $\Delta\bar{H}_H$ increases.

1. Introduction

Hydrides of metals and intermetallic compounds (IMCs) are widely used in different branches of science and engineering. Studies of the systems IMC–H_2 involve both kinetic and thermodynamics properties. Since the literature on this subject is vast, we cite only those references which relate directly to the work carried out in this paper.

The systems based on zirconium and hafnium with nickel and cobalt are prospective catalysts for hydrogenation processes [1, 2]. The thermodynamic data for these systems have previously been obtained with the help of a number of estimations (some of the values are given in Table 1) [3–13].

The formation enthalpies for the two-phase regions of "IMC–hydrogen" systems are commonly determined by means of the van't Hoff equation from the temperature dependence of the equilibrium dissociation pressure, though the calculation error may reach 74%–84% in this case (depending on the plateau extension, the accuracy of hydrogen content measurement, etc.).

Differential thermal analysis has also been used for obtaining the enthalpies of hydride formation via the desorption peak temperature of IMC hydrides according to the modified Nernst equation [14], which allows the ΔH determination error to be decreased to 3%–5% (depending on the accuracy of temperature measurement and the reproducibility of results).

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TABLE 1

Thermodynamics of IMC hydrides in two-phase regions

IMC	Region	ΔH (kJ (mol. $H_2)^{-1}$)	ΔS (J K^{-1} (mol. $H_2)^{-1}$)	T (K)	Method	Reference
ZrNi	α–β (H)	67.0		323	II	[3]
		95.5		423–523	I	[4]
		77.1		373–523	I	[5]
		69.1		565	II	[14]
		61.4			III	[15]
	α–mono (H)	47.5		323	IV	[16]
	Mono–β (H)	35.0		323	IV	[16]
ZrCo	α–β_1 (H)	75.4		323	II	[3]
		109.4		523–623	I	[4]
		83.3	134.9	423–573	I	[7]
		83.3	123.5	660	II	[14]
		69.2			III	[15]
	β_1–β_2 (H)	61.6	94.3	473–573	I	[7]
HfNi	α–mono	50.3		323	II	[3]
	Mono–β	45.0		323	II	[3]
HfCo	α–β	58.7		323	II	[3]

ΔH and ΔS are calculated: I, from the temperature dependence of the H_2 equilibrium pressure; II, from the transformation temperature at $P = 0.1$ MPa or from the pressure value in the two-phase region at the indicated temperature; III, from a semiempirical model based on the IMC electronic structure [15]; IV, from the calorimetric method [16]. Mono, monohydride phase.

Data from direct calorimetric determination of the integral enthalpies of formation of hydride phases are limited but are widely used for the systems $LaNi_5$–H_2 [17–21] and TiFe–H_2 [22]. Of the CrB structural type, only the ZrNi–H_2 system has been studied [16], but the authors used isothermal calorimetric studies with hydrogen determination by Sieverts' method. The results obtained require a lot of time and the problem of step-by-step increase in hydrogen content gives no opportunity to investigate the partial molar enthalpy behaviour on the phase boundaries.

The differential calorimetric method based on a standard instrument under non-isothermal conditions has been used until now for thermodynamic measurements in our work [23] and one other study [24]. The utilization of this instrument for kinetic studies and for the calculation of integral enthalpies has shown this method to be promising, but Susic [24] had no possibility to determine the quantity of hydrogen desorbed (or sorbed) by the hydride, which caused an incomparability of the results obtained with other published data as well as an incorrectness of some of the conclusions drawn from his work.

Therefore the main cause of the appearance of errors when using the calorimetric method is in the determination of the amount of hydrogen which takes part in the reaction according to the P–c–T technique, especially in the primary region of the α phase and in the final region of the β hydride. In the case of a wide "plateau" region, when the region of solid solution is small, the enthalpy of the phase transition turns out to be equal to the enthalpy of hydrogenation.

It appeared necessary to use a differential scanning calorimeter rather than the *P–c–T* technique, because this allowed us to exclude the influence of temperature differences in a sample, to give better stability and greater precision in heat measurement and also to cancel out heat effects due to changes in volume with pressure (*VdP* effects) [19, 20].

In this work, for the first time in the analysis of hydrogen evolved, the combination of a thermoconductometric apparatus with a differential scanning calorimeter has been used. This combination allows all the errors of the previous techniques of direct measurements of enthalpies to be eliminated and promises to be the most informative and simplest method for directly obtaining the dependence of the partial molar enthalpy of hydrogen dissolution on its content in the hydride and the value of the integral enthalpy.

2. Experimental details

2.1. *Sample preparation*

As initial intermetallic compounds, ZrNi, HfNi, ZrCo and HfCo were used. The intermetallic compounds were prepared by arc melting stoichiometric amounts of the pure metals under a helium atmosphere (99.985% quality). For the preparation of the alloys, zirconium and hafnium obtained by the iodide method as well as electrolytic nickel and cobalt were used. To obtain homogeneous samples, the ingots were remelted repeatedly. The homogeneity of the alloys was checked by X-ray diffraction.

The synthesis of IMC hydrides was carried out in a metallic vacuum device. The samples, having undergone a preliminary wash in acetone, alcohol and distilled water, were evacuated to 1.33 Pa for 1 h at a temperature of 1200–1300 K. The saturation with hydrogen was carried out at temperatures of 393–573 K and at a hydrogen pressure of 101.3–152.0 kPa. The IMC hydride $TiMoH_x$ served as hydrogen source. On cooling in a hydrogen atmosphere, the samples of hydrides obtained had a metallic lustre and were stable in air.

2.2. *Equipment, calibration and measurement procedure*

For simultaneous measurement of the changes of temperature and the heat evolved during the physicochemical transition in the substances studied, a differential scanning calorimeter (DSC 910 TA 990, Du Pont, U.S.A.) was used. The calibration of the DSC cell has been based on the thermal conductivity of sapphire and the melting heats of ultrapure metals (gallium indium and tin), which allows the calibration factor of the instrument to be obtained (E_{DSC}).

For the continuous quantitative determination of the sample mass change *vs.* temperature in the process of different transformations which proceed during the evolution or absorption of gaseous matter, the method of thermogravimetric analysis (TG-4433 model ultramicrobalance, Sartorius, F.R.G.) was used.

The installation scheme contained a Tsvet-110 chromatograph (U.S.S.R.) connected to the outlet from the DSC or TG unit. Argon was used as carrier gas. The method allows the relative quantities of hydrogen evolved from the hydride to be determined *vs.* temperature. As recorder, a thermoconductometric detector was used. The scheme of the installation is shown in Fig. 1. The carrier gas goes into the reference channel and the same gas which passes through the DSC or TG unit enters the working channel. At the moment the reaction is beginning, when gas evolves and enters the detector in the carrier gas flow, the detector bridge unbalances and the recorder registers the change in quality of the gas evolved with time. The instrument is calibrated against hydrogen which evolves from an IMC hydride of known composition. In this case the TG unit is used as the main unit and the quantity of hydrogen evolved is determined according to the initial sample mass. Thus the calibration factor of the instrument (E_K) is found.

Carrying out simultaneous calorimetric analysis and evolved hydrogen analysis (EHA) allows the absorbed heat and the quantity of gas evolved to be related as shown in ref. 23.

The argon flow rate and the weight of IMC hydride are chosen so that the hydrogen concentration will not influence the calibration factor of the DSC.

As a result of the experiments, DSC and EHA curves were obtained. The DSC curve characterizes the rate of heat loss and the EHA curve characterizes the hydrogen evolution rate. The quantity of hydrogen evolved from the hydride according to the EHA data was calculated from the equation

$$n = \frac{S_K}{m}\frac{R_Y}{R_X}\,0.6M_{\mathrm{IMC\text{-}H}}E_K \quad ((\mathrm{at.\ H})\ (\mathrm{mol.\ IMC})^{-1}) \qquad (1)$$

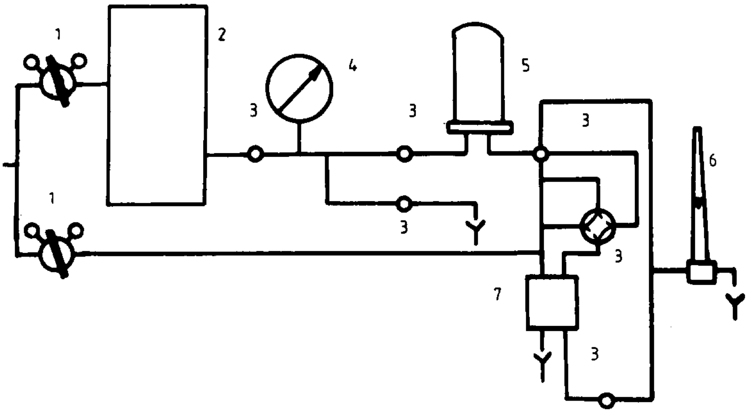


Fig. 1. Schematic diagram of the installation: 1, gas pressure regulator; 2, gas preparation unit; 3, gas valve; 4, standard pressure gauge; 5, cell with studied sample; 6, gas flowmeter; 7, thermoconductometric detector.

where S_K (cm^2) is the peak area on the recorder, m (mg) is the sample weight, R_X (mV cm^{-1}) and R_Y (mm h^{-1}) are the scale factors on the axes X and Y respectively, $M_{\text{IMC-H}}$ (g) is the molecular mass of IMC hydride and E_K (at. min^{-1}) is the instrument calibration factor.

The calculation of the peak area was carried out according to the peak height measurements:

$$S_K = \int_0^n \frac{d\alpha_K}{d\tau}\frac{R_X}{\lambda} K_K \quad (\text{cm}^2) \tag{2}$$

where $d\alpha_K/d\tau$ (cm) is the peak height of the ith measurement at time τ, K_K is the peak area normalization factor and λ (K min^{-1}) is the fixed heating rate.

The integral enthalpy is given by

$$\Delta H = \frac{\Delta H_Q M_{\text{IMC-H}}}{n/2} \times 10^{-3} \quad (\text{kJ (mol. H}_2)^{-1}) \tag{3}$$

where ΔH_Q is the enthalpy calculated according to the equation

$$\Delta H_Q = \frac{S_{\text{DSC}}}{m}\frac{R_X R_Y}{\lambda} \times 60 E_{\text{DSC}} \quad (\text{J (g IMC)}^{-1}) \tag{4}$$

Here E_{DSC} is the calorimetric calibration coefficient and S_{DSC} is the DSC peak area given by

$$S_{\text{DSC}} = \int_0^n \frac{d\alpha_Q}{d\tau} K_{\text{DSC}} \quad (\text{cm}^2) \tag{5}$$

where K_{DSC} is the DSC peak area coefficient.

The partial molar enthalpy is calculated from

$$\Delta \bar{H}_H = \frac{d\alpha_Q/d\tau}{d\alpha_K/d\tau} \quad \text{for the } n_i \text{ hydrogen atoms} \tag{6}$$

where $d\alpha_Q/d\tau$ is the heat absorption rate and $d\alpha_K/d\tau$ is the hydrogen desorption rate.

3. Results and discussion

3.1. Sorption processes in hydrogen

As a rule, absorption and desorption of hydrogen from IMC hydrides are accompanied by a change in the crystalline structure of the compound and by a phase transition at which heat is evolved or absorbed.

Typical DSC curves obtained during the sorption processes in hydrogen are shown in Figs. 2 and 3. The temperature ranges of the processes proceeding at atmospheric pressure and a fixed heating rate of 5 K min^{-1} are presented in Table 2.

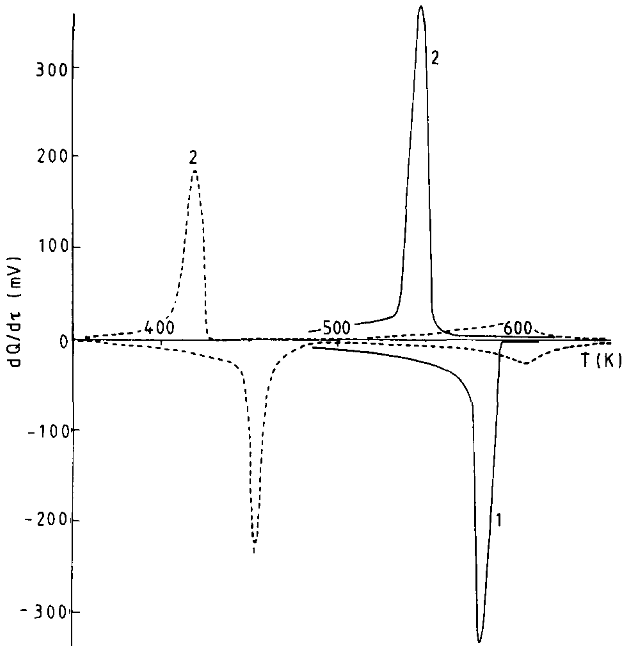


Fig. 2. DSC curves of (1) dehydrogenation and (2) hydrogenation for $ZrNiH_{3.0}$ (solid line) and $HfNiH_{3.0}$ (broken line) in hydrogen at atmospheric pressure; heating rate 5 K min^{-1}.

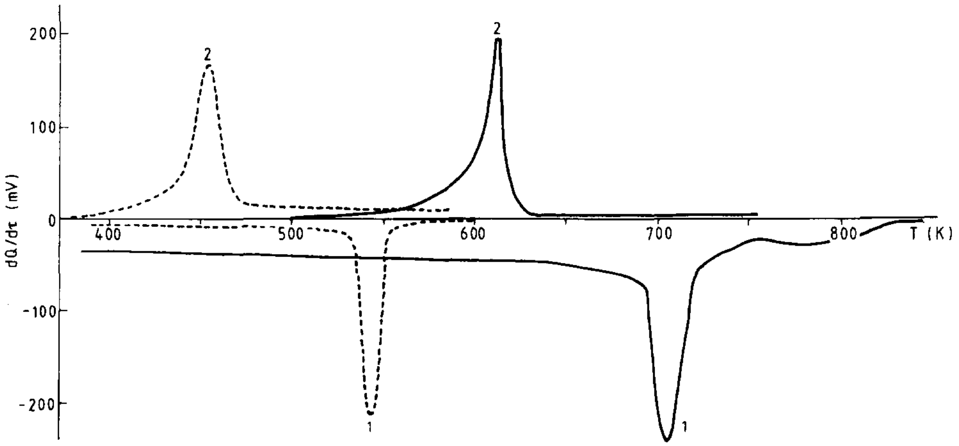


Fig. 3. DSC curves of (1) dehydrogenation and (2) hydrogenation for $ZrCoH_{3.0}$ (solid line) and $HfCoH_{3.0}$ (broken line) in hydrogen at atmospheric pressure; heating rate 5 K min^{-1}.

By comparing the data obtained from the *P–c–T* diagrams [3–9] with the X-ray phase analysis data [25, 26], it becomes possible to correlate the phase transition region (a "plateau" in the *P–c–T* diagrams) with the intervals of heat due to sorption or desorption in the DSC curves. In two-phase coexistence regions the following reactions take place:

TABLE 2

Integral enthalpies ΔH (kJ (mol. H_2)$^{-1}$) of studied systems (I) calculated according to the van't Hoff equation ($\Delta P = 0.16$–0.51 MPa) and (II) obtained by the calorimetric method (sample weight 100 mg, heating rate 5 K min^{-1}) in hydrogen

System	Reaction	x (mol. H_2)	Temperature (K)		Primary desorption II	First cycle of sorption			
			Absorption	Desorption		Absorption		Desorption	
						I	II	I	II
$HfNiH_x$	(7)	2.9	330–440	360–490	47.0	−45.4	−41.2	54.9	40.0
	(8)		450–640	510–670	41.1	−72.6	−60.8	72.4	47.2
$ZrNiH_x$	(9), (10)	2.9	470–560	490–730	77.1	−77.4	−80.6	76.6	64.2
$HfCoH_x$	(11)	2.0	370–470	400–590	61.0	−48.1	−51.9	68.7	43.5
$ZrCoH_x$	(12)	2.5	500–640	620–820	72.2	−68.1	−75.3	67.3	65.9

$$HfNiH_{3.0} = HfNiH_{1.0} + H_2 \pm \Delta H \qquad (7)$$

$$HfNiH_{1.0} = HfNi + \tfrac{1}{2}H_2 \pm \Delta H \qquad (8)$$

$$ZrNiH_{3.0} = ZrNiH_{1.0} + H_2 \pm \Delta H \qquad (9)$$

$$ZrNiH_{1.0} = ZrNi + \tfrac{1}{2}H_2 \pm \Delta H \qquad (10)$$

$$HfCoH_{3.0} = HfCo + \tfrac{3}{2}H_2 \pm \Delta H \qquad (11)$$

$$ZrCoH_{3.0} = ZrCo + \tfrac{3}{2}H_2 \pm \Delta H \qquad (12)$$

If in the P–c–T diagram the "plateau" which corresponds to reaction (10) is not pronounced compared to that corresponding to reaction (8), the sorption processes for HfNi and ZrNi are extremely different in the DSC curves.

When carrying out the sorption experiments, it is first necessary to remove the superficial oxide film which prevents the hydride from decomposition during long-term storage in air and is impermeable to gas at low temperatures. The removal of the oxide film decreases the activation energy of the subsequent hydrogenation and increases the rates of dissociative chemisorption and associative desorption [24, 27]. The temperature rise (in the medium of both hydrogen and inert gas) activates the hydride decomposition and the film becomes permeable to hydrogen. The energy barrier of the integral enthalpy of the hydrogen primary desorption (Table 2) is somewhat greater than that obtained in the subsequent cycle, the difference between the values being not more than the experimental accuracy.

In the primary heating of the hydride $ZrNiH_{3.0}$ (Fig. 4) an exo-effect is observed in the DSC curves which is accompanied by a mass increase of 0.08% (the temperature range is 350–410 K; the maximum deviation of temperature is 380 K at atmospheric pressure). This effect is due to hydrogen absorption in the quantity of 0.12 atom and is equal to 80–90 kJ (mol. $H_2)^{-1}$. The primary heating of the other systems is not accompanied by such an exo-effect.

The hysteresis character of the sorption processes causes a decrease in the maximum deviation temperature during absorption compared to that during desorption of hydrogen; for example, at atmospheric pressure and 5 K min^{-1} for the HfNi–H_2 system this decrease is 40° for a low temperature peak (reaction (7)) and 10° for a high temperature peak (reaction (8)).

In carrying out the calorimetric experiments in the hydrogen medium with the equipment used, an estimation of the gas quantity which is actually sorbed during the reaction of the IMCs did not seem to be possible; therefore the values of enthalpies obtained have a preliminary character. For the calculation of the values given in Table 2, it was accepted according to the TG analysis data obtained at atmospheric pressure of hydrogen that 2.9 moles of hydrogen take part in the process in HfNi–H_2 and ZrNi–H_2, 2.0 moles in HfCo–H_2 and 2.5 moles in ZrCo–H_2. In the table the results of the

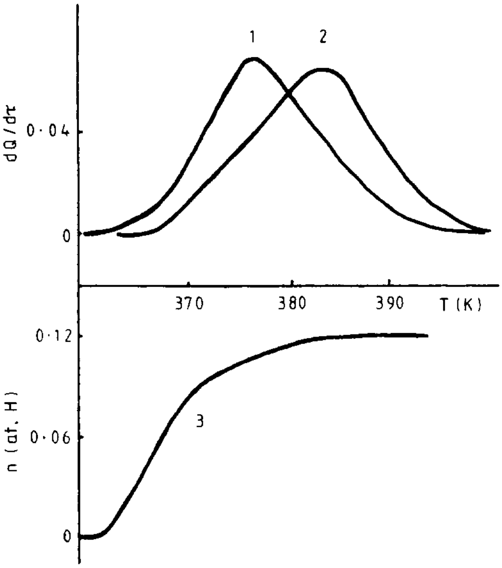


Fig. 4. DSC and TG curves of hydrogen desorption from $ZrNiH_{3.0}$ in hydrogen at a pressure of (1) 0.19 MPa, (2) 0.62 MPa and (3) atmospheric; heating rate 5 K min^{-1}.

calculation of the isosteric heats by using the van't Hoff equation are also presented.

Analysis of the data found in the literature (Table 1) shows that the assumption of a lack of temperature dependence causes a 5%–10% error at best. Comparison of the values obtained by the calorimetric method and those calculated according to the van't Hoff equation, *e.g.* for the HfNi–H_2 system, shows a 50%–60% error in the determination of enthalpy by the latter. The calculation carried out shows a limited suitability of the van't Hoff equation in general for the calculation of hydride systems as well as the erroneousness of the calculations when there is a dependence of the pressure on the hydrogen content of the IMC in a two-phase region, which in turn is confirmed by the course of the *P–c* isotherm.

According to the data in Table 2, the establishment of a correlation between ΔH_{abs} and ΔH_{des} from the calculated data is not possible. Taking into account the accuracy of the experiment (which is 3%–7%), the calorimetric integral enthalpies indicate a correlation $|\Delta H_{abs}| > \Delta H_{des}$ (in isobaric conditions an average of 10 kJ (mol. $H_2)^{-1}$). In this case the correlation of enthalpies remains in a continuous cycling process in the hydrogen medium.

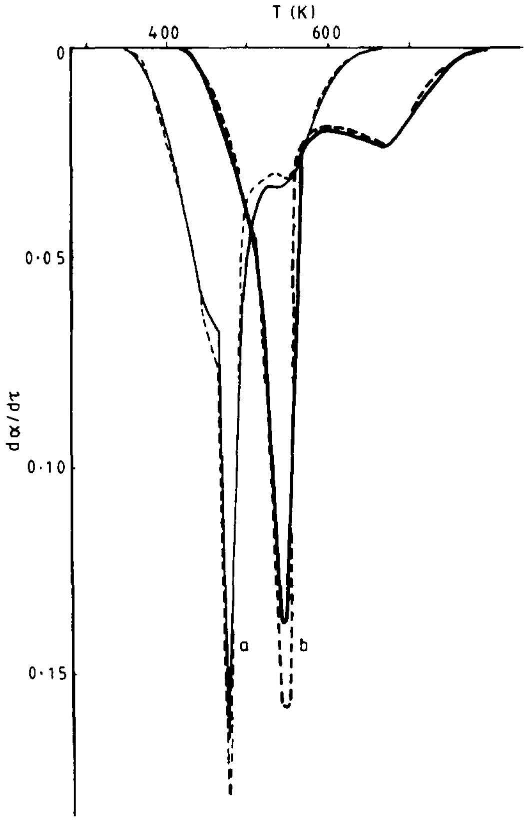
For the ZrNi–H_2 system the value of the integral entropy is 144.6 J K^{-1} (mol. $H_2)^{-1}$ in absorption and 134.0 J K^{-1} (mol. $H_2)^{-1}$ in desorption, which is close to the value of the configuration entropy for the IMC hydride, $\Delta S = 125.7 \pm 25.1$ J K^{-1} (mol. $H_2)^{-1}$ [28, 29]. The entropy effect is mainly connected with a high entropy value for gaseous hydrogen (129.9 J K^{-1} (mol. $H_2)^{-1}$ at room temperature) which is lost on introduction of hydrogen into a metallic lattice.

3.2. Desorption of hydrogen from IMC hydrides in inert gas

Figures 5 and 6 show the DSC and EHA curves obtained for the desorption of hydrogen from IMC hydrides in an argon atmosphere. The preliminary hydrogenation of the samples did not cause a change in the shape of the curves, which is practically the same for hydrogen evolved and heat absorbed. Some differences are connected with the influence of the hydride on the value of the thermal effect.

The values of the integral enthalpy of hydrogen desorption calculated according to the DSC and EHA data are presented in Table 3. When comparing the data of Tables 2 and 3, good agreement is seen for the values of the integral enthalpy of hydrogen desorption in argon and in hydrogen.

The dependence of the partial molar enthalpy of hydrogen dissolution on its content in the IMCs calculated by means of eqns. (1)–(6) is presented in Fig. 7.



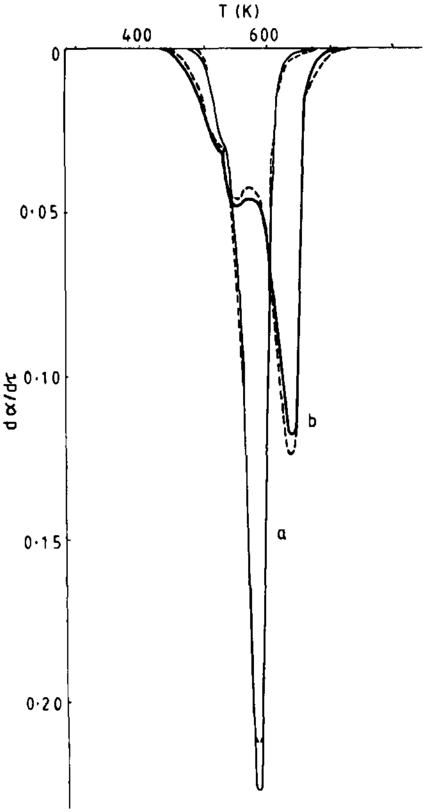


Fig. 5. Hydrogen desorption from (a) $HfNiH_{3.0}$ and (b) $ZrNiH_{3.0}$ in argon at a pressure of 0.53 MPa: solid line, DSC; broken line, EHA; heating rate 5 K min^{-1}.

Fig. 6. Hydrogen desorption from (a) $HfCoH_{3.0}$ and (b) $ZrCoH_{3.0}$ in argon at a pressure of 0.53 MPa: solid line, DSC; broken line, EHA; heating rate 5 K min^{-1}.

TABLE 3

DSC curve characteristic temperatures and enthalpies of hydrogen desorption (heating rate 5 K $\min^{-1}$, argon pressure 0.53 MPa)

System	T_0 (K)	T_{max} (K)	T (K)	$-\Delta H$ (kJ (mol. $H_2)^{-1}$)
HfNi–H_2	350	420	680	48.7 ± 3.2
ZrNi–H_2	400	530	780	83.6 ± 4.5
HfCo–H_2	420	560	690	59.0 ± 2.9
ZrCo–H_2	450	620	720	76.6 ± 4.4

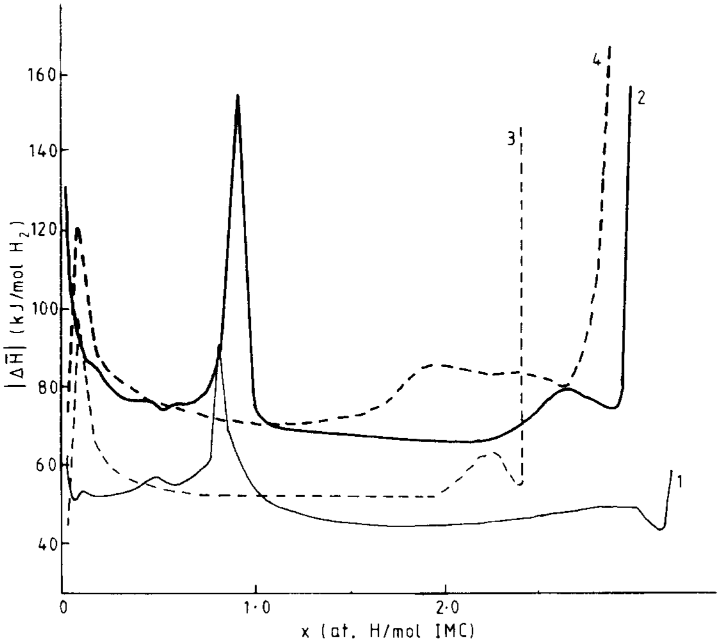


Fig. 7. Plot of $|\Delta\bar{H}_H|$ against hydrogen content in (1) HfNi, (2) ZrNi, (3) HfCo and (4) ZrCo; argon pressure 0.53 MPa.

In the crystalline lattice of CrB there are two different types of vacancies, the number of tetrahedral ones being twice as large as that of octahedral ones [15]. In the nickel-containing system the lattice type remains the same on hydrogen absorption, and because the second "plateau" of the *P–c* isotherm [3] is about twice as long as the first one, the authors of ref. 3 assume that the octahedral vacancies are filled first.

It is necessary to take into account that, in connection with small changes in conversion in the α solution and β hydride regions while using a small weight (about 100 mg) because of the small volume of the pans used in this calorimeter design, the dependence of the partial molar enthalpy of hydrogen dissolution obtained in these regions has a qualitative or semiquantitative character. However, this allows the data obtained to be compared with the data found in the literature from the results of studying IMC hydrides of other structural types. The main difficulty of the investigation of the IMC–H_2 system in the region of hydrogen content where the equilibrium pressure is extremely small [16] was overcome by thermoconductometric determination of the hydrogen evolved. It is necessary to point out that desorption is a quasi-equilibrium process and the danger of formation of a metastable hydrogen distribution in isobaric conditions does not arise.

In the primary region of hydrogen sorption a sharp decrease in the value of the partial molar enthalpy of hydrogen dissolution is observed whereas the hydrogen content in the IMC increases, which agrees well with the results for other IMCs (see *e.g.* refs. 18, 21 and 30). The decrease $|\Delta\bar{H}_H|$ in the region $0<x<0.1$–0.2 indicates that between the hydrogen atoms repulsive forces will appear which cause an even distribution of atoms in the metallic matrix of the IMC.

In the α solution region ($0<x<0.23$–0.25) the hydrogen chemisorption process takes place. The values of $|\Delta\bar{H}_H|=\Delta\bar{H}_H^I$ for dissolved hydrogen in this region are given in Table 4. When the hydrogen content increases to $x=0.23$–0.25, the $|\Delta\bar{H}_H|$ value decreases sharply to $\Delta\bar{H}_H^{pII}$; in this case hydrogen dissolves as an α solution in the IMC.

After the formation of the α solution, during further saturation with hydrogen in the region $0.25<x<0.8$, a certain constancy of $|\Delta\bar{H}_H|$ is observed which is connected with the first "plateau" on the P–c isotherm [3] (for nickel-containing hydrides) and with the phase transformation "α solution–monohydride $HfNiH_{1.0}$ or $ZrNiH_{1.0}$". The existence of a monohydride phase was already proved by X-ray diffraction *in situ* studies [25, 26]. In the region of hydrogen content $0.8<x<1.0$ a peak of the partial molar enthalpy of hydrogen dissolution in the IMC is reached. The increase and subsequent sharp decrease in exothermicity are caused by the completion of the formation of a new phase, $HfNiH_{1.0}$ or $ZrNiH_{1.0}$, and by the commencement of the transitory region from the monohydride phase to the β phase. The range of $\Delta\bar{H}_H^{II}$ values is given in Table 4.

The two-phase region ($1.0<x<2.1$) for the nickel-containing IMC hydrides is characterized by the constancy of the partial molar enthalpy ($\Delta\bar{H}_H^{pIII}$, Table 4).

TABLE 4

Partial molar enthalpies $\Delta\bar{H}_H$ (kJ (mol. H_2)$^{-1}$) of hydride decomposition

System	$-\Delta\bar{H}_H^I$	$-\Delta\bar{H}_H^{pII}$	$-\Delta\bar{H}_H^{II}$	$-\Delta\bar{H}_H^{pIII}$	$-\Delta\bar{H}_H^{III}$
HfNi–H_2	60–70	50–60	70–90	45–50	40–50
ZrNi–H_2	140–160	75–80	130–160	60–70	100–120
HfCo–H_2	90–110	45–55			150–170
ZrCo–H_2	120–140	65–70		75–85	160–170

In the region near the boundary (with the $\alpha+\beta$ region) a slight decrease in $|\Delta\bar{H}_H|$ (by 8–10 kJ (mol. $H_2)^{-1}$) is observed. Comparison with the P–c–T data has shown that precisely in these regions a change in inclination of isotherms takes place. It is possible that the cause of this phenomenon is the non-homogeneity of the sample formed in the process of hydrogenation.

In ref. 30 in the region $0.2<x<0.4$ for the $LaNi_5$–H_2 system (*i.e.* near the boundary of the α and $\alpha+\beta$ regions) a discontinuity was discovered in the dependence of the partial molar enthalpy of hydrogen dissolution on its content in the IMC, which is connected with a phase transition. The authors explain the sharp change in $\partial(\Delta H)/\partial x$ by a strong attraction between hydrogen atoms in this region and by a possible formation of some hydride in the α solution region (up to the formation of the two-phase boundary).

For the nickel-containing hydrides in the region of hydrogen content $2.5<x<3.0$ there is an enriched part of the two-phase region. The sharp increase and subsequent decrease in $|\Delta\bar{H}_H|$ are due to the completion of hydride formation ($\Delta\bar{H}_H^{III}$).

In the HfCo–H_2 and ZrCo–H_2 systems the number of octahedral vacancies is half that of tetrahedral ones and it is possible that the first desorption peak (Fig. 6) in the DSC curves (both in argon and in hydrogen) is connected with the hydrogen desorption from octahedral positions. The desorption from the vacancies of tetrahedral type proceeds with a simultaneous reconstruction of the crystalline lattice.

In the region of coexistence of two phases in the HfCo–H_2 system ($0.4<x<1.8$–2.1) the partial molar enthalpy is constant.

The phase transition on hydrogen introduction into HfCo proceeds in a single stage; that into HfNi, because of its lower symmetry, in two stages. The character of the change in partial molar enthalpy for HfCo corresponds completely to the shape of the isotherm on the P–c diagram [3].

The character of the change in partial molar enthalpy on hydrogen desorption from $ZrCoH_{3.0}$ is similar to that obtained for $HfCoH_{3.0}$ (the two differ in the existence of two β hydride phases in the former). In the region of coexistence of the two phases, $\alpha+\beta_1$ at a hydrogen content $0.25<x<1.65$ ($\Delta\bar{H}_H^{pII}$) and $\beta_1+\beta_2$ at a hydrogen content $2.2<x<2.5$ ($\Delta\bar{H}_H^{pIII}$), there is no dependence of $\Delta\bar{H}_H$ on the hydrogen concentration of the IMC. In the region of the β_2 phase the subsequent saturation with hydrogen up to 3.0 atoms causes a sharp increase in the $|\Delta\bar{H}_H|$ value. The data obtained are in accordance with the P–c–T measurements [3]. In the regions near the boundaries α–$(\alpha+\beta_1)$ and $(\beta_1+\beta_2)$–β_2 the partial molar enthalpy of dissolution has a discontinuous character. The increase in $\Delta\bar{H}_H$ in the hydrogen concentration region $1.7<x<1.9$ corresponds to the β_1–β_2 phase transition. Comparison of the calorimetric results with those calculated from P–c–T data partial molar enthalpies for the ZrCo–H_2 system [7] has shown that for the experimental method the values are greater by 8–10 kJ. This may be due to the fact that the technique used allows the measurements to be carried out with a greater accuracy in the regions of phase transformations.

4. Conclusions

Studies carried out on the IMC–H_2 systems based on zirconium and hafnium with nickel and cobalt are of interest from the point of view of the importance of these systems both as absorbents and catalysts and as a prototype for developing a technique to study the physics and chemistry of hydrides.

As regards the number of theoretical models, the thermodynamics of the IMC hydrides is now considerably advanced, though not sufficiently so for the interpretation of many irregularities obtained experimentally. The combination of thermoanalytical methods in physicochemical studies allows the fullest information to be obtained about the course of absorption or desorption processes. It also appeared that an advantage of the calorimetric technique in obtaining the thermodynamic characteristics of IMC–H_2 systems is the possibility of avoiding errors due to the non-ideal behaviour of the IMC–H_2 system. In this case the use of an instrument which works in the differential mode allows the main experimental errors to be avoided which exist in many calorimetric experiments, without making additional corrections for the thermal effect of gas introduction into the system and for the pressure change during the sorption or desorption experiments, which is especially important for the single-phase regions. Temperature scanning allows the time expenditure to be cut for determination of enthalpy. The determination of the hydrogen quantity by the thermoconductometric method increases the accuracy of the experiment compared to Sieverts' method used earlier.

The values of integral enthalpy obtained by the calorimetric method are somewhat higher than those determined from the P–c–T measurements, which is due to the ΔH_H values in single-phase regions in the DSC measurements.

The character of the change in partial molar enthalpy of hydrogen dissolution in IMCs is correlated with the dependence discovered for other systems.

There is a tendency for the value of the partial molar enthalpy of hydrogen dissolution to be decreased with an increase in hydrogen content in the α solution. When hydrogen accumulates, primary filling of vacancies takes place, preferentially of those which are surrounded by atoms of a hydride-forming metal. In the regions near the $\alpha-(\alpha+\beta)$ and $(\alpha+\beta)-\beta$ boundaries the partial molar enthalpy has a discontinuous character. In the phase transformation region the $\Delta\bar{H}_H$ value does not depend on the composition when the laws of ideal dissolution are observed for the given IMC–H_2 system, the region conforming to the "plateau" of the P–c–T diagram. When a new phase is formed (monohydride, β-hydride), $|\Delta\bar{H}_H|$ increases.

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