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Synthesis, properties and Mössbauer study of $ZrFe_{2-x}Ni_x$ hydrides ($x = 0.2–0.8$)

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ABSTRACT

Interaction of $ZrFe_{2-x}Ni_x$ ($x = 0.2$, 0.4, 0.6, and 0.8) pseudobinary intermetallic compounds with hydrogen was studied. It was found that these compounds can accumulate up to 1.7–1.8 wt.% H_2 at room temperature. For all investigated $ZrFe_{2-x}Ni_x$–H_2 systems, thermodynamic functions of the β-hydride → α-solution phase transition and changes of metal matrix volume during formation of hydrides were calculated. It was shown that increase in Ni content leads to reduction of both desorption pressures and starting pressures of reaction with hydrogen in the first hydrogenation cycle compared to $ZrFe_2$. Mössbauer investigations, which have been carried out for all alloys as well as hydrides, revealed that Curie temperatures (T_c) and average hyperfine fields (HF_{av}) of initial alloys decrease with Ni content increase, while isomer shifts (IS) remain constant. Absorption of H_2 results in significant increase in IS together with some increase in T_c and HF_{av} for all samples. The decomposition of the hydride phases to intermetallic phases while heating from 78 K to room temperature was found to be a two-step process involving formation of the hydride phases with intermediate hydrogen content.

1. Introduction

A significant number of works was devoted to investigation of hydrogen interaction with Laves phases ZrB_2 (B = transition metal) in the recent 50 years. This can be accounted for their attractive hydrogen storage capacity and the stability to hydrogenolysis up to high temperatures. The application of high hydrogen pressures makes it possible to synthesize a new hydride phases and to enlarge our knowledge of hydrides chemistry.

$ZrFe_2$ is a strong ferromagnetic with the temperature of magnetic ordering $T_c = 630$ K [1]. The Mössbauer investigations of this compound were carried out in several works [2–4]. Some works were dealt with the influence of substitution of Fe by other elements (Al [5], Si [6], Mn [7], Co [8,9]) in $ZrFe_2$ on hyperfine magnetic interactions. Investigations of $ZrFe_2$ doped with Ni were performed in works [10,11].

However, Mössbauer studies of pseudobinary $ZrFe_2$-based hydrides were described insufficiently because of their instability at ambient conditions. Although $ZrFe_2$ hydride was investigated in Ref. [4], $ZrFe_{2-x}Ni_x$ hydrides were not studied yet. The only Mössbauer research, which has been carried out on $ZrFe_{2-x}Ni_x$ hydrogen α-solutions, was reported in Ref. [11].

Thus, the investigation of the hydrogen interaction with pseudobinary $ZrFe_{2-x}Ni_x$ ($x = 0.2$, 0.4, 0.6, and 0.8) intermetallics at high hydrogen pressures and hyperfine magnetic interactions in these alloys and their hydrides was the main goal of the present work.

2. Experimental

Samples were prepared by alloying mixtures of pure initial metals in the arc furnace on a copper water-cooled bottom with unspent tungsten electrode in an argon atmosphere at a pressure of 1–1.5 atm. The samples were remelted three (or four) times to insure homogeneity followed by annealing for 240 h at 1173 K in evacuated quartz tube and quenching in cold water. The structure of the alloys was examined by powder X-ray diffraction (XRD) on DRON-3 diffractometer (Cu K_α). The refinement of diffraction profiles was performed using the Rietveld method.

The EDX analysis of the chemical composition and the homogeneity of alloys were performed on LEO Supra 50VP SEM (cathode with field electron emission) equipped with Oxford INCA Energy + system (the resolution of the Si (Li) detector is 129 eV on Mn K_α line 5.894 eV).

The hydrogen sorption properties were studied by measuring PC (pressure–composition) absorption and desorption isotherms in a high hydrogen pressure apparatus (up to 3000 atm). A detailed description of the apparatus and the experimental procedure could be found elsewhere [12].

Thermodynamic parameters of desorption reaction were calculated with van't Hoff equation using fugacity values f_p corresponding to experimental dissociation pressure values p at different temperatures T:

$$RT\ln(f_p) = \Delta_r H - T\Delta_r S$$

All hydride samples were passivated before XRD and Mössbauer investigations. The high pressure vessel was cooled down to 78 K in liquid nitrogen (to prevent possible desorption) and the pressure was reduced to the atmospheric value. Then hydrides were dwelled for at least an hour in the open air at 78 K. After that, the samples were taken out from vessel and stored in liquid nitrogen. This passivation

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Table 1
XRD data of $ZrFe_{2-x}Ni_x$ and corresponding hydrides.

Compound	a (Å)	V (Å^3)	ΔV/V (%)
$ZrFe_2$ [16]	7.064(1)	352.46(3)	
$ZrFe_2H_{3.5}$ [16]	7.595(3)	438.1(3)	24.3
$ZrFe_{1.8}Ni_{0.2}$	7.058(1)	351.59(1)	
$ZrFe_{1.8}Ni_{0.2}H_{3.5}$	7.576(1)	434.90(5)	23.7
$ZrFe_{1.6}Ni_{0.4}$	7.052(1)	350.74(1)	
$ZrFe_{1.6}Ni_{0.4}H_{3.6}$	7.596(1)	438.33(4)	25.0
$ZrFe_{1.4}Ni_{0.6}$	7.041(1)	349.03(1)	
$ZrFe_{1.4}Ni_{0.6}H_{3.6}$	7.607(1)	440.22(3)	26.1
$ZrFe_{1.2}Ni_{0.8}$	7.032(1)	347.65(2)	
$ZrFe_{1.2}Ni_{0.8}H_{3.7}$	7.600(1)	438.99(4)	26.3

ΔV/V – relative increase in unit cell volume of intermetallic at hydrogenation.

technique of hydrides with air oxygen is effective and allows to slow down considerably the decomposition process of hydride phases with high dissociation pressures (>100 atm) at room temperature [13–16].

The crystal structure of the hydrides was examined by XRD. The samples were removed from liquid nitrogen immediately before the measurements, which were carried out at room temperature for the shortest time possible in order to avoid their decomposition. The XRD data of hydrides was used later for an adjustment of PC-isotherms so as to take into account the volume change of the sample upon hydrogenation.

The Mössbauer spectra were obtained on an electrodynamic type spectrometer with constant acceleration (Ms-1104Em, Rostov-Na-Donu, Russia) and ^{57}Co(Rh) as a source at 78 and 298 K. All isomer shifts (IS) are given relative to α-Fe at room temperature. An average error in IS values was ±0.05 mm/s.

3. Results and discussion

3.1. Hydrogen sorption properties

The substitution of Fe by Ni in $ZrFe_2$ leads to the decrease of the lattice parameters of cubic C15 Laves phase (Table 1) in accordance with metal atomic radii (R_{Fe} = 1.26 Å, R_{Ni} = 1.24 Å) and correlates well with the data obtained in Ref. [5,11,17]. According to the EDX analysis, the composition of all samples corresponded to calculated one.

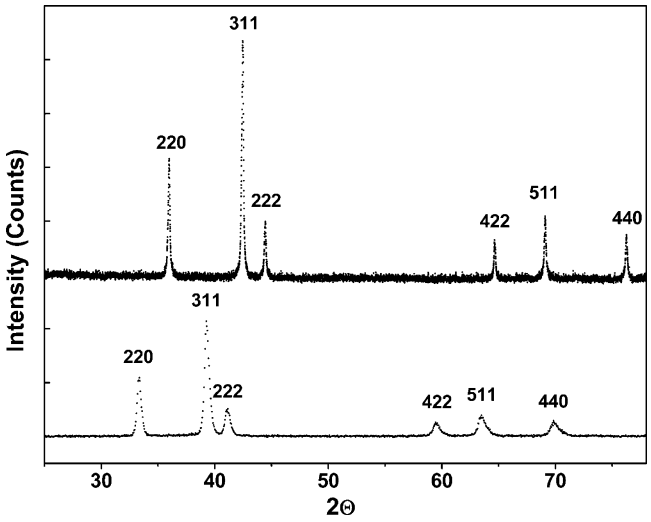

Fig. 1. XRD patterns of $ZrFe_{1.8}Ni_{0.2}$ (top) and $ZrFe_{1.8}Ni_{0.2}H_{3.5}$ (bottom).

The XRD patterns of $ZrFe_{1.8}Ni_{0.2}$ and the corresponding hydride $ZrFe_{1.8}Ni_{0.2}H_{3.5}$ are shown in Fig. 1 as an example. Absorption of hydrogen did not change the crystal structure of intermetallics but led to an increase of their unit cell volumes of 24–26%. The XRD data of $ZrFe_{2-x}Ni_x$ hydrides is also shown in Table 1. A small increase in hydrogen capacity of alloys was observed with increasing Ni content. Accordingly, relative increase in unit cell volume of alloys after hydrogenation (ΔV/V) was also observed.

Hydrogen desorption isotherms for $ZrFe_{2-x}Ni_x$–H_2 systems at various temperatures are shown in Fig. 2; hydrogen sorption properties of $ZrFe_{2-x}Ni_x$ are listed in Table 2. As follows from this data,

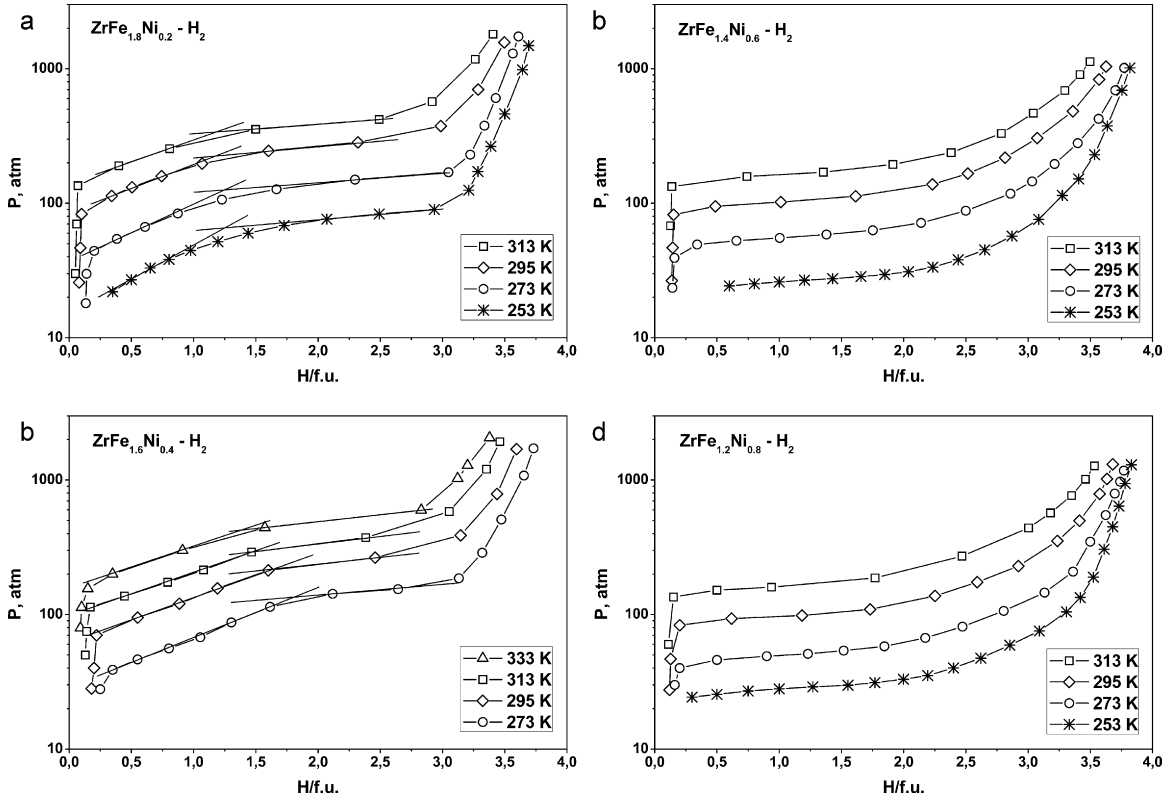

Fig. 2. Desorption isotherms in $ZrFe_{2-x}Ni_x$–H_2 systems at various temperature: (a) x = 0.2; (b) x = 0.4; (c) x = 0.6; (d) x = 0.8.

Table 2
Hydrogen sorption properties of $ZrFe_{2-x}Ni_x$.

Compound	P_0 (atm)	P_1 abs/des (atm)	P_e abs/des (atm)	H/f.u.$_{press}$/wt.% H_2	ΔH (kJ/mol H_2)	ΔS, J/(K mol H_2)
$ZrFe_2$ [16]	800	1120/–	690/325	3.5_{1800}/1.72	21.3	121
$ZrFe_{1.8}Ni_{0.2}$	700	560/140	355/175	1.2_{200}/0.6	22.6 ± 0.8	120 ± 4
		660/245	510/280	3.5_{1550}/1.72	20.8 ± 0.7	119 ± 4
$ZrFe_{1.6}Ni_{0.4}$	700	520/95	375/120	1.6_{215}/0.78	22.0 ± 0.7	115 ± 3
		590/225	455/255	3.6_{1700}/1.74	18.7 ± 0.9	111 ± 5
$ZrFe_{1.4}Ni_{0.6}$	600	650/95	350/120	3.6_{1050}/1.77	21.6 ± 0.8	114 ± 4
$ZrFe_{1.2}Ni_{0.8}$	600	705/100	435/115	3.7_{1300}/1.80	21.7 ± 0.6	114 ± 3

P_0 – starting pressure of reaction with hydrogen in first hydrogenation cycle at 295 K, P_1 – equilibrium absorption and desorption plateau pressures in first cycle at 295 K, P_e – equilibrium absorption and desorption plateau pressures of activated sample at 295 K. H/f.u.$_{press}$ – hydrogen storage capacity at a giving pressure (press) and temperature of 295 K.

desorption pressures and starting pressures of initial hydrogenation decrease while hydrogen capacity increases with increasing Ni content.

The shape of the desorption isotherms for $ZrFe_{1.8}Ni_{0.2}$ and $ZrFe_{1.6}Ni_{0.4}$ alloys differs greatly from that for $ZrFe_{1.4}Ni_{0.6}$ and $ZrFe_{1.2}Ni_{0.8}$ alloys, which exhibit only one slope of plateau in the two-phase region, whereas in the case of $x = 0.2$ and 0.4 the whole plateau can be represented by two differently sloping regions, identified by straight lines in Fig. 2. According to [18] such a shape of an isotherm indicates the existence of the two hydride phases on the plateau. At 295 K the compositions corresponding to the first hydride phase can be expressed as $ZrFe_{1.8}Ni_{0.2}H_{1.2}$ and $ZrFe_{1.6}Ni_{0.4}H_{1.6}$, the second phase – $ZrFe_{1.8}Ni_{0.2}H_{3.5}$ and $ZrFe_{1.6}Ni_{0.4}H_{3.6}$. Similar formation of several hydride phases was reported repeatedly, e.g. [19,20]. Alternatively, it is possible to suppose the formation of the extended solid solution of H_2 in the $ZrFe_{1.8}Ni_{0.2}$ and $ZrFe_{1.6}Ni_{0.4}$ alloys.The occurrence of two plateaux makes it difficult to analyze the influence of nickel addition on the hydrogen desorption enthalpy of the $ZrFe_{2-x}Ni_x$–H_2 systems. As follows from the obtained data, the substitution of iron for nickel does not change markedly the value of the reaction enthalpy of hydrogen desorption. The decrease of unit cell volume of alloys with increasing Ni content (Table 1) should lead to destabilization of hydride phases. However, absorption and desorption pressures and starting pressures of $ZrFe_{2-x}Ni_x$ reaction with hydrogen are lower than those of $ZrFe_2$ [16]. Additional study may help to elucidate this behavior as well as to explain some differences in desorption pressures, hydrogen capacities and β-hydride → α-solution phase transition enthalpies of these alloys obtained in this work and reported previously in Ref. [17]. The authors of Ref. [17] tried to reduce the stability of $ZrFe_2$-based hydrides by substitution of Fe by Ni and found that increasing Ni content led to increase of hydrogen desorption pressures due to reduction of unit cell volume of alloys. Authors of Ref. [16] reported that the equilibrium desorption pressure of $ZrFe_2$ is 325 atm at 296 K. Thus, it seems unlikely that the substitution of 10 at.% Fe by Ni in $ZrFe_2$ ($ZrFe_{1.8}Ni_{0.2}$) may lead first to decrease of equilibrium desorption pressure by 2 orders – to ~3 bar (303 K) [17], and then to increase of desorption pressure.

3.2. Mössbauer investigations

3.2.1. Intermetallic compounds

The Mössbauer spectra of $ZrFe_{2-x}Ni_x$ measured at 78 K and hyperfine field (HF) distribution curves P(H) are shown in Fig. 3a–d. The hyperfine field distributions are to become wider with x increase.

As it is follows from Fig. 3a–d, the Curie temperatures (T_c) decreased with Ni content increase, which agrees well with the previous data on magnetism in this system [1]. All samples are characterized by wide HF distributions. This could be explained by magnetic dilution because of substitution of Fe by Ni, which was reported to be non-magnetic in Laves phases [21]. Accordingly, the contributions of spectral paramagnetic components increase with Ni content increase.

Average hyperfine fields (HF_{av}) were also considerably decreased with Ni content increase (from 190 to 100 kOe for compositions with $x = 0.2$ and $x = 0.8$, accordingly) that correlates with the data obtained in [10,11]. This could be explained by the fact that magnetic properties of Laves phases ZrB_2 are caused by significant electrons transfer from less electronegative Zr to more electronegative B-component (Fe or Ni). For Ni, unlike Fe, this transference leads to filling of the d-band and, thus, increase in Ni content leads to HF_{av} decrease [3].

Isomer shifts ($\delta = -0.08$ mm/s at $T = 78$ K), in the range of accuracy, were found to be insensitive to Ni content for all intermetallics, which agrees with literature data [10]. It is justifiable because the Ni and Fe atoms differ from each other only in configuration of the 3d-electrons which influence weakly the isomer shift.

The Mössbauer spectrum of $ZrFe_{1.8}Ni_{0.2}$ was composed of two Zeeman sextets with relative area ratio of 1:3 and the HF distribution (Fig. 3a). The sextets (subspectra 1 and 2 in Fig. 3a) of different apparent quadrupole shifts and HF but identical IS ($\delta = -0.08$ mm/s at $T = 78$ K) correspond to the two Fe sites in a cubic C15 Laves phase, which are distinguishable if [1 1 1] is the direction of easy magnetisation axis, as it is in parent $ZrFe_2$ [2,4]. The presence of the HF distribution is pointing out on co-existence of [1 0 0] easy magnetisation axis in the alloy.

If Ni content is $x \geq 0.4$, magnetic components of Mössbauer spectra were fitted by HF distributions only. This assumes the [1 0 0] easy magnetisation axis for these intermetallics. Therefore, the easy magnetisation axis changes its direction from [1 1 1] to [1 0 0] as the Ni concentration increases from $x = 0$ to $x = 0.4$. This agrees well with the previous Mössbauer investigations on substituted $ZrFe_2$ based intermetallics, viz. $ZrFe_{2-x}Al_x$ [5], $ZrFe_{2-x}Si_x$ [6], $ZrFe_{2-x}Co_x$ [8,9].

3.2.2. Hydrides

The Mössbauer spectra of $ZrFe_{2-x}Ni_x$ hydrides measured at 78 K and corresponding HF distributions P(H) are shown in Fig. 4a–d. Note that spectral components are significantly broadened.

Hydrogen absorption leads to large increase in IS more than 0.60 mm/s compared to alloys. At the average value of $\delta = 0.58$ mm/s at 78 K, the isomer shifts of hydrides are independent of Ni content. This value is close to the one reported for $ZrFe_2H_{3.5}$ [4]. For the latter, this unusually large for metal-like compounds IS was explained by a combination of two factors: firstly, it is an increase in the unit cell volume at hydrogenation, and, secondly, there is some additional reduction of the s-electrons charge density at the Fe nuclei at hydrogen absorption because of partial transference of s-electrons from Fe nuclei to hydrogen atoms, i.e. occurrence of bond ionicity. With regards to close values of hydrogen capacities for all $ZrFe_{2-x}Ni_x$ alloys (3.5–3.7 H/f.u.) and similar relative unit cell volume changes ($\Delta V/V = 24$–26%), it is reasonable to assume that the above factors are responsible for the large IS observed as well.

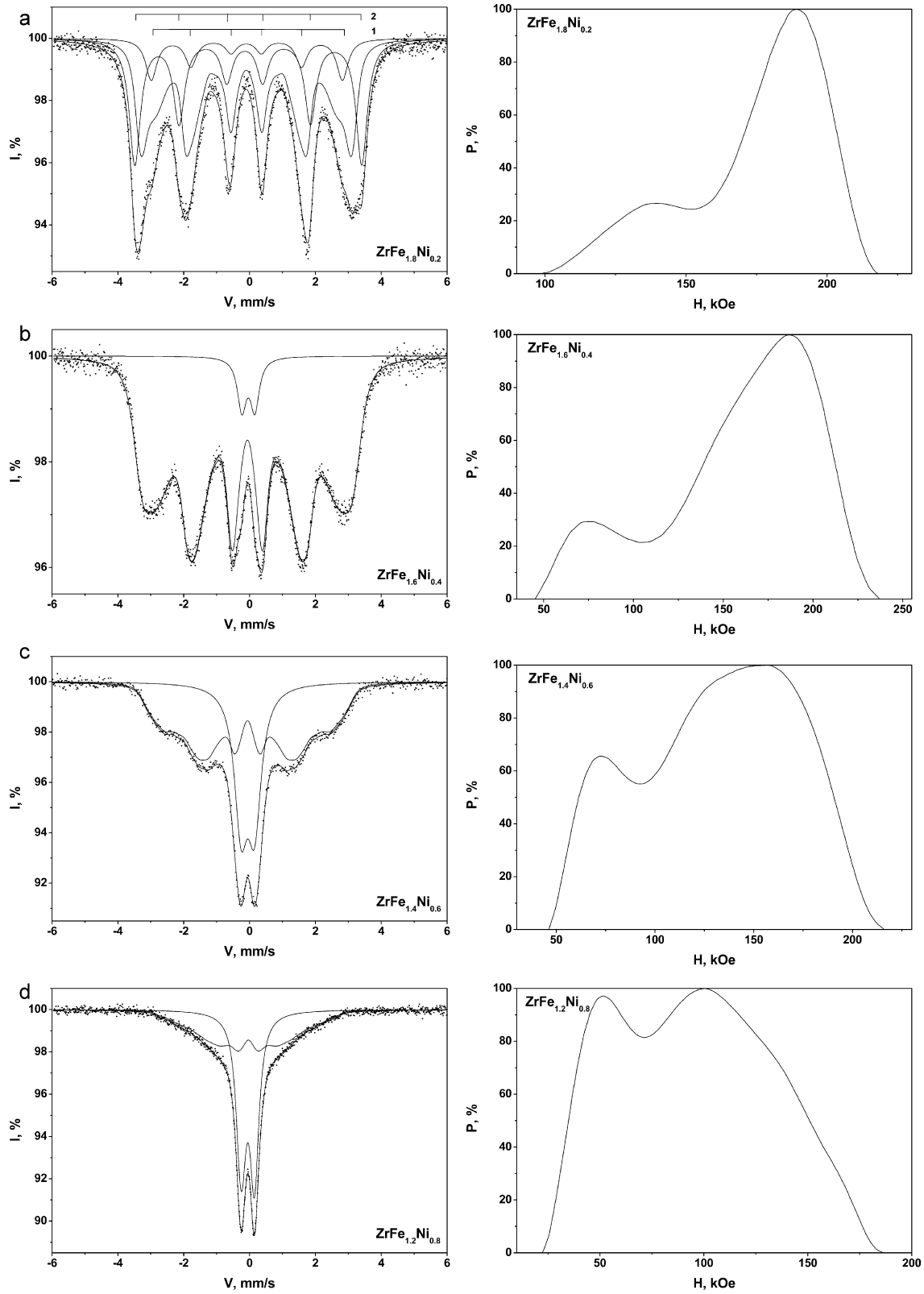

Fig. 3. Mössbauer spectra of $ZrFe_{2-x}Ni_x$ at 78 K and hyperfine field distribution curves P(H): (a) $x = 0.2$; (b) $x = 0.4$; (c) $x = 0.6$; (d) $x = 0.8$.

As it follows from Fig. 4a–d, spectra of all hydrides are magnetically splitted at 78 K. Thus, formation of hydrides resulted in T_c increase compared to intermetallics. HF_{av} increased up to 270–280 kOe. Here again, the similar increase in HF value has been previously observed for hydrogenated $ZrFe_2$ [4] that was explained by increase in magnetic moment of Fe atoms in hydrides.

By measurements of Mössbauer spectra while heating the $ZrFe_{1.4}Ni_{0.6}H_{3.6}$ sample from 78 K to room temperature and further dwelling under ambient conditions, a two-step process of hydride phase decomposition was revealed. The spectra at different stages of the decomposition process are shown in Fig. 5: (a) after dwelling under ambient conditions for one day (measured at 298 K); (b)

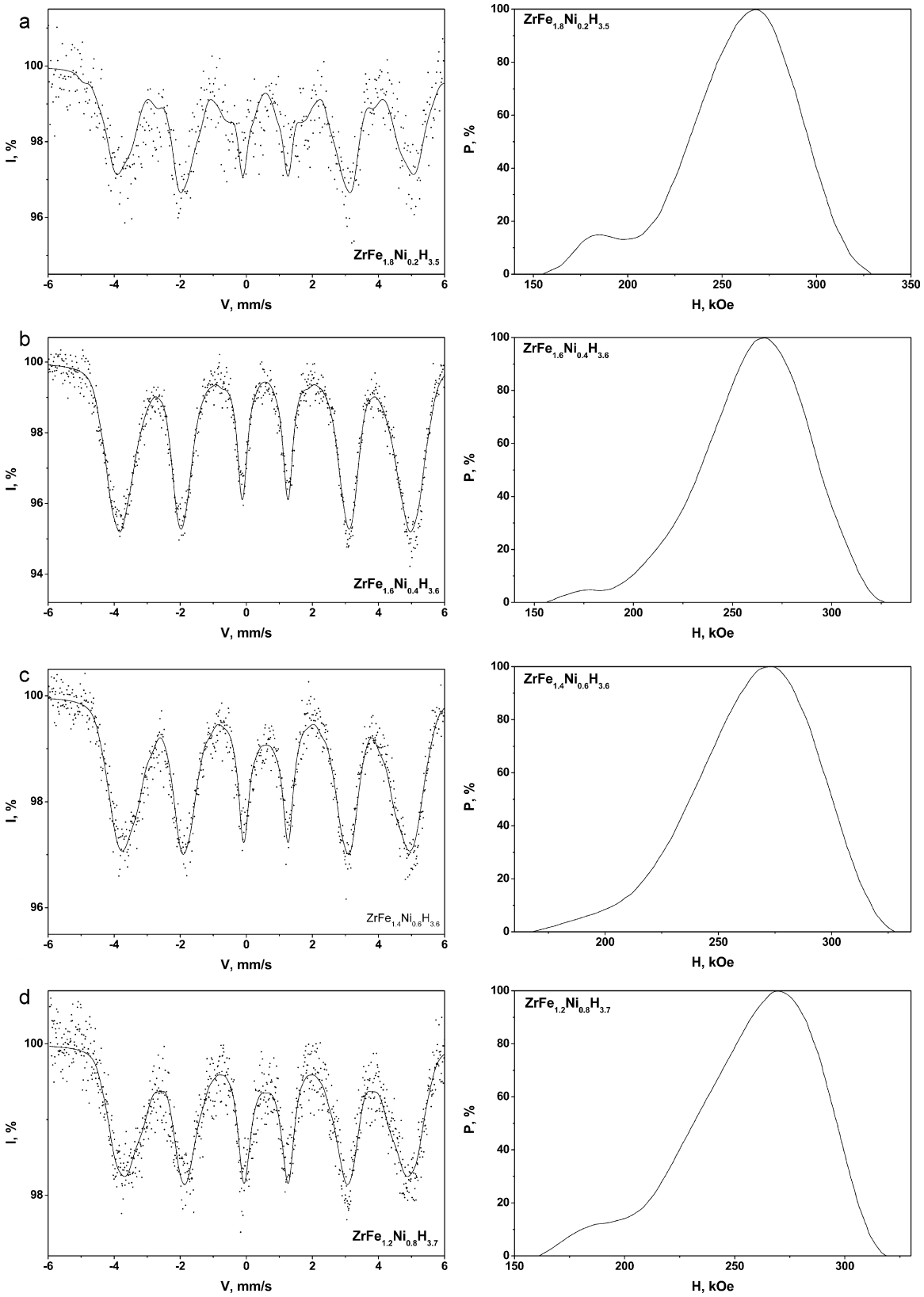

Fig. 4. Mössbauer spectra of $ZrFe_{2-x}Ni_x$ hydrides at 78 K and hyperfine field distribution curves P(H): (a) $x = 0.2$; (b) $x = 0.4$; (c) $x = 0.6$; (d) $x = 0.8$.

after two days under ambient conditions (298 K); (c) after two days under ambient conditions (78 K).

As one can see, dwelling of initial hydride phase under ambient conditions leads to its decomposition to another intermediate hydride phase with lower hydrogen content (quadrupole doublet in Fig. 5a). Its content reaches only 50% for day of dwelling what confirms the efficiency of hydride passivation with air oxygen. The T_c of the intermediate hydride phase is lower than that of initial hydride phase which was found to be magnetically ordered at 298 K (HF distribution in Fig. 5a). On the contrary, the intermediate hydride

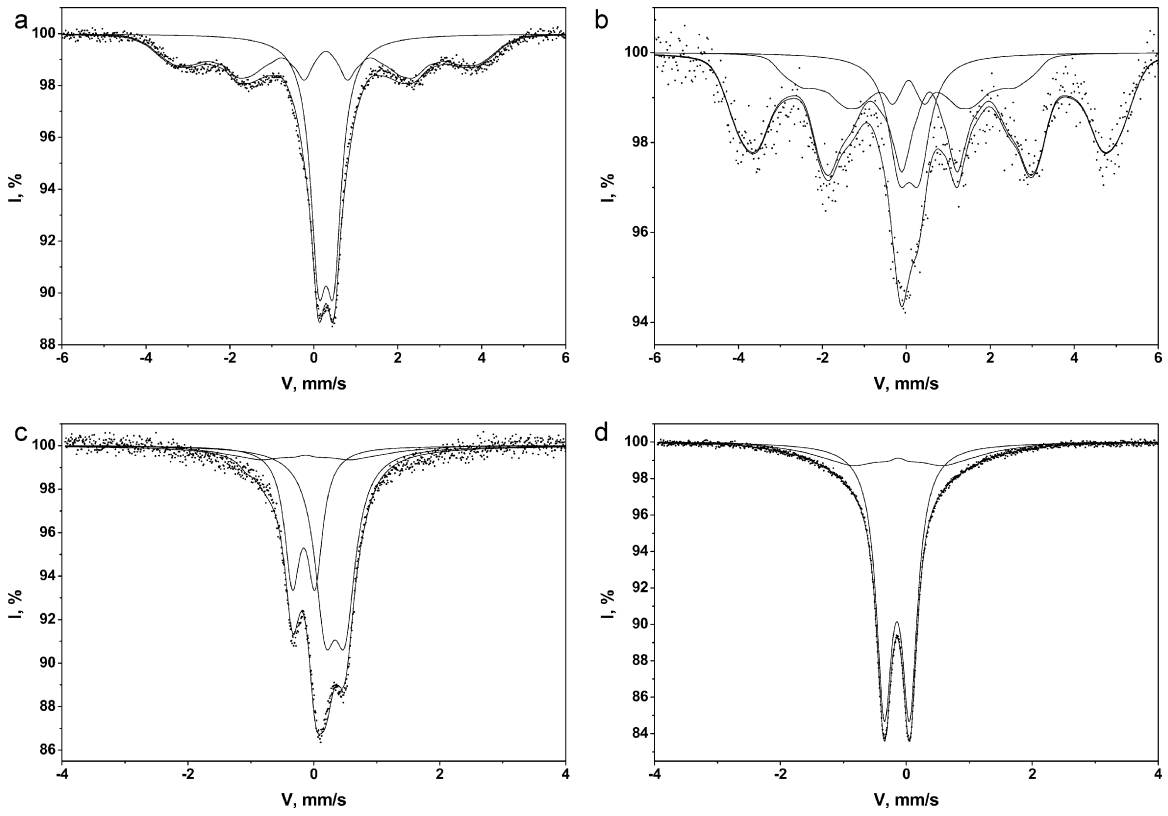

Fig. 5. Mössbauer spectra at different stages of the decomposition process of $ZrFe_{1.4}Ni_{0.6}H_{3.6}$: (a) after dwelling under ambient conditions for one day (measured at 298 K); (b) after two days under ambient conditions (298 K); (c) after two days under ambient conditions (78 K); (d) Mössbauer spectrum of $ZrFe_{1.4}Ni_{0.6}$ (298 K).

is paramagnetic at room temperature. At $\delta = 0.30$ mm/s at 298 K, the IS of this phase is lower than that of the initial hydride phase ($\delta = 0.40$ mm/s; 298 K), which presumably correlates with its lower hydrogen content (Fig. 5a).

After two days, the initial hydride decomposed completely and only hydride with lower hydrogen content remained, which underwent further decomposition to the parent intermetallic phase (Fig. 5b). The spectrum (Fig. 5b) was fitted by two quadrupole doublets and HF distribution. One of the doublets ($\delta = -0.18$ mm/s) and HF distribution ($\delta = -0.17$ mm/s) correspond exactly to initial intermetallic $ZrFe_{1.4}Ni_{0.6}$ (see Fig. 5d). The second doublet corresponds to paramagnetic intermediate hydride phase at 298 K ($\delta = 0.30$ mm/s).

The Mössbauer spectrum (78 K) of the sample dwelled under ambient conditions for two days is shown in Fig. 5c. Note that the intermediate hydride phase is ferromagnetic ordered at this temperature (Fig. 5c). The IS of this phase is $\delta = 0.50$ mm/s (78 K) that is less than IS of saturated hydride phase ($\delta = 0.58$ mm/s) at the same temperature (Fig. 4c). The HF_{av} (250 kOe) is also less than the same HF_{av} of the saturated hydride (270–280 kOe). This spectrum includes also a spectrum of partially ferromagnetic ordered $ZrFe_{1.4}Ni_{0.6}$ with $\delta = -0.05$ mm/s that is shown in Fig. 5c. The comparison of spectra (Figs. 5c and 3c) demonstrates clearly this fact.

The similar behavior was observed for all other hydride samples. Note that both initial and intermediate hydride decomposition periods were increased with Ni content increase that correlates well with better stability of hydrides with higher Ni content (Table 2).

4. Conclusions

In the present work, interaction of pseudobinary intermetallics $ZrFe_{2-x}Ni_x$ ($x = 0.2$, 0.4, 0.6, and 0.8) with hydrogen was studied. It was found that these compounds can accumulate up to 1.7–1.8 wt.% H_2 at room temperature. For all investigated systems $ZrFe_{2-x}Ni_x$–H_2, thermodynamic functions of the β-hydride → α-solution phase transition and changes of metal matrix volume during formation of hydrides were calculated. Two plateaus corresponding to two probably different hydride phases with different hydrogen content are distinguished on the desorption isotherms of the samples with $x = 0.2$ and 0.4. It was established that desorption pressures and starting pressures of initial hydrogenation reaction decrease with Ni content increase.

Mössbauer investigations of intermetallics revealed that the Curie temperatures and average hyperfine fields decrease with Ni content increase, while isomer shifts are independent of it. Hydrogen absorption leads to a significant increase in IS for all the samples. T_c and HF_{av} also increase compared to initial alloys.

A two-step process of hydride phase decomposition was revealed while heating hydrides from 78 K to room temperature and dwelling under ambient conditions.

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