Hydrogen ordering effects in Laves-phase YFe₂

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Abstract. Mössbauer spectroscopy and X-ray diffraction measurements were performed before and after hydrogenation of YFe₂ 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 YH₃ (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 ⁵⁷Fe 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 Zr₃Fe, Zr₂Fe, ZrFe and ZrFe₂ 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 ZrFe₂ along with the hydride formation of ZrH₂ [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 xₘₐₓ = 1.9 at.H/at.Me (Me – alloy atom). Owing to the formation of TiH₃, the TiFe phase becomes significantly poor in titanium and evolves into the TiFe₂. 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-
decomposition of the YFe₂ Laves phase due to high related to an ordering of hydrogen atoms in interstitials at different hydrogen content. These structures are owing to the large variety of crystal structures obtained up to 5H per formula unit (f.u.) and is interesting by the volume effect. The YFe₂ compound can absorb increase the Fe-Fe interatomic distances which can be lattice. Increasing hydrogen content 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 YFe₂ 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 interstitials sites which leads either to superstructures or to a distortion of the cubic C15 parent structure. Also the decomposition of the YFe₂ 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 ⁵⁷Fe Mössbauer spectra (MS).

Experimental summary

The appropriate samples of the YFe₂₋ₓ 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, at a maximum H₂ pressure close to 1 x 10⁵ 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 H₂-charging process, the specimens were easily ground to a fine powder (less than 40 μm) destined directly for Mössbauer absorbers. Finally, the ⁵⁷Fe MS of hydrogen-free and hydrogenated samples were measured at room temperature in transmission geometry using a standard constant-acceleration spectrometer with a ⁵⁷Co 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 YFe₂ 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 (CuKα radiation and graphite monochromator). Unfortunately, the sample of the Y₀.₃₅Fe₀.₆₅ alloy turned out not pure YFe₂ 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 YFe₂ (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 YFe₂.

All the measured ⁵⁷Fe 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 Y₀.₃₅Fe₀.₆₅ and Y₀.₃₅Fe₀.₆₅H, 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

<p>| Table 1. Atomic concentrations of yttrium (y) and hydrogen (x) in the samples of YₓFe₁₋ₓHₓ alloys (x = H/Me, where Me denotes an alloy atom) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>y</th>
<th>YₓFe₁₋ₓ</th>
<th>x</th>
<th>YₓHₓ (J%)</th>
<th>pYFe₂ (J%)</th>
<th>YFe₂ (J%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>TA</td>
<td>93</td>
<td>31 (1)</td>
<td>44 (1)</td>
<td>29 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>57</td>
<td>29</td>
<td>23 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>52 (1)</td>
<td>5</td>
<td>4 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>58 (2)</td>
<td>TA</td>
<td>36 (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4 (2)</td>
</tr>
</tbody>
</table>

* YₓFe₂₋ₓ – (fcc) structure type D8 with a = 1.2087 nm.
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to the hyperfine fields of 18.44 ± 0.16 T and 18.06 ± 0.26 T, respectively. It is in good agreement with another result of Mössbauer study on ⁵⁷Fe for YFe₂. In [2, 12] it has been reported that the population ratio between the 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 Y₃H₀₉ 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. 1. The ⁵⁷Fe Mössbauer spectra of the Y₀.₃₅Fe₀.₆₅(a) and Y₀.₃₅Fe₀.₆₅Hₓ alloys with different hydrogen concentration x = 0.38 (b), 0.47 (c), 0.55 (d) and 0.97 (e) measured at room temperature.

Fig. 2. Average hyperfine field <B> (a) and the average ⁵⁷Fe isomer shift <IS> (AV – marked) with respect to α-Fe (b) as a function of hydrogen concentration (x) in Y₀.₃₅Fe₀.₆₅Hₓ alloys. The dashed lines are guides to the eye visualizing the general trend in the data for <B>, <IS> and IS of the individual six-line pattern (B₁, B₂ and B₃) in each spectrum of the Y₀.₃₅Fe₀.₆₅Hₓ alloys. The values of <B> and IS for YFe₂ (△), YFe₃ (●) and Y₆Fe₂₃ (▽) are shown [14].
Hyperfine magnetic fields derived from the fit of the $^{57}$Fe Mössbauer spectra in $Y_{0.35}Fe_{0.65}H_x$ samples at 300 K (in brackets the maximal uncertainty of $B$ is given result from the variance of the fit)

<table>
<thead>
<tr>
<th>$y$</th>
<th>$x$</th>
<th>$B_1$ (T)</th>
<th>$B_2$ (T)</th>
<th>$B_3$ (T)</th>
<th>$B_4$ (T)</th>
<th>$B_5$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>0.38</td>
<td>21.07(17)</td>
<td>20.53(11)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.47</td>
<td>25.39(17)</td>
<td>20.87(15)</td>
<td>18.72(29)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.55</td>
<td>25.50(30)</td>
<td>22.05(26)</td>
<td>18.99(23)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.97</td>
<td>32.98(11)</td>
<td>29.93(11)</td>
<td>27.33(27)</td>
<td>25.29(37)</td>
<td>23.03(72)</td>
<td>–</td>
</tr>
</tbody>
</table>

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 interstitials 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 $d_{Fe-Fe}$ 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-reach structures $Y_{m}Fe_{n}$ ($n > m$) derived from the C15 structure. The $^{57}$Fe MS of all hydrogenated samples showed only the $Y_{m}Fe_{n}$ 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 $YH_x$ ($c = 0.9; 2.5$) rather than to an ordering of hydrogen in the YFe$_2$-H hydride, as can be expected.

**References**

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