

Hydrogen ordering effects in Laves-phase YFe_2

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Abstract. Mössbauer spectroscopy and X-ray diffraction measurements were performed before and after hydrogenation of YFe_2 Laves phase in order to investigate the effect of hydrogen on their structural and magnetic properties. The experimental results show an instant change of both the lattice parameters and the hyperfine field. The results are interpreted due to the phase decomposition of the parent intermetallic in the aftermath of creation of stoichiometric hydrides YH_c ($c = 0.9; 2.5$).

Key words: hydrides • Laves phase • Mössbauer spectroscopy

Introduction

This investigation forms part of the studies of the influence of hydrogen on the structural and magnetic properties of iron alloys with transition metals and rare earth by means of ^{57}Fe Mössbauer spectroscopy. For example, in V-Fe alloys with too low iron content to be ferromagnetic (<20 at.% Fe), the local magnetic order can be induced owing to an increase of the mutual interactions between magnetic moments of iron atoms, mainly because of anisotropic expansion of the lattice in the aftermath of capture of the hydrogen atoms in interstitials [14, 16]. In Zr-Fe alloys, many intermetallic compounds such as Zr_3Fe , Zr_2Fe , ZrFe and ZrFe_2 are formed depending on the range of the alloy concentration. The magnetic properties of the system have been created or improved due to hydrogenation mainly by means of decomposition of the paramagnetic zirconium-rich compounds into ferromagnetic ZrFe_2 along with the hydride formation of ZrH_2 [14, 17]. On the other hand, in Ti-Fe alloys [15] the magnetic transition occurs at 67 at.% Fe. The effect of hydrogen on the magnetic properties is visible particularly in the narrow range of the alloy concentration where the TiFe intermetallic compound exists. This compound can react with hydrogen up to maximum hydrogen content $x_{\text{max}} = 1.9$ at.H/at.Me (Me – alloy atom). Owing to the formation of TiH_2 , the TiFe phase becomes significantly poor in titanium and evolves into the TiFe_2 . Moreover, the absorption of hydrogen often leads to the formation of Fe-rich microprecipitates at grain boundaries and can determine the magnitude of magnetic susceptibil-

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Received: 9 July 2012
Accepted: 15 October 2012

Table 1. Atomic concentrations of yttrium (y) and hydrogen (x) in the samples of $Y_yFe_{1-y}H_x$ alloys ($x = H/Me$, where Me denotes an alloy atom)

y	0.35			
x	0.38	0.47	0.55	0.97

ity [7, 18]. This way, the local neighborhood of iron atoms in TiFe locally becomes similar to this in pure metallic iron.

In this paper are presented initial results of hydrogen effect on the magnetic properties of Y-Fe alloys. In the Y-Fe system the following compounds occurs: YFe_2 , YFe_3 , Y_6Fe_{23} , Y_2Fe_{17} . All of these stable compounds are ferromagnetic [5, 19]. Neutron diffraction [11] and NMR investigations [13] showed that magnetic moments are different on crystallographically inequivalent sites, demonstrating a dependence of the Me moment on its local environment. Because of the itinerant character of $3d$ magnetism, the magnetic properties of yttrium compounds are strongly dependent on the crystal structure and lattice parameters. In this field the hydrogenation of the well known YFe_2 compound seems to be interesting in particular since it makes it possible to study the influence of hydrogen on the magnetic Fe sublattice. Increasing hydrogen content makes it possible to increase the Fe-Fe interatomic distances which can be considered as applying an “inverse pressure” expressed by the volume effect. The YFe_2 compound can absorb up to 5H per formula unit (/f.u.) and is interesting owing to the large variety of crystal structures obtained at different hydrogen content. These structures are related to an ordering of hydrogen atoms in interstitial sites which leads either to superstructures or to a distortion of the cubic C15 parent structure. Also the decomposition of the YFe_2 Laves phase due to high susceptibility of hydrogen to coupling with yttrium is expected. Both phenomena can lead to essential redistribution of alloy atoms in the vicinity of Fe probe and should be visible in the ^{57}Fe Mössbauer spectra (MS).

Experimental summary

The appropriate samples of the Y_yFe_{1-y} alloy were prepared from the constituent pure elements (Fe: 99.99% and Y: 99.9%) by several arc melting under argon atmosphere followed by vacuum annealing of the initially crushed material for 100 h at 1100 K. Hydrogenation was performed during slow cooling of the samples several times in the range of temperature 900 K – 450 K,

Table 2. The X-ray diffraction phase analysis in the samples of $Y_{0.35}Fe_{0.65}$ and $Y_{0.35}Fe_{0.65}H_x$ alloys (J – relative reflection intensity of $K_\alpha - Cu$; TA – trace amount; c – stoichiometry of the hydride: $0.9^{(1)}$, $2.5^{(2)}$; y and x – atomic concentrations of yttrium and hydrogen)

y	Y_yFe_{1-y}		x	$Y_yFe_{1-y}H_x$				
	αY (J%)	YFe_2 (J%)		YH_c (J%)	αY (J%)	YFe_2 (J%)	YFe_3 (J%)	Y_mFe_n (J%)
0.35	TA	93	0.38	31 ⁽¹⁾	TA	57	TA	
			0.47	44 ⁽¹⁾	TA	29	23	
			0.55	52 ⁽¹⁾	5	4	37	TA*
			0.97	58 ⁽²⁾		TA	36	4*

* Y_6Fe_{23} – (fcc) structure type D8 with $a = 1.2087$ nm.

at a maximum H_2 pressure close to 1×10^5 Pa. Next, the samples were annealed at 450 K for a long time and slowly cooled to room temperature. The content of hydrogen (x) has been measured with an accuracy of 1% by recording the pressure variation in the calibrated volumes of the reaction quartz tubes. Because of the brittleness of the melted samples after H_2 -charging process, the specimens were easily ground to a fine powder (less than 40 μm) destined directly for Mössbauer absorbers. Finally, the ^{57}Fe MS of hydrogen-free and hydrogenated samples were measured at room temperature in transmission geometry using a standard constant-acceleration spectrometer with a ^{57}Co in a Rh source.

Results and discussion

The compositions of the measured samples are given in Table 1. The aim of choice such concentration of the components was the preparation of the sample representing the YFe_2 intermetallic compound. It is common knowledge that this compound is a cubic Laves phase with C15-type crystal structure formed peritectically in a small composition range between 65.0 and 68.0 at.% Fe after annealing at 1143 K for 125 h [1].

The structural characterization of all obtained samples was realized by X-ray diffraction (XRD) using powder diffractometer (CuK_α radiation and graphite monochromator). Unfortunately, the sample of the $Y_{0.35}Fe_{0.65}$ alloy turned out not pure YFe_2 single phase probably because too short time of annealing has been applied compared to the standard time of preparation that usually equals several weeks, as reported in [1, 12]. Nevertheless, the X-ray investigation (see Table 2) revealed mainly the YFe_2 (C15) compound along with a trace (<1%) of αY solid solution (A3). The lattice parameter was obtained as 0.7359 ± 0.0002 nm and the interatomic distances were found to be 0.3184 nm (Y-Y), 0.2599 nm (Fe-Fe) and 0.3048 nm (Y-Fe). These values differ from the corresponding lattice parameters obtained in [1], but the difference is no more than 0.1% and the phase composition of the sample has, therefore, been fully justified as to be appropriate to the YFe_2 .

All the measured ^{57}Fe MS were analysed in compliance with possible phases formation in the Y-Fe system and consist of the superposition of several sets of Lorentzians. The measured spectra for the $Y_{0.35}Fe_{0.65}$ and $Y_{0.35}Fe_{0.65}H_x$ samples with different hydrogen concentration are presented in Fig. 1a–e. The spectrum for the uncharged alloy (Fig. 1a) consists of two six-line patterns at population ratio 1:3 that are corresponding

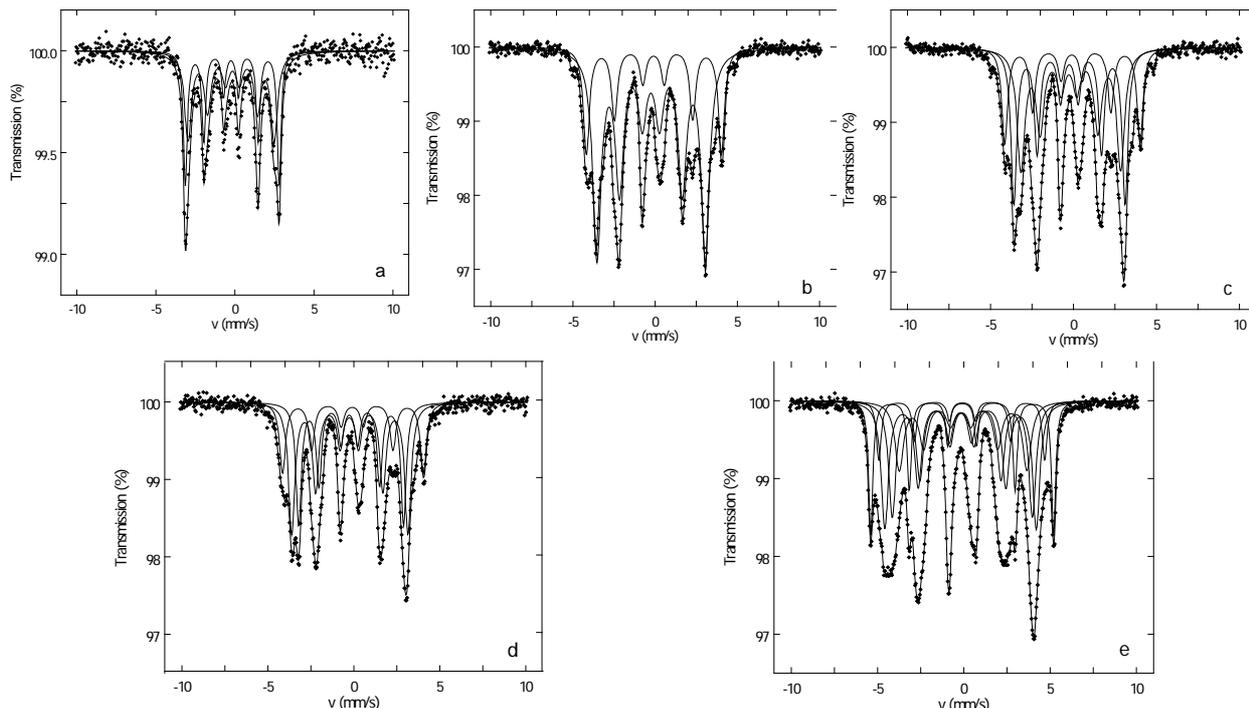


Fig. 1. The ⁵⁷Fe Mössbauer spectra of the Y_{0.35}Fe_{0.65} (a) and Y_{0.35}Fe_{0.65}H_x alloys with different hydrogen concentration $x = 0.38$ (b), 0.47 (c), 0.55 (d) and 0.97 (e) measured at room temperature.

to the hyperfine fields of 18.44 ± 0.16 T and 18.06 ± 0.26 T, respectively. It is in good agreement with another results of Mössbauer study on ⁵⁷Fe for YFe₂. In [2, 12] it has been reported that the population ratio between two six-line patterns corresponds to a direction of easy magnetization along the <111> and exhibits two hyperfine fields of 21.2 T and 20.8 T at 4.2 K and 18.5 T and 18.2 T at room temperature.

At the lowest hydrogen concentration (Fig. 1b), the main contribution descended from YFe₂ is still detected in the spectrum along with a trace of α Y and YFe₃ (hexagonal Ni₃Pu type structure). However, the intensity of YFe₂ in XRD patterns has been reduced

compared with the uncharged sample (Fig. 1a) by ca. 30%, probably because of a distinct contribution from the substoichiometric YH_{0.9} hydride. At higher hydrogen contents (Fig. 1c–e) the ⁵⁷Fe MS become more complicated reflecting gradual growth of participation of Fe-rich compounds. Initially, at $x = 0.47$ the YFe₃ contribution in addition to YFe₂ has been confirmed by X-ray diffraction measurements. At $x = 0.97$, the YFe₂ contribution disappears almost completely and new phases, in exchange for YFe₂, have been recognized as the YFe₃ (hexagonal) with a trace of the Y₆Fe₂₃ (fcc, structure type D8). The hyperfine parameters derived from the fits of the measured ⁵⁷Fe MS are in agree-

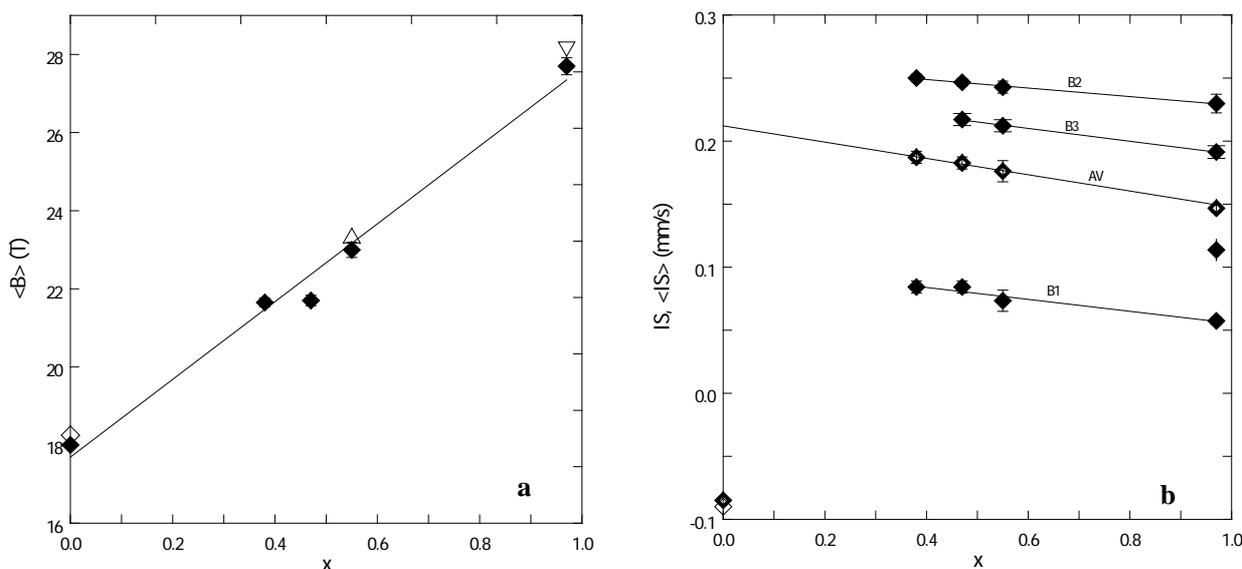


Fig. 2. Average hyperfine field $\langle B \rangle$ (a) and the average ⁵⁷Fe isomer shift $\langle IS \rangle$ (AV – marked) with respect to α -Fe (b) as a function of hydrogen concentration (x) in Y_{0.35}Fe_{0.65}H_x alloys. The dashed lines are guides to the eye visualizing the general trend in the data for $\langle B \rangle$, $\langle IS \rangle$ and IS of the individual six-line pattern (B_1 , B_2 and B_3) in each spectrum of the Y_{0.35}Fe_{0.65}H_x alloys. The values of $\langle B \rangle$ and IS for YFe₂ (\diamond), YFe₃ (Δ) and Y₆Fe₂₃ (∇) are shown [14].

Table 3. Hyperfine magnetic fields derived from the fit of the ^{57}Fe Mössbauer spectra in $\text{Y}_{0.35}\text{Fe}_{0.65}\text{H}_x$ samples at 300 K (in brackets the maximal uncertainty of B is given result from the variance of the fit)

y	x	B_1 (T)	B_2 (T)	B_3 (T)	B_4 (T)	B_5 (T)
0.35	0.38	21.071(17)	20.533(11)	–	–	–
	0.47	25.392(17)	20.871(15)	18.721(29)	–	–
	0.55	25.501(30)	22.050(26)	18.990(23)	–	–
	0.97	32.981(11)	29.931(32)	27.332(27)	25.293(37)	23.032(72)

ment with the data obtained from Mössbauer effect investigation of Y-Fe compounds [6]. In Table 3 are collected values of the hyperfine magnetic fields B_i corresponding to each subspectrum in the spectra of hydrogenated samples.

The composition dependence of the average hyperfine field in the $\text{Y}_{0.35}\text{Fe}_{0.65}\text{H}_x$ samples is presented in Fig. 2a together with the marked values of the average hyperfine field calculated from the ^{57}Fe MS of YFe_2 , YFe_3 and Y_6Fe_{23} [6]. As seen, a good compatibility is visible especially for the samples in which the existence of one of YFe_2 , YFe_3 or Y_6Fe_{23} compounds was confirmed by X-ray analysis. If it is assumed that almost all hydrogen atoms can react with atoms of yttrium, which were initially bonded in full in the binary YFe_2 compound, at higher hydrogen concentration more yttrium atoms can be involved in the formation of yttrium hydride through the commitment of yttrium from the lattice of YFe_2 . It leads gradually to reduce the YFe_2 phase and to raise new Fe-rich phases of Y_mFe_n ($n > m$), in turn. It seems reasonable owing to the extremely high value of the enthalpy of yttrium hydride formation (e.g., -205 kJ/mol hydride for $\text{YH}_{2.5}$) compared to the enthalpy of hydrides formation from the compounds of YFe_3 (-73 kJ/mol H_2), YFe_2 (-96 kJ/mol H_2) and YFe (-147 kJ/mol H_2) [3].

Another problem that is worth of short comment is the growth of the overall magnetic order in the aftermath of volume expansion ($\Delta V/V$) of the crystal lattice due to hydrogen absorption. There is a well established fact that in metals and in binary intermetallic compounds the isomer shift (IS) is almost a linear function of the fractional change in volume [8, 9]. Since the isomer shift experiences change of interatomic distances, it is useful to compare its concentration dependence both, in hydrogen-free and hydrogenated system (Fig. 2b). From the review published by Kalvius *et al.* [10], an increase in volume of 10% should lead to a value of IS being shifted by about 0.15 mm/s in the positive direction. On the other hand, in most of the intermetallic compounds based on $3d$ and $4d$ elements the change of the IS after charging with hydrogen is approximately equal to $+0.4$ mm/s relative to α -Fe and the increase of atomic volume upon hydrogen absorption is usually of the order of 20% [4]. It is doubtful, however, whether one is justified in applying such volume correction. The volume increase accompanying the hydrogen absorption is mainly due to the additional space required by H atoms. If more space becomes available to the Fe atoms after H_2 take up it will, at best, be only a smaller fraction of $\Delta V/V$. In fact, as seen from Fig. 2b, the estimated change of the average isomer shift $\Delta\langle\text{IS}\rangle$ is no more than $+0.3$ mm/s after hydrogenation. What is more, the average isomer shift $\langle\text{IS}\rangle$ is a linear function of hydrogen concentration (AV – dashed line)

and instead of grow, diminish slightly towards higher hydrogen contents. This is a little unexpected behavior, since it is known that in the range up to 3.5 H/f.u. the atoms of hydrogen are in a structure of C15 only in interstitial sites of A2B2 type. It may be explained if assume that some part of the hydrogen atoms locate also in the lattice of lower symmetry, as in this case, in the YFe_3 created at higher hydrogen concentration instead of the anticipated growth of the YFe_2 -H hydride. This phase crystallizes in a hexagonal structure with a $d_{\text{Fe-Fe}}$ distance estimated at 2.38–2.51 nm [1]. In the structure of lower-symmetry the hydrogen uptake can easily lead to anisotropic expansion of the lattice that is likely to help Fe-Fe pairs to generate localized moments. This gives rise to magnetic interactions, so strong that they can determine the overall magnetic properties of the system, which is reflected a significant increase in the average hyperfine field (Fig. 2a).

Conclusion

In this work the influence of hydrogen absorption on the structural and magnetic properties of the as-prepared YFe_2 sample has been studied. Both, the XRD and Mössbauer measurements showed a significant change of crystallographic and magnetic structure upon hydrogenation. It has been observed a gradual evolution of the phase structure of the samples from the single Laves phase YFe_2 towards the mixture of Fe-rich structures Y_mFe_n ($n > m$) derived from the C15 structure. The ^{57}Fe MS of all hydrogenated samples showed only the Y_mFe_n contributions. This result allows to assume that one of the possibility to explain such behavior is the yttrium atoms commitment to creation of stoichiometric hydrides YH_c ($c = 0.9; 2.5$) rather than to an ordering of hydrogen in the YFe_2 -H hydride, as can be expected.

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