S.M. FILIPEK*,**, RU-SHI LIU***, N. KURIYAMA****, N. TAKEICHI****, H. TANAKA****,
I.I. BULYK*****, H.-T. KUO******, M.-H. TU***, M. KOCHMAN*

HYDRIDES FORMED IN ZrCo$_2$ – BASED INTERMETALLIC COMPOUNDS UNDER HIGH HYDROGEN PRESSURE

WODORKI WYTWARZANE POD WYSOKIMI CIŚNIENIAMI WODORU ZE ZWIĄZKÓW MIĘDZYMETALICZNYCH NA OSNOWIE ZrCo$_2$

The hydrides of zirconium based pseudobinary alloys $Zr(Co_{1-x}T_x)_2$, (T = Fe, V or Cr) and $Zr_{1-x}R_xCo_2$ (R = Y, La, Pr) were synthesized under 1.2 GPa of hydrogen pressure. It was revealed that partial substitution of cobalt by V, Cr or Fe increases hydrogen absorption capacity and stability of derived hydrides. Especially, it was found that $ZrCo_{1.8}V_{0.2}$ alloy exposed to high hydrogen pressure can absorb 50% more hydrogen than pure $ZrCo_2$ and the hydride $ZrCo_{1.8}V_{0.2}H_y$ has surprisingly high stability. Substitution of zirconium by Y, La or Pr in $ZrCo_2$ alloys improved hydrogen absorption but hydrides derived from La and Pr substituted alloys were less stable than $ZrCo_2H_2$. Only for $Zr_{0.7}Y_{0.3}Co_{0.2}H_y$ the hydrogen absorption was higher and desorption rate markedly smaller comparing $ZrCo_2H_2$.

Keywords: Hydrides, High hydrogen pressure, Laves phases

Pod wysokim ciśnieniem wodoru rzędu 1.2 GPa otrzymano szereg wodorków na osnowie pseudobinarnych stopów cyrkonu o następujących składach: $Zr(Co_{1-x}T_x)_2$, (T = Fe, V or Cr) oraz $Zr_{1-x}R_xCo_2$ (R = Y, La, Pr). Wykazano, że częściowe podstawienie kobaltu wanadem, chromem lub żelazem zwiększa zdolność absorpcyjną stopów i stabilność tworzących się wodorków. W szczególności okazało się, że pod wysokim ciśnieniem wodoru $ZrCo_{1.8}V_{0.2}$ absorbuje o 50% więcej wodoru aniżeli $ZrCo_2$, a co więcej otrzymany z tego stopu wodorek ma nieoczekiwanie wysoką stabilność. Częściowe zastąpienie cyrkonu itrem, lantanem lub prazeodymem podwyższało wprawdzie zdolność absorpcyjną wodoru ale jednocześnie otrzymane wodorki zawierające lantan lub prazeodym były mniej stabilne aniżeli $ZrCo_2H_2$. Jedynie dla $Zr_{0.7}Y_{0.3}Co_{0.2}H_y$ odnotowano wyższą absorpcję wodoru i niższą szybkość jego desorpcji aniżeli w przypadku $ZrCo_2H_2$.

1. Introduction

Studies of hydrogen absorption in ZrT_2 intermetallic (T – transition metal) compounds and their pesudobinary derivatives attracted great interest due to their potential application as hydrogen storage materials [1-4]. High hydrogen absorption capacity at moderate hydrogen pressures has been found for $ZrCr_2$ [5,6], $ZrMn_2$ [7], $ZrNi_2$ [8] and ZrV_2 [9]. On the other hand Laves C15 alloys, $ZrFe_2$ and $ZrCo_2$ for long time were considered as non-hydride forming materials. However, it was revealed [10,11] that at 100°C they can react with hydrogen forming hydrides but high hydrogen pressures are necessary: 300 MPa(H$_2$) for $ZrFe_2H_4$ and more than 400 MPa(H$_2$) for $ZrCo_2H_2$. Then, from PC-isotherms measurements it was found that at 20°C the equilibrium absorption/desorption pressures for $ZrFe_2$ – H$_2$ system were much lower – only 69.9/32.9 MPa(H$_2$) [12]. Consequently it seemed attractive to modify thermodynamic parameters of hydride formation by substitut-

ing one or both components of the parent alloy by another metal. For instance it could be expected that replacing part of iron in $ZrFe_2$ alloy by vanadium or chromium would reduce equilibrium desorption pressure and increase hydrogen absorption capacity. Results of hydrogen sorption measured under high hydrogen pressure for a variety of pseudobinary alloys derived from $ZrFe_2$, $ZrCr_2$, $TiFe_2$ [13,14] and $TiCo_2$ [15], were published recently.

In this work we were focused on possible improvement of hydrogen sorption capacity and stability of $ZrCo_2$ based hydrides. Having this in mind we investigated two groups of pseudobinary alloys: one in which zirconium was substituted by yttrium, lanthanum or praseodymium and another one in which cobalt was partly substituted by iron, chromium or vanadium. For the $Zr(Co_xFe_{1-x})_2$ – hydrogen system we present new results which are complementary to report published [16] already.

*   INSTITUTE OF PHYSICAL CHEMISTRY, POLISH ACADEMY OF SCIENCES, 01-224 WARSAW, POLAND

** INSTITUTE OF HIGH PRESSURE PHYSICS PAS, 01-142 WARSAW, POLAND

***   DEPARTMENT OF CHEMISTRY, NATIONAL TAIWAN UNIVERSITY, TAIPEI, TAIWAN, ROC

****   NATIONAL INSTITUTE OF ADV. IND. SCIENCE AND TECHN. IKEDA, OSAKA 563-8577, JAPAN

*****   KARPENKO PHYSICO-MECHANICAL INSTITUTE OF THE NAS OF UKRAINE, LVIV, UKRAINE

******   ACADEMIA SINICA, TAIPEI,TAIWAN

2. Experimental

The stoichiometric compositions of pure metals were arc-melted and remelted several times in pure argon atmosphere. The received ingots were placed in evacuated and sealed quartz tubes and annealed in 850°C during 7 days. After rapid quenching to room temperature the bulk alloys were crushed and their structure and homogeneity were checked by means of x-ray diffraction (XRD) and microprobe analysis. Parent samples were put in the high pressure apparatus described elsewhere [16,17] and treated at 100°C in vacuum for 24 hours before the hydrogen charging. The hydrogenation was usually conducted at pressures up to 1.2 GPa(H_2) and 100°C for 5 days. Then temperature has been reduced to 25°C and samples were kept at this temperature under pressure for next two days. Before pressure release the apparatus was cooled down to -50°C; then the pressure was reduced to the atmospheric value and the samples were immediately taken to x-ray diffraction measurements. The XRD measurements were performed at room temperature by using a D8 Brucker diffractometer (Cu Kα wavelength), equipped with a rear graphite monochromator. The measured range was $25° < 2\theta < 50°$ for samples stable or metastable. For samples unstable which could decompose during the time of measurement a narrow range $39° < 2\theta < 44°$ has been used. For these samples (all alloys with high Co content) the measurements within the narrow range of diffraction angles was necessary to observe a rapid evolution of the main peak (311) of C15 structure, starting from pure β hydride, through two phase ($\beta + \alpha$) part until its final position, identical with that of the parent sample. Let us mention that initially measurements were conducted in the full range $20° < 2\theta < 90°$ and we could not identify any peaks belonging to the hydride phase in Zr-Co based alloys with high Co concentration. For the same reason the results of hydrogen induced volume expansions of Zr(Fe$_{1-x}$Co$_x$)$_2$ alloys, which we published earlier [16] are visibly smaller than those in the present paper.

3. Results and discussion

3.1. Hydrides of ZrCo$_{2-x}$Fe$_x$ intermetallic compounds

Cell parameters, molecular volumes and volume expansion upon hydride formation in ZrCo$_{2-x}$Fe$_x$ intermetallic com-

pounds are presented in the Table 1. Let us remark that in this work the volume changes and hydrogen concentrations of ZrCo$_2$ and ZrFe$_2$ hydrides were slightly higher than in previous reports [10,14,16]. Obtaining higher values was possible not only by higher hydrogen pressure during the samples treatment but also due to very careful, rapid preparation of hydrides for XRD examinations.

The *in situ* P-C measurements proved that hydrides of both ZrCo$_2$ and ZrFe$_2$, formed under high hydrogen pressure are thermodynamically unstable and decompose when kept without contact with air [12,16]. However, there is substantial difference between behavior of both hydrides when left in contact with air at room temperature [10,11]. The β-ZrCo$_2$H$_2$ (we will use β symbol for hydrides and α for solid solution of hydrogen in the parent phase) decomposes completely within few hours. In the case of β-ZrFe$_2$H$_4$ a self-ignition occurred sometimes what means that its surface became very active after exposure to hydrogen pressure. However, when surface was poisoned by formation of thin oxide layer it protected the hydride from further desorption. Therefore the β-ZrFe$_2$H$_4$ can be stored longer than one year without any structural changes. Substitution of iron by cobalt reduces hydrogen absorption capacity and destabilizes the hydride. For instance the β-ZrFe$_{1.8}$Co$_{0.2}$H$_{4.2}$ is not stable. In the initial stage the hydrogen desorption from the β-ZrFe$_{1.8}$Co$_{0.2}$H$_{4.2}$ results only in contraction of the β-phase molecular volume. During first 10 days the hydrogen concentration in the β-phase falls down to 3H/f.u. (f.u. = formula unit) and the α-phase (solid solution of hydrogen in the parent alloy) starts to precipitate. From this moment the lattice parameter and hydrogen concentration in the β-phase remain constant and hydrogen desorption continues for about one year and proceeds as a sluggish phase transition from β-hydride to α-solid solution. Similar process (but much faster) has been observed also for β-ZrFe$_{0.5}$Co$_{1.5}$H$_{2.8}$ hydride; precipitation of the α-phase occurred when concentration of hydrogen in the β-hydride decreased to 2.1H/f.u. Let us notice a relatively large range of hydrogen concentration available in the β-hydrides of both ZrFe$_{1.8}$Co$_{0.2}$ and ZrFe$_{0.5}$Co$_{1.5}$ alloys. It cannot be excluded that similar property have also ZrFe$_{0.2}$Co$_{1.8}$ and ZrCo$_2$ but initial desorption from their β-hydrides could be too fast and cannot be observed.

TABLE 1

Cell parameters, volumes and volume expansion for ZrCo$_{2-x}$Fe$_x$ intermetallic compounds and corresponding hydrides. The H content is estimated with a cell volume increase of 2.7 Å^3/H atom

Sample	Cell parameters a (Å) /c (Å)/	Volume V (Å^3)	Volume expansion (%)	Comment
ZrFe$_2$	7.064	352.5		
β ZrFe$_2$H$_{4.3}$	7.632	444.5	26.1	*Metastable at ambient conditions*
ZrFe$_{1.8}$Co$_{0.2}$	7.046	349.8		
β ZrFe$_{1.8}$Co$_{0.2}$H$_{4.1}$	7.601	439.2	25.5	*The first XRD run: only single β phase*
β ZrFe$_{1.8}$Co$_{0.2}$H$_3$	7.455	414.3	18.4	*After 10 days: $\alpha + \beta$ phase coexistence*
ZrFe$_{0.5}$Co$_{1.5}$	6.987	341.1		
β ZrFe$_{0.5}$Co$_{1.5}$H$_{2.8}$	7.377	401.4	17.7	*XRD directly after pressure treatment*
β ZrFe$_{0.5}$Co$_{1.5}$H$_{2.1}$	7.288	387.2	13.5	*After 24 hours in ambient cond.($\alpha + \beta$).*
ZrFe$_{0.2}$Co$_{1.8}$	6.971	338.7		
β ZrFe$_{0.2}$Co$_{1.8}$H$_{2.3}$	7.299	388.9	14.8	*Rapid decomposition*
ZrCo$_2$	6.960	337.1		
β ZrCo$_2$H$_{2.3}$	7.286	386.8	14.7	*Rapid decomposition*

Cell parameters, volumes and volume expansion for $ZrCo_{2-x}T_x$ intermetallic compounds (T = Cr or V) and corresponding hydrides. The H content is estimated with a cell volume increase of 2.7 Å^3/H atom

Sample	Cell parameter (Å)	Volume V (Å^3)	Volume change (%)	Comment
$ZrCo_2$	6.960	337.1		
$\beta ZrCo_2H_{2.3}$	7.286	386.8	14.7	*Rapid decomposition*
$ZrCo_{1.8}V_{0.2}$	6.990	341.6		
$\beta ZrCo_{1.8}V_{0.2}H_{3.6}$	7.488	419.9	22.9	*The first XRD run; only β phase.*
$\beta\ ZrCo_{1.8}V_{0.2}H_{2.2}$	7.301	389.2	13.9	*After 3 weeks at ambient cond.; only β phase.*
$ZrCo_{1.8}Cr_{0.2}$	6.983	340.6		
$\beta\ ZrCo_{1.8}Cr_{0.2}H_{2.3}$	7.311	390.8	14.7	*The first XRD run; only β phase.*
$\alpha ZrCo_{1.8}Cr_{0.2}H_x$	6.989	341.4	0.2	*After 2 hours at ambient cond.; only α phase.*
$ZrCo_{0.5}Cr_{1.5}$	7.013	344.9		
$\beta\ ZrCo_{0.5}Cr_{1.5}H_{3.8}$	7.530	426.9	23.8	*The first XRD run; only β phase.*
$\beta\ ZrCo_{0.5}Cr_{1.5}H_{3.7}$	7.520	425.3	23.3	*After 2 days $\alpha + \beta$;*

3.2. Hydrides of $ZrCo_xT_{2-x}$ intermetallic compounds (T = V or Cr)

The data for $ZrCo_{1.8}V_{0.2}$, $ZrCo_{1.8}Cr_{0.2}$, $ZrCo_{0.5}Cr_{1.5}$ and their hydrides are presented in the Table 2.

Results given in Table 2 confirm positive influence of substitution of cobalt by chromium or vanadium on hydrogen absorption and stability of $ZrCo_2$ based hydrides. At small chromium addition ($ZrCo_{1.8}Cr_{0.2}$ alloy) the effect is insignificant. However, it became remarkable for $ZrCo_{0.5}Cr_{1.5}$ where concentration of hydrogen (3.8H/f.u.) is much higher than in $ZrCo_2H_{2.3}$. Desorption of hydrogen from $ZrCo_{0.5}Cr_{1.5}H_{3.8}$ occurs mainly through direct transition from the β-hydride to the α solid solution; in this case the solubility of hydrogen in the β-hydride has a narrow range.

The behavior of $ZrCo_{1.8}V_{0.2}H_x$ is unusual. Substitution of cobalt by small amount of vanadium not only markedly increases the hydrogen absorption (by 50%) but also expands the range of hydrogen solution in the β-phase and enhances its stability. After storage at ambient conditions for three weeks the concentration of hydrogen in the β hydride was reduced from 3.6 to 2.2 H/f.u. but precipitation of the α phase did not occur. Such strong influence of small vanadium addition on properties of $ZrCo_2$ based hydride is very different from that of chromium and any other element.

3.3. Influence of substitution of zirconium by yttrium or rare earth – the case of $Zr_{1-x}R_xCo_2$(R = La, Pr, Y) – hydrogen systems

It was proved [13] that alloying $ZrFe_2$ with yttrium or dysprosium decreased the hydrogen absorption pressure without reduction of the hydrogen storage capacity. Moreover, the rare earth in $Zr_{1-x}Re_xFe_2$ (Re = Y or Dy) alloys played a catalytic role in the hydrogen absorption which proceeded without an induction period. Similar effect could be expected for $Zr_{1-x}R_xCo_2$ alloys investigated in this work. Results obtained for $Zr_{1-x}R_xCo_2$ (R = La, Pr, Y) – hydrogen systems are summarized in the Table 3.

Cell parameters, volumes and volume expansion for $Zr_{1-x}R_xCo_2$ (R = La, Pr, Y) and corresponding hydrides. The H content is estimated with a cell volume increase of 2.7 Å^3/H atom

Sample	Cell parameter a (Å)	Volume V (Å^3)	Volume expansion (%)	Comment
$ZrCo_2$	6.960	337.1		
$\beta\ ZrCo_2H_{2.3}$	7.286	386.8	14.7	*Rapid decomposition*
$Zr_{0.9}La_{0.1}Co_2$	6.929	332.7		
$\beta Zr_{0.9}La_{0.1}Co_2H_{2.3}$	7.264	383.3	15.2	*Rapid decomposition*
$Zr_{0.8}La_{0.2}Co_2$	6.909	329.8		
$\beta Zr_{0.8}La_{0.2}Co_2H_{2.4}$	7.258	382.3	15.9	*Rapid decomposition*
$\alpha\ Zr_{0.8}La_{0.2}Co_2H_x$	6.942	334.6	1.4	
$Zr_{0.7}La_{0.3}Co_2$	6.888	326.8		
$\beta\ Zr_{0.7}La_{0.3}Co_2H_{2.6}$	7.265	383.5	17.3	*Rapid decomposition*
$\alpha\ Zr_{0.7}La_{0.3}Co_2H_x$	6.949	335.6	2.7	
$Zr_{0.9}Pr_{0.1}Co_2$	6.943	334.6		
$\beta Zr_{0.9}Pr_{0.1}Co_2H_{2.0}$	7.235	378.7	13.2	*Rapid decomposition*
$Zr_{0.8}Pr_{0.2}Co_2$	6.908	329.7		
$\beta\ Zr_{0.8}Pr_{0.2}Co_2H_{2.2}$	7.221	376.6	14.2	*Rapid decomposition*
$Zr_{0.7}Y_{0.3}Co_2$	6.950	335.7		
$\beta\ Zr_{0.7}Y_{0.3}Co_2H_{2.6}$	7.319	392.1	16.8	*Sluggish decomposition*
$\alpha\ Zr_{0.7}Y_{0.3}Co_2H_x$	7.018	345.7	3.0	

Since the main peak (311) from C15 structure of hydrides has moved during measurements toward higher angles it can be expected that real values of hydrogen concentration *in situ* under high pressure conditions could be even higher from those given in the Table 3. Excluding $Zr_{0.7}Y_{0.3}Co_2H_{2.6}$ which was relatively stable and its decomposition has been completed after 3 days, all other hydrides were extremely unstable. For example, as can be seen on Fig. 1, the hydride peak (311) from $Zr_{0.7}La_{0.3}Co_2H_{2.6}$ disappeared after the first XRD run (less than 3 min.). The $Zr_{0.8}Pr_{0.2}Co_2H_{2.2}$ decomposed within 10 min.
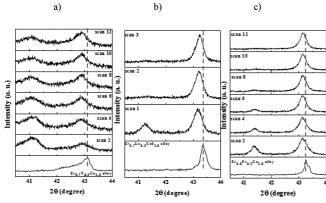

Fig. 1. XRD scanning of main peaks (311) of $Zr_xR_{1-x}Co_2$ (above $2\theta = 43^0$) and their hydrides (near $2\theta = 41^0$), the red lines show position of (311) peaks for parent alloys; a) $Zr_{0.7}Y_{0.3}Co_2H_y$, b) $Zr_{0.7}La_{0.3}Co_2H_y$, c) $Zr_{0.8}Pr_{0.2}Co_2H_y$. Time of one scan was ~3 min

4. Conclusions

Several pseudobinary $ZrCo_2$ based alloys, in which zirconium or cobalt were substituted by another elements, formed hydrides when exposed to high hydrogen pressure (1.2 GPa and 100°C). Substitution of cobalt by metals like V, Cr and Fe increases hydrogen absorption capacity and stability of synthesized hydrides. The strongest effect has vanadium as substituting element. Among β-$ZrCo_xFe_{1-x}H_y$ hydrides the β-$ZrFe_{1.8}Co_{0.2}H_y$ (3<y<4.1) and β-$ZrFe_{0.5}Co_{1.5}H_y$ (2.1<y<2.8) are characterized with a large range of available hydrogen concentration. Similar property has been found also for β-$ZrCo_{1.8}V_{0.2}H_y$ (where 2.2<y<3.6) but not for β-$ZrCo_{1-x}Cr_xH_y$. Partial substitution of zirconium by yttrium, lanthanum or praseodymium slightly increases hydrogen absorption capacity but hydrides formed in this kind of pseudobinary alloys are, excepting β-$Zr_{0.7}Y_{0.3}Co_2H_{2.6}$, extremely unstable at ambient conditions. Unfortunately, the Sievert's type apparatus for measuring hydrogen absorption/desorption isotherms is reported only for pressure range limited to 0.3 GPa(H_2) [14] thus much smaller than necessary pressure range. One possible suggestion for *in situ* measurements is application of hydrogen charged DAC (diamond anvil cell).

REFERENCES

[1] D. Shaltiel, I. Jacob, D. Davidov, J. Less-Common Met. **53**, 117-131 (1977).

[2] J.L. Soubeyroux, D. Fruchart, A.S. Biris, J. Alloys Compd. **293-295**, 48 (1995).

[3] S.B. Gesari, M.E. Pronsato, A. Visintin, A. Juan, J. Phys. Chem. C **114** (39), 16832-16836 (2010).

[4] M. Dorogova, T. Hirata, S.M. Filipek, Solid State Commun. **125**, 587-589 (2003).

[5] K. Morimoto, M. Saga, H. Fujii, et al., J. Phys. Soc. Jpn. **57** (2), 647-654 (1988).

[6] M. Dorogova, T. Hirata, S.M. Filipek, H. Bala, J. Phys.: Condens. Matter **14**, 11151 (2002).

[7] V.A. Skripov, T.J. Udovic, J.J. Rush, Phys. Rev. B, **76** (10), 104305 (2007).

[8] R. Griessen, A. Driessen, D.G. De Groot, J. Less-Common Met. **103**, 235-244 (1984).

[9] A.N. Bogdanova, A.V. Irodova, G. Andre, F. Bouree, Acta Cryst. **A61**, C319 (2005).

[10] S.M. Filipek, I. Jacob, V. Paul-Boncour, et al., Polish J. Chem. **75**, (12), 1921-1926 (2001).

[11] S.M. Filipek, V. Paul-Boncour, A. Percheron-Guegan, I. Jacob, J. Phys., Cond. Matter. **14** , (44) 11261 (2002).

[12] T.A. Zotov, E.A. Movlaev, S.V. Mitrokhin, V.N. Verbetsky, J. Alloys Compd. **459**, 220-224 (2008).

[13] R.B. Sivov, T.A. Zotov, V.N. Verbetsky, The influence of Y, Gd and Dy doping on hydrogen sorption properties of $ZrFe_2$, in. A.A. Yakimchuk (Ed.), Interaction of Hydrogen Isotopes with Structural Materials (IHISM-08 Junior), Sarov, 201-208 (2009).

[14] T.A. Zotov, R. Sivov, E.A. Movlaev, S.V. Mitrokhin, V.N. Verbetsky, J. Alloys Compd. **509S**, S839-S843 (2011).

[15] H.T. Kuo, R.S. Liu, S.M. Filipek, R. Wierzbicki, R. Sato, C.L. Chan, H.D. Yang, J.F. Lee, Inorg. Chem. **48**, 11655-11659 (2009).

[16] S.M. Filipek, V. Paul-Boncour, N. Kuriyama, N. Takeichi, H. Tanaka, R.-S. Liu, R. Wierzbicki, R. Sato, H.T. Kuo, Solid State Ionics **181**, 306-310 (2010).

[17] S.M. Filipek, A.B. Sawaoka, Kooatsu Gijyutu (JHPI) **30**, (6), 43-49 (1992).