Hydrogen absorption effects in the $Zr(Fe_{0.5}Cr_{0.5})_2$ compound

J.A.H. Coaquira [a], H.R. Rechenberg [a,*] and J. Mestnik Filho [b]

[a] *Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, Brazil*
[b] *Instituto de Pesquisas Energéticas e Nucleares, CP 11049, 05422-970 São Paulo, Brazil*

$Zr(Fe_{0.5}Cr_{0.5})_2$ Laves phase samples have been made to absorb different hydrogen amounts up to 3.3 H/f.u. XRD showed all $ZrFeCrH_y$ samples to have the C14 structure and, for $0 < y < 2.6$, to be composed of a H-poor α-phase and a H-rich β-phase having different c/a ratios. Both phases could be distinguished in the Mössbauer spectra. The β-phase fraction was determined both from X-ray and Mössbauer analysis, with excellent agreement. β-phase lattice constants and hyperfine parameters vs. y exhibited a small jump at $y \approx 1.75$, suggesting a phase transition. Mössbauer spectra of $ZrFeCrH_{3.3}$ in the 78–350 K range revealed that, for Fe at the $6h$ site, quadrupole splitting and linewidth increased for decreasing temperature. These effects were attributed to H atomic jump diffusion, and an activation energy of ≈ 70 meV was estimated.

1. Introduction

$Zr(Fe_x Cr_{1-x})_2$ Laves phase compounds are noted for their high hydrogen storage capability, which is a maximum for $ZrCr_2$ but remains significant for Fe concentrations up to $x \approx 0.7$ [1]. These compounds crystallize in the C14 hexagonal structure in the $0.2 < x < 0.8$ range [2]. The presence of Fe as a constituent element makes these materials ideally suited for a Mössbauer study of the microscopic changes induced by hydrogen absorption. Studies on the structural, hyperfine and magnetic properties of $Zr(Fe_x Cr_{1-x})_2$ ($0.3 \leqslant x \leqslant 0.7$) compounds and their hydrides have been reported recently [3,4]. In this article we report a detailed investigation on the $Zr(Fe_{0.5}Cr_{0.5})_2$ compound (ZrFeCr for short) loaded with different amounts of hydrogen, as well as on the temperature dependence of hyperfine parameters in the $ZrFeCrH_{3.3}$ hydride.

2. Experiment

ZrFeCr samples were prepared by melting together the pure elements in an arc furnace under argon atmosphere. The hydrogen charging was carried out in a Sievert-type facility at a pressure of ~ 1 atm of high purity H_2. Finely pulverized samples were activated by heating in vacuum at 800°C and exposed to hydrogen gas while

* Corresponding author.

cooling down slowly to room temperature (RT). A weighed fraction of the sample was outgassed to determine the amount of absorbed hydrogen. Intermediate H concentrations were obtained by removing controlled hydrogen aliquots at RT, until the required gas pressure was reached. X-ray diffractograms were collected in the $20° < 2\theta < 90°$ range using Cu K_α radiation and were analyzed with the Rietveld refinement method. Mössbauer spectra were obtained with a liquid-nitrogen cryostat, using a $^{57}Co(Rh)$ source kept at room temperature.

3.   Results and discussion

XRD analysis revealed the ZrFeCr sample to be single-phased with the hexagonal C14 structure (space group $P6_3/mmc$), and the same structure was retained after H uptake for all samples. The $ZrFeCrH_{2.6}$ hydride showed a 19% cell volume expansion relative to ZrFeCr. Samples with smaller H contents yielded doubled diffraction lines, evidencing coexistence of a H-poor (α-phase) and a H-rich one (β-phase). The β-phase volume fraction in $ZrFeCrH_y$, as determined from the Rietveld analysis, was found to increase linearly with y. Figure 1 displays lattice constants vs. y for both phases. The α-phase a and c are constant and ~0.3% larger than for the hydrogen-free sample. The expanded β-phase lattice constants, on the other hand, exhibit a small but noticeable jump at $y \approx 1.75$. It is noteworthy that the c/a ratio is distinctly smaller for the β-phase (=1.631) than for the α-phase (=1.640).

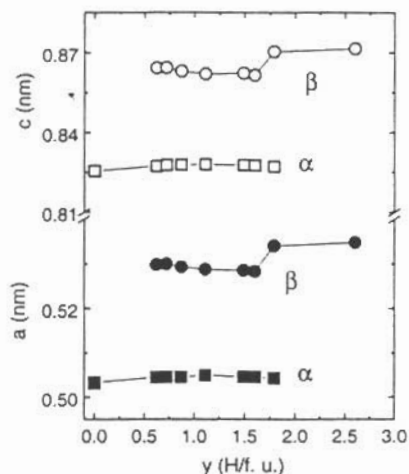

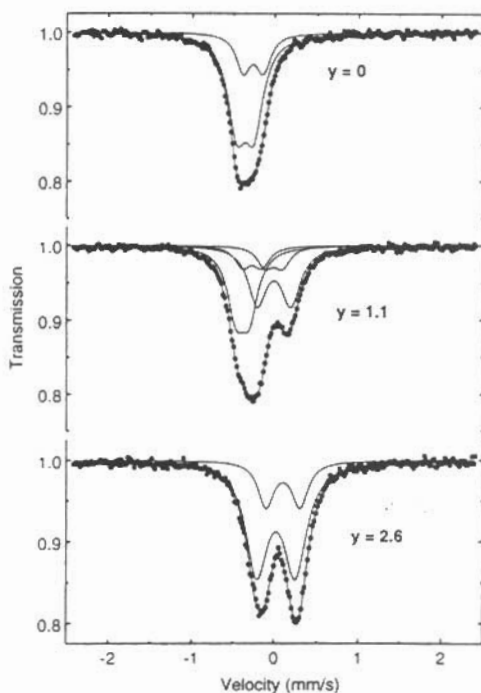Figure 1. $ZrFeCrH_y$ lattice constants against y. Squares: α-phase, circles: β-phase.

Figure 2. ZrFeCrH$_y$ room-temperature Mössbauer spectra.

Room-temperature Mössbauer spectra of ZrFeCrH$_y$ samples with $y = 0$, 1.1 and 2.6 are displayed in figure 2. The $y = 0$ spectrum was fitted with two doublets in the 1 : 3 area ratio, corresponding to the $2a$ and $6h$ sites which can be randomly occupied by Fe and Cr [5] in the C14 lattice. The ZrFeCrH$_{2.6}$ spectrum could be decomposed in a similar way. For all intermediate H concentrations the spectrum was a superposition of four doublets, corresponding to both α- and β-phases, as exemplified by the $y = 1.1$ sample in figure 2. With the 1 : 3 site occupancy ratio as only constraint, the β-phase fractional amount was determined from the Mössbauer spectral fits for all samples. Excellent agreement with the X-ray data was obtained, as shown in figure 3.

A comparison of the hyperfine parameters in the alloy and in the hydride reveals an isomer shift (IS) increase of about 0.38 mm/s at both sites, as well as a substantial quadrupole splitting (QS) increase. The QS change is most pronounced at the $6h$ site, owing to the fact that H atoms only occupy A2B2-type interstices [5]: indeed, since the B corners of such tetrahedra are predominantly $6h$, Fe atoms at such sites are much
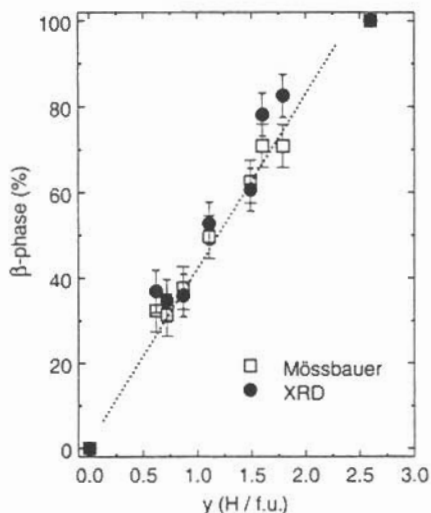
Figure 3. β-phase fraction in ZrFeCrH$_y$ against y as determined from X-ray diffractograms and Mössbauer spectra.

more likely to have H as a close neighbor, thereby undergoing electronic perturbations, as compared to $2a$ Fe atoms. A more detailed discussion of these features is given in [3]. The present experiments have, furthermore, revealed that the IS and QS at the β-phase in ZrFeCrH$_y$ are not quite y-independent, but exhibit a small, jump-like increase near $y = 1.75$. This anomaly and the lattice constant jump mentioned above are suggestive of some phase transition occurring within the β-phase for increasing H content, which demands further investigation.

Mössbauer spectra were measured in the 78–350 K temperature range both for ZrFeCr and another hydride sample of composition ZrFeCrH$_{3.3}$. QS vs. T data for both samples are shown in figure 4. For the hydrogen-free alloy, QS was constant or decreased slightly on account of thermal expansion. In the hydride, Fe($2a$) behaved in a similar way as in the hydrogen-free alloy, but the Fe($6h$) site, in contrast, exhibited a remarkable QS increase for decreasing temperature.

As mentioned above, Fe at the $6h$ site is most likely to be perturbed by a H atom. It is, therefore, plausible that the observed anomalous behavior is related to a thermally activated process involving H atomic motion. In order to describe the [57]Fe QS temperature dependence, a simple model was used [6] in which the observed QS is a time average over two configurations: a more distorted one, corresponding to a H atom sitting in an interstitial site, and a more symmetrical one in which the H is
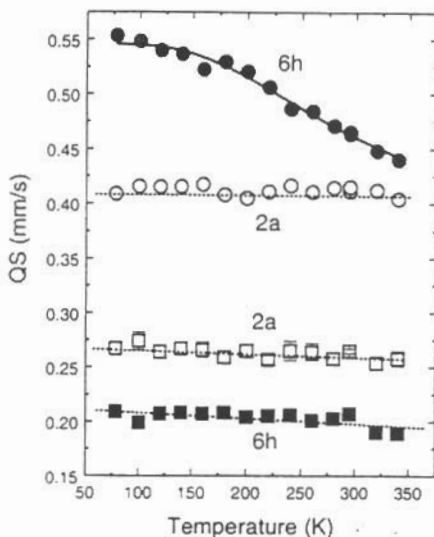
Figure 4. Quadrupole splitting against temperature, for ZrFeCr (squares) and $ZrFeCrH_{3.3}$ (circles). Dotted lines are visual guides. Full curve is fit with eq. (1).

jumping between two neighboring sites. Thus,

$$QS(T) = \frac{QS_{eq}\tau_r + QS_{tr}\tau_j}{\tau_r + \tau_j}, \tag{1}$$

where QS_{eq} and QS_{tr} are QS values for the equilibrium and transitional configurations respectively, τ_r is the H atom's residence time at the equilibrium site, and τ_j is the time it takes to jump over the potential barrier separating two equilibrium positions. It is assumed that $\tau_r = \tau_0 \exp(E/kT)$ (with $\tau_0 \approx 10^{-13}$ s) and τ_j is a constant of order 10^{-12} s. It can be noted that both characteristic times are much smaller than the "interaction time" $\hbar/\Delta E_{hf}$, so the fast fluctuation regime actually applies [7]. The data shown in figure 4 could be satisfactorily fitted with an activation energy $E = 72(4)$ meV.

In addition to the QS, the linewidth W of the $6h$ subspectra was found to increase from 0.32 mm/s at 340 K to 0.42 mm/s at 80 K. A similar phenomenon was observed some time ago in the ^{181}Ta Mössbauer spectra of $TaH_{0.018}$ [8], and was explained by assuming the W temperature dependence to be due to isomer shift fluctuations induced by diffusional jumps of a neighboring H atom, leading to an Arrhenius-type behavior $\delta W \sim \exp(U/kT)$. Our data did not accurately follow such a law, nevertheless a parameter $U = 60(10)$ meV could be estimated. From the similarity of the

two independently determined activation energies it becomes evident that the same phenomenon is involved, i.e., atomic jump diffusion of H affecting only the $6h$ Fe site in a significant manner.

The activation energies estimated above are unusually small for such large hydrogen concentrations. For example, activation energies in the 150–200 meV range have been determined from proton spin–lattice relaxation time measurements in C14-type $ZrCr_2H_y$ with $y \approx 3$ [9]. In order to better understand the hydrogen motion in $Zr(Fe,Cr)_2$ hydrides, it would be of interest to extend this investigation to other techniques, more sensitive than Mössbauer spectroscopy for that purpose.

Acknowledgements

References

[1] D. Shaltiel, I. Jacob and D. Davidov, J. Less-Common Met. 53 (1977) 117.
[2] K. Kanematsu, J. Phys. Soc. Japan 29 (1970) 864.
[3] J.A.H. Coaquira, H.R. Rechenberg and J. Mestnik Filho, J. Alloys Compounds 288 (1999) 42.
[4] J.A.H. Coaquira, H.R. Rechenberg and J. Mestnik Filho, J. Magn. Magn. Mater. 196/197 (1999) 677.
[5] O. Canet, M. Latroche, F. Bourée-Vigneron and A. Percheron-Guégan, J. Alloys Compounds 210 (1994) 129.
[6] K. Negita, N. Nakamura and H. Chihara, Chem. Phys. Lett. 63 (1979) 187.
[7] F.E. Wagner and G. Wortmann, in: *Hydrogen in Metals I*, eds. G. Alefeld and J. Völkl (Springer, Berlin, 1978) p. 145.
[8] A. Heidemann, G. Kaindl, D. Salomon, H. Wipf and G. Wortmann, Phys. Rev. Lett. 36 (1976) 213.
[9] A.V. Skripov, M.Yu. Belyaev and A.P. Stepanov, Solid State Commun. 78 (1991) 909.