Polish J. Chem., **75**, 1921–1926 (2001)

Investigation of $ZrFe_2$ and $ZrCo_2$ Under Very High Pressure of Gaseous Hydrogen and Deuterium

by S.M. Filipek[1*], I. Jacob[2], V. Paul-Boncour[3], A. Percheron-Guegan[3], I. Marchuk[1], D. Mogilyanski[2] and J. Pielaszek[1]

[1]*Institute of Physical Chemistry of the Polish Academy of Sci., 01-224 Warsaw, Poland*
[2]*Dept. of Nuclear Engineering, Ben-Gurion University of Negev, Beer Sheva 84105, Israel*
[3]*Laboratoire de Chimie Metallurgique et Spectroscopie des Terres Rares, C.N.R.S., 2-8 rue H. Dunant, 94320 Thiais, France*

(Received July 12th, 2001; revised manuscript September 3rd, 2001)

New hydrides and deuterides of Laves cubic phases $ZrFe_2$ and $ZrCo_2$ were synthesized by high hydrogen (deuterium) pressure technique. For both Laves phases the symmetry of lattice does not change but a large expansion of lattice parameter (by 8% for $ZrFe_2$ and by 4.5% for $ZrCo_2$) occurs during hydrides (deuterides) formation. In contrast to the relatively stable hydride (if stored in an inert atmosphere) formed in $ZrFe_2$, the $ZrCo_2H_2$ decomposes easily at 25°C. Large lattice expansion of $ZrFe_2$ during the deuteride formation changes only slightly its magnetic properties.

Key words: hydrides, deuterides, Laves phase, high pressure

Laves phases belong to those groups of intermetallic compounds, which from more than 50 years, are intensively investigated due to their interesting structural, magnetic and electronic properties [1]. About 30 years ago the raising interest concerning the phenomena associated with hydrogen absorption in these materials has also been noticed [2]. Some of Laves phases can accommodate large number of hydrogen (deuterium) atoms even at moderate pressures. This can be (or already is) utilized in various practical applications, as hydrogen storage, electrical batteries, hydrogen getters, catalysts *etc*. The hydrogen absorption modifies usually strongly the properties of Laves phases. For instance in $ErFe_2$ [3] or YFe_2 [4,5], subsequent structural transformations were detected for increasing the hydrogen concentration. Applying the high pressure technique, we were able to obtain pure orthorhombic phases $ErFe_2H_5$, $ErFe_2D_5$ and YFe_2H_5 respectively [5]. However, there exists a category of Laves phases, in which the solubility of hydrogen (deuterium) at normal conditions is rather small and formation of hydrides (deuterides) was not expected. $ZrFe_2$ and $ZrCo_2$ can be given as an example [6]. On the other hand, relatively high absorption of hydrogen under high pressure conditions in amorphous Zr_{12}-Fe_{88} (our unpublished data) suggested that high hydrogen pressure technique can stimulate hydrogen absorption in the crystalline $ZrFe_2$ to the level, where transformation into hydride be-

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[*] Author for correspondence.

comes possible. This has encouraged us to check the possibility of hydride (deuteride) formation in $ZrFe_2$ and $ZrCo_2$ at high chemical potential of hydrogen or deuterium (*i.e.* by exposure to hydrogen/deuterium of about 1.0 GPa).

EXPERIMENTAL

The $ZrFe_2$ and $ZrCo_2$ alloys were prepared under argon atmosphere by melting the weighted fractions of metals in an arc furnace with a water-cooled copper hearth. The quality of the samples was checked by XRD, by microprobe analysis and by preliminary neutron diffraction experiments at NRCN (Nuclear Research Center-Negev). Each alloy was crushed into fine powder and introduced to metallic capsule which was placed inside the piston-cylinder high pressure apparatus described elsewhere [7]. The pressure of hydrogen or deuterium during experiments was usually not higher than 1.5 GPa, temperature was stabilized in the range up to 150°C by using external heating and a temperature control system. The samples were exposed to the hydrogen (deuterium) gas at a given pressure/temperature condition for time usually not longer than one month. After exposure was finished, the apparatus was cooled down to –60°C, pressure was reduced, samples were discharged and then stored in liquid nitrogen until their further investigations. This procedure was undertaken to avoid a possible desorption of hydrogen and decomposition of the hydride (deuteride). The X-ray diffraction measurements were performed at room temperature, but immediately after samples were taken out from the liquid nitrogen. The magnetic measurements were performed on a DSM8 magneto-susceptometer with an applied fields up to 1.6 T. The change of the magnetization as a function of temperature was measured with an applied field of 1 T and from 4.2 to 300 K. Measurements at higher temperature were not available, due to desorption of deuterium.

RESULTS AND DISCUSSION

Hydrogen pressures lower than 0.3 GPa were insufficient for hydride formation in both alloys investigated. However, at 1.1 GPa (H_2) $ZrFe_2$ and $ZrCo_2$ reacted with hydrogen (or deuterium) and formed hydrides (deuterides) after a three weeks exposition at 100°C. This pressure was much higher than the equilibrium formation pressures of deuterides and hydrides of both $ZrFe_2$ and $ZrCo_2$ intermetallics. For instance at 100°C the equilibrium hydrogen pressure for $ZrFe_2$ hydride formation was only 0.35 GPa. One can expect that deuterides will be formed at higher pressure than corresponding hydrides. At present the isotopic effect related to formation and decomposition of hydrides (deuterides) is under investigation and will be discussed later.

In any case the 1.1 GPa (H_2/D_2) was sufficient for synthesis of hydrides or deuterides in both intermetallics investigated. Moreover, the XRD measurements data did not reveal any difference between the structure of hydrides and corresponding deuterides.

The diffractograms of $ZrCo_2$ hydride and deuteride as well as $ZrFe_2$ deuteride are given in Fig. 1, Fig. 2 and Fig. 3 respectively. From XRD data it has been estimated that the initial cubic lattice of the $ZrFe_2$ (lattice parameter = 7.072 Å [6]) expands to 7.637±0.001 Å, thus, approximately by about 8%. The corresponding increase in volume per formula unit (f.u.) is 11.47 $Å^3$. The lattice of $ZrCo_2$ expands approximately by 4.5%, namely from 6.945 Å [8] to 7.267±0.001 Å. The corresponding volume increase per formula unit (f.u.) is 5.82 $Å^3$.

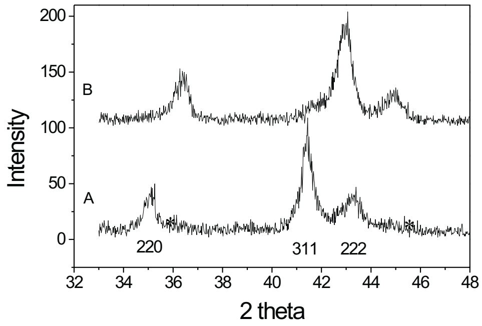

Figure 1. XRD patterns of ZrCo$_2$H$_2$ sample: A) Pure hydride – just after removing from liquid nitrogen; B) After one hour at room temperature – hydride decomposed to starting material.

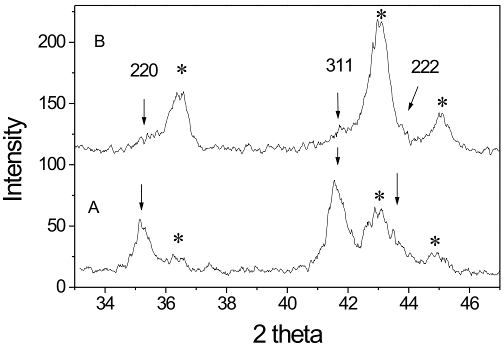

Figure 2. XRD patterns of ZrCo$_2$D$_x$ sample: A) Short time after removing from liquid nitrogen and B) after one hour. The arrows indicate the deuteride with corresponding hkl indexation and the stars the ZrCo$_2$ phase.

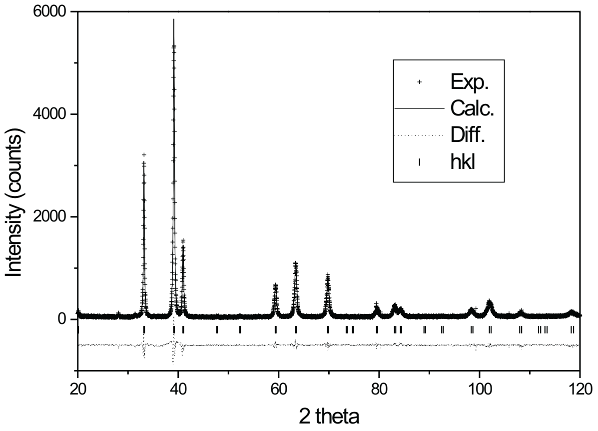

Figure 3. Refined pattern of ZrFe$_2$ deuteride (23 h D$_2$ at 100°C and 1.08 GPa). Single phase deuteride is observed. Concentration of deuterium has been estimated for 4 D/f.u.

Direct measurements of mass increase *in situ* inside the high pressure vessel in order to find the hydrogen (deuterium) uptake were not possible. On the other hand, the determination of hydrogen (deuterium) concentration out of high pressure apparatus was very difficult and not reliable, due to highly unstable character of the samples (fast decomposition, oxidation or self-ignition). An appropriate method of analytical procedure is under preparation now. Meanwhile, the quantity of the absorbed hydrogen is estimated from the induced lattice expansion of the intermetallic compounds. It is well known (see for example [9–11]), that the volume, accommodating one hydrogen atom in the metal lattice, is quite constant especially for transition metals. The most cited value is (2.8±0.2) $Å^3$/(H atom). This value depends to some extent on the type of the crystal lattice in general and the type of the occupied interstitial sites, in particular. It is worthwhile to examine the expansion associated with hydrogen absorption in other Zr-based Laves-phase compounds. We utilize for this purpose an extensive compilation [2] of crystallographic data. Averaging the eleven data [12–18], cited therein, for the expansion of ZrB_2 alloys (B = V, Cr, Mn) upon hydrogenation, yields approximately 2.85 $Å^3$/(H atom). It may be noted [2] that most of the V_H values for ZrV_2 are lower than those for $ZrCr_2$ and $ZrMn_2$. This is probably associated with the different types of interstitial sites occupied in those intermetallic compounds. There is a definite trend during the passage from ZrV_2 to $ZrMn_2$. In contrast to ZrV_2, where both (2Zr, 2B) and (1Zr, 3B) tetrahedral sites are occupied by hydrogen, in $ZrMn_2$ hydrogen locates predominantly in (2Zr, 2B) sites [19]. We believe that this trend may continue for $ZrFe_2$ and $ZrCo_2$, namely in these alloys the hydrogen atoms would occupy the (2Zr, 2B) sites only. The validity of the mentioned trend may be checked by neutron diffraction experiments on $ZrFe_2D_x$ and $ZrCo_2D_x$. In any way, we adopt the average value of V_H (2.85 $Å^3$/(H atom) for the estimation of the hydrogen absorption in $ZrFe_2$ and $ZrCo_2$. As mentioned earlier, the lattice of the $ZrFe_2$ expands approximately by 8% upon hydrogenation and the corresponding increase in volume per formula unit (f.u.) is 11.47 $Å^3$. Thus, one can estimate that four hydrogen atoms per f.u. should be absorbed what corresponds to formula $ZrFe_2H_4$. The lattice of $ZrCo_2$ expands approximately by 4.5%. The corresponding volume increase per formula unit (f.u.) is 5.78 $Å^3$ and two hydrogen atoms per f.u. are, therefore, estimated to be absorbed ($ZrCo_2H_2$). The apparent smaller hydrogen absorption in $ZrCo_2$ may be explained by two reasons. First, the escaping tendency of the absorbed hydrogen in $ZrCo_2$ is very high – our X-ray results indicate that all the hydrogen virtually leaves the $ZrCo_2$ compound in about one hour after exposure to ambient atmosphere (Fig. 1 and Fig. 2). Second, the necessary hydride-formation pressure in $ZrCo_2$ is probably higher than in $ZrFe_2$ (either for stability or hysteresis reasons), in accordance with the observed behavior from ZrV_2 to $ZrCr_2$ and to $ZrMn_2$. More specifically, ZrV_2 and $ZrCr_2$ absorb hydrogen under 1 atm of H_2, while it is necessary to use higher hydrogen pressures (tens of atmospheres) in order to enhance the hydrogen absorption in $ZrMn_2$, in spite of its relatively low equilibrium pressure [20,21].

Magnetic properties of $ZrFe_2$ deuteride: The deuteride $ZrFe_2D_4$ was sufficiently stable and did not decompose even after 24 hours of storage at room temperature. However, the decomposition accelerates rapidly with temperature increase. Sometimes self-ignition of this deuteride took place when exposed to air. For this reason measurements above 300 K are not available. The magnetic properties of Laves phases depend usually strongly on the interatomic distance of magnetic element. Taking into account the large increase of lattice constant during formation of deuteride it seemed interesting to compare the magnetic properties of $ZrFe_2$ and $ZrFe_2D_4$. $ZrFe_2$ is ferromagnetic with T_C of 628 K, and a saturation magnetization of 1.72 μ_B/Fe at 290 K. Hydrogen (Deuterium) absorption under high pressure leads to the formation of a hydride (deuteride) with about 4 D/f.u. Magnetic measurements, between 4.5 and 300 K, indicate that the deuteride remains ferromagnetic. At 4.5 K, the deuteride displays a moment of 1.88 μB/Fe, compared to 1.78 μB/Fe for $ZrFe_2$ (Fig. 4), whereas they exhibit similar moments of 1.7 μB/Fe at 290 K. Increasing the temperature leads, therefore, to a faster decrease of the magnetization for the deuteride (Fig. 5). This can be related to a decrease of T_C. However, due to the unstability of this deuteride above room temperature, it was not possible to determine its Curie temperature. These results are in agreement with those observed for another Laves phases hydrides (deuterides). For instance, in YFe_2 up to 3.5 H/f.u. an increase of the saturation magnetization at 4.5 K, but a decrease of Tc was observed [22].

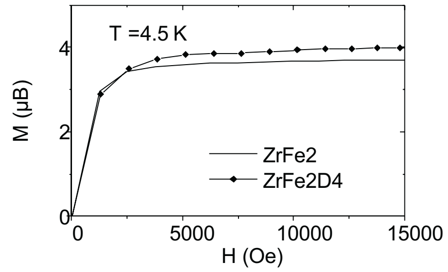

Figure 4. Magnetization of $ZrFe_2$ and $ZrFe_2D_4$ at 4.5 K.

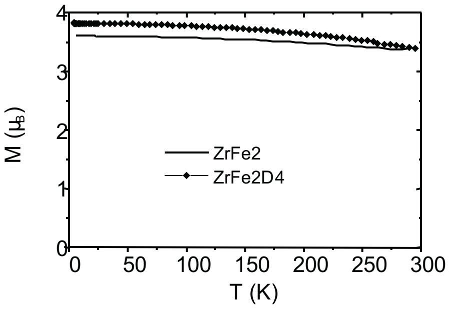

Figure 5. Thermomagnetization curves of $ZrFe_2$ and $ZrFe_2D_4$.

CONCLUSIONS

New hydrides and corresponding deuterides were found in $ZrFe_2$ and $ZrCo_2$ intermetallic compounds. Both, the hydrides and the deuterides are formed leading to a discontinuous increase of the lattice parameter without changing the initial (cubic) structure. Number of hydrogen (deuterium) atoms accomodated in $ZrFe_2$ and $ZrCo_2$ intermetallics was estimated as 4 and 2 respectively. In contrast to $ZrFe_2H_4$, that is relatively stable at normal conditions (when stored without contact with air), the $ZrCo_2H_2$ rapidly decomposes at 25°C. This instability and lower accommodation of hydrogen atoms can be attributed to the smaller size of the sites available for hydrogen in $ZrCo_2$. $ZrFe_2D_4$ is ferromagnetic showing at 290 K a moment of 1.7 μB/Fe, thus, similar to the hydrogen-free $ZrFe_2$. However, the saturation magnetization of deuteride at 4.5 K was slightly higher, what suggests that the deuterium uptake might reduce T_C.

Acknowledgment

Authors highly appreciate the partial support of this work by the Israeli Council of Higher Education.

REFERENCES

1. Raynor G.V., *Progr. Metal Phys.,* **1**, 34 (1949).
2. Yvon K. and Fischer P., in L. Schlapbach (ed.), *Topics in Applied Physics*, Vol. 63: *Hydrogen in Intermetallic Compounds I,* Springer-Verlag, Berlin-Heidelberg, 1988, p. 87.
3. Shashikhala K., Raj P. and Sathyamoorthy A., *Mater. Res. Bull.*, **13**, 957 (1996).
4. Paul-Boncour V., Guenee L., Latroche M., Escorne M., Percheron-Guegan A., Reichl Ch. and Wiesinger G., *J. Alloys Comp.*, **253–254**, 272 (1997).
5. Paul-Boncour V., Filipek S.M., Percheron-Guegan A., Marchuk I. and Pielaszek J., *J. Alloys Comp.*, **317–318,** 83 (2001).
6. Israel A., Jacob I., Soubeyroux J.L., Fruchart D., Pinto H. and Melamud M., *J. Alloys Comp.*, **253–254**, 265 (1997).
7. Baranowski B. and Filipek S.M., *Synthesis of Metal Hydrides in: High Pressure Chemical Synthesis,* (Jurczak J. and Baranowski B., Eds) Elsevier, Amsterdam (1989), pp. 55–100.
8. Israel A., Soubeyroux J.L., Fruchart D. and Jacob I., unpublished results; A. Israel, Investigation of Atomic Bonding Strengths in the Anomalous Hydrogen Absorbers $Zr(Al_xB_{1-x})_2$ by Nuclear Resonant Photon Scattering and Neutron Diffraction, Ph. D. Thesis, BGU (1997).
9. Baranowski B., Majchrzak S. and Flanagan T.B., *J. Phys. F,* **1**, 258 (1971).
10. Peisl H., in *Topics of Applied Physics*, vol. 28, G. Alefeld and J. Voelkl (eds.), Springer-Verlag, Berlin 1978, p. 53.
11. Fukai Y., *The Metal-Hydrogen System*, Springer-Verlag, Berlin, 1992.
12. Didisheim J.J., Yvon K., Fisher P. and Shaltiel D., *J. Less Common Met.*, **73**, 355 (1980).
13. Didisheim J.J., Yvon K., Fisher P. and Tissot P., *Solid State Commun.*, **38**, 637 (1981).
14. Didisheim J.J., Yvon K., Shaltiel D., Fisher P., Bujard P. and Walker E., *Solid State Commun.*, **32** (8D), 1087 (1979).
15. Fruchart D., Rouault A., Shoemaker C.B. and Shoemaker D.P., *J. Less Common. Met.*, **73**, 363 (1980); *Phys. Status Solidi*, A57, K119 (1980).
16. Yartys V.A., Burnasheva V.V., Semenenko K.N., Fadeeva N.V. and Solov'ev S.P., *Int. J. Hydrogen Energy*, **7**, 957 (1982).
17. Irodova A.V., Lavrova O.A., Laskova G.V. and Padurets L.N., *Sov. Phys.-Sol. State*, **24**, 22 (1982).
18. Didisheim J.J., Yvon K., Shaltiel D. and Fisher P., *Solid State Comm.*, **31**, 47 (1979).
19. Jacob I., Bloch J.M., Shaltiel D. and Davidov D., *Solid State Comm.*, **35**, 155 (1980).
20. Pebler A. and Gulbransen E.A., *Trans. Metall. Soc. AIME,* **239**, 1593 (1967).
21. Shaltiel D., Jacob I. and Davidov D., *J. Less Common Met.*, **53**, 117 (1977).
22. Paul-Boncour V. and Percheron-Guegan A., *J. Alloys Comp.*, **293–295**, 237 (1999).