Nanostructured Metal Hydrides for Hydrogen Storage Studied by *In Situ* Synchrotron and Neutron Diffraction

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ABSTRACT

This work was focused on studies of the metal hydride materials having a potential in building hydrogen storage systems with high gravimetric and volumetric efficiencies of H storage and formed / decomposed with high rates of hydrogen exchange. *In situ* diffraction studies of the metal-hydrogen systems were explored as a valuable tool in probing both the mechanism of the phase-structural transformations and their kinetics. Two complementary techniques, namely Neutron Powder Diffraction (NPD) and Synchrotron X-ray diffraction (SR XRD) were utilised. High pressure *in situ* NPD studies were performed at D₂ pressures reaching 1000 bar at the D1B diffractometer accommodated at Institute Laue Langevin, Grenoble. The data of the time resolved *in situ* SR XRD were collected at the Swiss Norwegian Beam Lines, ESRF, Grenoble in the pressure range up to 50 bar H₂ at temperatures 20-400°C.

The systems studied by NPD at high pressures included deuterated Al-modified Laves-type C15 ZrFe_{2-x}Al_x intermetallics with x = 0.02; 0.04 and 0.20 and the CeNi₅-D₂ system. D content, hysteresis of H uptake and release, unit cell expansion and stability of the hydrides systematically change with Al content. Deuteration exhibited a very fast kinetics; it resulted in increase of the unit cells volumes reaching 23.5 % for ZrFe_{1.98}Al_{0.02}D_{2.9(1)} and associated with exclusive occupancy of the Zr₂(Fe,Al)₂ tetrahedra.

For CeNi₅ deuteration yielded a hexahydride CeNi₅D_{6.2} (20°C, 776 bar D₂) and was accompanied by a nearly isotropic volume expansion reaching 30.1% ($\Delta a/a=10.0\%$; $\Delta c/c=7.5\%$). Deuterium atoms fill three different interstitial sites including Ce₂Ni₂, Ce₂Ni₃ and Ni₄. Significant hysteresis was observed on the first absorption-desorption cycle. This hysteresis decreased on the absorption-desorption cycling.

A different approach to the development of H storage systems is based on the hydrides of light elements, first of all the Mg-based ones. These systems were studied by SR XRD. Reactive ball milling in hydrogen (HRBM) allowed synthesis of the nanostructured Mg-based hydrides. The experimental parameters (P_{H_2} , T, energy of milling, ball / sample ratio and balls size), significantly influence rate of hydrogenation. The studies confirmed (a) a completeness of hydrogenation of Mg into MgH₂; (b) indicated a partial transformation of the originally formed α -MgH₂ into a metastable γ -MgH₂ (a ratio α/γ was 3/1); (c) yielded the crystallite size for the main hydrogenation product, α -MgH₂, as close to 10 nm. Influence of the additives to Mg on the structure and hydrogen absorption/desorption properties and cycle behaviour of the composites was established and will be discussed in the paper.

INTRODUCTION

Recent R&D on hydrogen storage have resulted in a new method, “hybrid” H storage, yielding improved by up to 50 % overall H storage system efficiency [1]. In present work we have focused on metal hydrogen systems where one can significantly increase hydrogen storage capacity of the MH on application of high H₂ pressures. H storage capacities of the MH suitable for such systems are highly pressure-dependent, when pressures increase to a few hundred bar.

Characterisation of such systems can be efficiently performed by performing *in situ* diffraction studies of the metal-hydrogen interactions in the pressure cells loaded by hydrogen gas. Using deuterated samples and neutron scattering allows to “see” hydrogen environment and to probe metal-H/D and H-H/D-D interactions via establishing a pressure-dependant changes of the phase-structural composition of the materials. Such works, despite providing a very interesting and important scientific insight, meet obvious technical challenges. Thus, the list of particular metal hydride systems studied by *in situ* NPD at high D₂ pressures is rather limited. The system mostly focused during the earlier research is the LaNi₅-D₂ system where systematic studies at different applied high pressure experimental conditions were performed (see [2] as example). However, broadening of the materials field would be much desirable allowing overseeing a broader picture of the behaviours of the high pressure hydrides. Such a task was aimed in present work where a structural analogue of La-containing intermetallic, CeNi₅-D₂ system was studied by *in situ* NPD at pressures up to 1000 bar.

Zr-based Laves phase compounds ZrFe₂ and ZrCo₂ can be hydrogenated only using high applied hydrogen pressures, up to 3000 bar, giving ZrFe(Co)₂D_{~3} [3]. These deuterides were studied *ex situ* by NPD and their crystal structures were solved. Al substitution for Fe in ZrFe₂ significantly modifies the hydrogenation behaviours decreasing equilibrium pressures of hydrogen and increasing stability of the hydrides [4]. The range of the studied ZrFe_{2-x}Al_x materials was limited to the alloys with a rather large content of Al; thus, the equilibrium pressures of hydrogen desorption were well below 100 bar [4]. In present work we were focused on the experimental study of the systems in which Al content was very low, below 0.1 at.Al/f.u. Zr(Fe,Al)₂, thus aiming to synthesize the hydrides where the stability was expected to be only slightly increased as compared to ZrFe₂-H₂ system.

The other focus of the *in situ* studies of the metal-hydrogen systems is in studies of the nanoscale materials, as they exhibit extremely high specific surface and form nanocomposites consisting of small crystallites of a metal hydride and nanoscale dopants, facilitating hydrogen exchange rates and lowering kinetic barriers for the phase-structural transformations. Synthesis of the nanomaterials with controlled content of doping catalysers was proved to be especially successful for the Mg based alloys where complementing high H storage capacity of Mg, 7.6 wt.% H, by increased rates of H charge and discharge will help in building practical systems for H storage based on this light metal. *In situ* synchrotron XRD of the phase-structural transformations in the systems of Mg alloys and hydrogen gives valuable input in establishing the mechanism of the transformations, their kinetics as related to the nanostructuring. Reactive Ball Milling in hydrogen is a valuable tool in synthesis of the nanostructured Mg-based hydrides. These hydrides were studied by *in situ* SR XRD in our previous works [5,6]. In present paper we would like to report some new experimental data in the area. The focus will be on the V-catalysed processes of hydrogenation of Mg and its alloys.

EXPERIMENTAL DETAILS

Materials used: The CeNi₅ and Zr(Fe,Al)₂ alloys were prepared by arc melting using starting materials with a purity of at least 99.9%. X-ray diffraction pattern (Siemens D 5000 diffractometer, Cu K α ₁ radiation) showed that the samples prepared were single phases with correspondingly CaCu₅-type and MgCu₂ types of structures. The magnesium metal used was a grit of 50–150 mesh (0.1–0.3 mm) from Fluka (purity 99+%).

RBM in hydrogen: Hydrides were synthesized and processed by application of high-energy RBM in a Fritsch Pulverisette P6 planetary mill. The samples were placed into a custom-built Duplex SS 2377 (austenitic–ferritic steel) vial. The sample-to-balls weight ratio was ~ 1:80. The vial was initially evacuated and filled with 30 bar H₂. The milling was performed at 500 rpm. To monitor the hydrogenation process, the milling was paused (typically in 15-20 min intervals) and the vial, after cooling to room temperature, was connected to a Sieverts-type apparatus to monitor the amount of hydrogen absorbed; the vial was then refilled with hydrogen, and milling was continued. A complete hydrogenation of the Mg powder was reached in 6 hours, and in less than 2 h for its composite with 10-35 wt.% of the BCC-type V₇₅Ti₁₀Zr_{7.5}Cr_{7.5} alloy.

In situ SR XRD experiments: *In situ* SR-XRD studies of the Mg-based hydride nanocomposites were performed at the Swiss Norwegian Beam Lines (SNBL), at the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

The measurements were performed using a set-up designed for *in situ* studies of the chemical processes occurring in hydrogen gas or in vacuum (see Ref. [7] and references therein). A small amount of the sample was put into a 0.5 mm quartz glass capillary (0.01 mm wall thickness), filling approximately 3-5 mm of the capillary. The capillary was seal-proof connected to the gaseous system using either a carbon ferrule, or a 1/8" Swagelok VCR fitting via a T-piece; the latter was attached to the goniometer head. Vacuum was created using a turbomolecular vacuum pump. Experimental data at BM01A were collected using a MAR2300 image plate detector. The wavelength and sample-to-detector distance were calibrated using LaB₆ as a reference material. The collection of one diffraction data set took 10 s. Powder diffraction data were analysed by the Rietveld whole-profile refinement method using the General Structure Analysis System (GSAS) [8] and Fullprof [9] softwares.

Crystallite size and strains: The sizes of the crystallites and strains in the materials were evaluated from the refinements of the Rietveld powder profile parameters using the following equations [10]: $D_V = \lambda/(\beta_s - \cos\theta)$; $e = \beta_D/(4 - \tan\theta)$, where D_V is a volume-weighted crystallite size, λ is the wavelength, β is the integral width of the reflection, θ is the Bragg angle and e is the microstrain. To obtain the integral width of the size-broadened and strain-broadened profiles, the size-broadening and micro-strain broadening profile coefficients were converted according to the procedure described in Ref. [10]. The instrumental contribution to the line broadening was evaluated by refining the profile parameters for LaB₆. During the refinements, only Lorentzian size-broadening and strain broadening profile parameters were refined.

In situ NPD measurements: Powder neutron diffraction data were collected with the D1B diffractometer at ILL, Grenoble ($\lambda = 2.52$ Å). More information about the *in situ* neutron powder diffraction can be found in the following review [11]. The scheme of the experimental setup is presented in Figure 1 and consists of a high-pressure Sievert's hydrogenator connected to a high-pressure sample cell made of a zero coherent scattering alloy (Zr-Ti) with a stainless steel inner liner. High pressures were achieved by the use of multistage, heat-based deuterium intensifier (maximum H₂ pressure 2 kbar). The *in situ* apparatus allowed simultaneous

measurement of deuterium concentration in the sample and assessment of the crystal structure via neutron diffraction.

Figure 1. High pressure 1000 bar setup for the NPD studies. MV1 – A valve that isolates high purity hydrogen from the metal hydride reservoir (R1) to the LP section of the rig. MV2 – A valve that allows gas evacuation from the rig. MV3 – External gas supply valve. MV4 – A valve that isolates the LP and the HP sections of the rig. MV5 – A valve that isolates the HP reservoir from the rig. MV6 – A valve attached to the HP reservoir. MV7 – A valve isolating the sample volume (V2) from the reference volume (V1). MV8 – A valve isolating the sample volume from the rest of the rig. R1 – A volume filled with LaNi_5 , used to store H_2 or D_2 . The volume is used to purify the hydrogen and to intensify the gas to up to 200 bar using a heat pump. R2 – A volume filled by the alloy that stores H_2 at higher pressure (200 bar) and intensifies the pressure to 1000 bar using heat. V1 – Reference volume, temperature stabilized by water loop. V2 – Sample volume designed to operate inside a vacuum furnace.

RESULTS

CeNi₅ - D₂ system

Initial sample was characterised by SR XRD (SNBL; BM01A; $\lambda=0.7350 \text{ \AA}$) as a single phase alloy containing the CeNi_5 intermetallic compound with hexagonal unit cell; $a=4.88415(7)$; $c=4.00016(7) \text{ \AA}$. First deuteration was tried without preliminary activation of the alloy and took place on application of high deuterium pressures. Our observations of the absorption-desorption processes can be summarized as follows:

- Both deuterium absorption and desorption are characterized by presence of clear plateaux on the P - C diagrams;
- A solid solution of deuterium in CeNi_5 , $\alpha\text{-CeNi}_5\text{D}_{\sim 0.5}$, is formed first and extends until the level of pressure of 600 bar D_2 . Then the $\beta\text{-CeNi}_5\text{D}_{\sim 6}$ is formed.
- During the first deuteration, the midpoint of the plateau for the $\alpha \rightarrow \beta$ transformation at 20 °C is observed at 632 bar D_2 ;
- For the desorption, the midpoint of the plateau pressure for the $\beta \rightarrow \alpha$ transformation is significantly lowered, being 117 bar D_2 at 60 °C;

- During the second deuteration, midplateau pressure for $\alpha \rightarrow \beta$ transformation at 30 °C is significantly decreased to just 237 bar D₂;
- The observed regularities illustrating a significant hysteresis in D absorption/desorption concluded from analysis of the NPD pattern (see Figures 2, 3) are in good agreement with the reference data [12].

Figure 2. First deuterium absorption and desorption by CeNi₅ from the PND data.

Figure 3. *In situ* NPD ($\lambda=2.52$ Å) of deuterium desorption from the β -CeNi₅D_{6.3} deuteride. α -CeNi₅D_{0.5} becomes visible at 147 bar D₂.

α -CeNi₅D_{0.5}: During the formation of the α -solid solution the hexagonal unit cell slightly expands; $\Delta a/a=0.3\%$; $\Delta c/c=0.6\%$; $\Delta V/V=1.1\%$; $a=4.8969(6)$; $c=4.0261(6)$ Å; $V=83.61(2)$ Å³ [D1B; $\lambda=2.52$ Å]. From Rietveld profile refinements of the NPD data we conclude that D atoms exclusively occupy the Ce₂Ni₂ 6*m* tetrahedra. Positional parameters for D are: $x=0.118(5)$; $y=2x$; $z=1/2$; $n=0.085(7)$. Interestingly, only this interstitial site meets geometrical criterion for size limitation of the H-occupied sites, radius >0.4 Å: $r=0.42$ Å. The other, vacant, sites have radii below 0.3 Å. It is worth to point out a difference between site occupancies in the α -LaNi₅D_{0.42} [13] and α -CeNi₅D_{0.5} solid solutions. Indeed, in the LaNi₅-based solid solution D atoms occupy two different sites, 6*m* (~2%) and 12*n* (3%), in contrast to the α -CeNi₅D_{0.5} where only the 6*m* sites are partially filled by D atoms. From volumetric data of D absorption the limiting D content in α -solid solution is higher, 0.84 at.D/CeNi₅. An observed difference between the volumetric data and crystal structure refinements can be caused by presence of very small amount of the β -deuteride phase in the sample (ca. 5%) which starts to be formed already at 613 bar D₂. Such small quantities are difficult to confidently identify using the NPD data with a relatively low resolution.

β -CeNi₅D_{6.2}: Analysis of the NPD pattern showed a completeness of the transformation into the β -deuteride at pressure of 776 bar D₂. During the deuteration, the unit cell expands by 30.1 %, with $\Delta a/a=10.0$ % and $\Delta c/c=7.5$ %. Refinements yielded an excellent fit between the experimental and calculated data (see Figure 4). Three different interstitial sites are filled by D atoms, including Ce₂Ni₂ tetrahedra 6*m*; Ce₂Ni₁₂Ni₂ sites 6*i* (half of the octahedra Ce₂Ni₁₂Ni₂) and tetrahedra Ni₄ 4*h*. Crystal structure data for the CeNi₅D_{6.3} are presented in Table I.

Figure 4. NPD profile refinement of the diffraction pattern for a saturated $\text{CeNi}_5\text{D}_{6.3}$ deuteride (776 bar D_2 , 20 °C).

We observe that in the saturated deuteride $\text{CeNi}_5\text{D}_{6.3}$, the unit cell parameters, $a=5.374(2)$; $c=4.3013(7)$ Å, are rather close to the values for LaNi_5D_6 [14]. This contrasts to a large shrinking of the unit cells when to replace La in LaNi_5 by Ce to form CeNi_5 . Thus, a Ce valence evolution towards a trivalent state is taking place upon hydrogenation to form $\text{CeNi}_5\text{D}_{\sim 6}$. Furthermore, it seems that only *in situ* technique applied in present work was able to collect the correct crystallographic data for the deuteride. Indeed, in the work [12] where a stabilization of the high pressure hydride by SO_2 was applied, the experimentally measured values of the unit cell parameters were much smaller ($a=5.368$; $c=4.235$ Å) indicating a partial H desorption from the sample following a pressure decrease. Finally, we have observed appearance of anisotropic diffraction peak broadening upon first hydrogenation of CeNi_5 , during $\alpha\text{-CeNi}_5\text{D}_{\sim 0.5} \rightarrow \beta\text{-CeNi}_5\text{D}_{\sim 6}$ transformation. The anisotropic strain broadening is absent in the initial period of hydrogenation, until the β -deuteride appears and remains after further desorption-absorption cycling. Similar effect was observed in hydrogen-cycled pure and substituted LaNi_5 and attributed to dislocation-induced strain occurring after first hydrogenation [15]. The anisotropic peak broadening was modelled using the method applied in [16].

Table I.

Crystal structure data for $\beta\text{-CeNi}_5\text{D}_{6.3}$ (20°C, 776 bar D_2 , D1B diffractometer at ILL).

Space group $P6/mmm$. $a=5.374(2)$; $c=4.3013(7)$ Å; $V=107.58(5)$ Å³.

Isotropic atomic displacement factors B_{iso} were fixed for Ce and Ni (1.0 Å²) and for D (2.0 Å²).

Atom	Site	x/a	y/b	z/c	Occupancy at. D/unit cell	Interatomic Me-D distances, Å
Ce	1a	0	0	0		
Ni1	2b	$\frac{1}{3}$	$\frac{2}{3}$	0		
Ni2	3g	$\frac{1}{2}$	0	$\frac{1}{2}$		
D1	6i	$\frac{1}{2}$	0	0.143(3)	2.97(11) occup. 50%	Ce - D1 2.76 Ni1 - D1 1.67 Ni2 - D1 1.54
D2	6m	0.137(2)	0.274(4)	$\frac{1}{2}$	2.66(8) occup. 44%	Ce - D2 2.50 Ni2 - D2 1.71
D3	4h	$\frac{1}{3}$	$\frac{2}{3}$	0.38(-)	0.62(4) occup. 16%	Ni1 - D3 1.64 Ni2 - D3 1.64

ZrFe_{2-x}Al_x – D₂ system

ZrFe₂ intermetallic compound crystallizes with MgCu₂-type C15 FCC structure. Three different alloys containing 0.02; 0.04 and 0.20 at.Al/f.u. ZrFe_{2-x}Al_x were synthesized by arc melting. SR XRD studies showed that Fe substitution by Al in Zr(Fe,Al)₂ alloys increases the unit cell parameter without change of the Laves-type of the crystal structure, from $a=7.072$ Å for ZrFe₂[4] to $a=7.08492(8)$ Å for ZrFe_{1.98}Al_{0.02}, $a=7.08658(7)$ Å for ZrFe_{1.96}Al_{0.04} and $a=7.0978(1)$ Å for ZrFe_{1.80}Al_{0.20}.

The hydrogenation/deuteration performance was studied at pressures of deuterium up to 1600 bar D₂. Corresponding deuterides were synthesized and studied by *in situ* neutron powder diffraction measurements at D1B instrument, ILL, Grenoble, France. From volumetric measurements performed in *in situ* setup, maximum D storage capacity reached 3.4 at.D/f.u. for ZrFe_{1.98}Al_{0.02}.

Deuteration resulted in expansion of the unit cells reaching $\Delta V/V=23.5$ % ($a=7.6003(5)$ Å) for ZrFe_{1.98}Al_{0.02}D_{2.9(1)}; 23.2% ($a=7.5966(5)$ Å) for ZrFe_{1.96}Al_{0.04}D_{2.9(2)} and 18.6% for ZrFe_{1.8}Al_{0.2}D_{2.7(2)} ($a=7.5141(5)$ Å). Detailed data on the crystal structures are given in the Table II. Deuteration proceeds via formation of a two-phase region instead of a continuous solid solution and reaches saturation around 1000 bar D₂. A significant hysteresis was observed between the pressures of D₂ desorption and absorption during measurements of the isotherms (see Figure 5). From refinements of the NPD data (Figure 6) we conclude that D atoms occupy the Zr₂Fe(Al)₂ tetrahedra 96g ($x=0.32$; $y=x$; $z=0.13$; occupancy ~24%). Interatomic distances Me-D within the tetrahedra are: $\delta(\text{Zr-D})=2.01\text{--}2.08$; $\delta(\text{Fe-D})=1.75$ Å. The latter distances do not exclude a possibility of occupancy of the Al-substituted sites by H/D.

In situ studies demonstrated a very fast kinetics of H/D exchange in the material. From NPD data it was found that initial intermetallic alloys and their corresponding deuterides are ferromagnetic. Magnetic moments of Fe at room temperature slightly increase from the alloy (1.9 μ_B) to the corresponding deuteride (2.2 μ_B), similarly to ZrFe₂ based deuteride.

Figure 5. Deuterium absorption-desorption isotherms for ZrFe_{1.98}Al_{0.02} at 20 °C.

Figure 6. NPD profile refinements of the diffraction pattern for a saturated ZrFe_{1.98}Al_{0.02}D_{2.9} deuteride (963 bar D₂, 20 °C).

Table II.

Crystal structure data for the $\text{ZrFe}_{2-x}\text{Al}_x$ ($x=0.02; 0.04; 0.20$) compounds and their corresponding deuterides (at 20 °C). Space group $Fd-3m$. Zr in $8a$ ($\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$); Fe(Al) in $16d$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$).

Composition and D ₂ pressure	a , Å	$\Delta a/a$, %	$\Delta V/V$, %	$\Delta V/\text{at.D}$, Å ³	Positions of D atoms (96g: x, x, z)	Interatomic Me-D distances, Å
$\text{ZrFe}_{1.98}\text{Al}_{0.02}$	7.08492(8)					
$\text{ZrFe}_{1.98}\text{Al}_{0.02}\text{D}_{2.9(1)}$ 963 bar	7.6003(4)	7.3	23.5	3.59	$x=0.319(1)$ $z=0.126(1)$ occup. 24(1)%	Zr-D 2.08 Zr-D 2.01 Fe(Al)-D 1.75
$\text{ZrFe}_{1.96}\text{Al}_{0.04}$	7.08658(7)					
$\text{ZrFe}_{1.96}\text{Al}_{0.04}\text{D}_{2.9(2)}$ 989 bar	7.5966(5)	7.2	23.2	3.56	$x=0.319(1)$ $z=0.126(1)$ occup. 24(1)%	Zr-D 2.09 Zr-D 2.00 Fe(Al)-D 1.75
$\text{ZrFe}_{1.8}\text{Al}_{0.2}$	7.0978(1)					
$\text{ZrFe}_{1.8}\text{Al}_{0.2}\text{D}_{2.7(2)}$ 953 bar	7.5141(5)	5.9	18.6	3.09	$x=0.324(7)$ $z=0.129(4)$ occup. 23(2)%	Zr-D 2.11 Zr-D 1.98 Fe(Al)-D 1.70

In situ SR XRD studies of hydrogen absorption-desorption processes in Mg-based hydride nanocomposites

Mg and Mg alloys can be easily hydrogenated during reactive ball milling (RBM) in H₂ gas, to yield nanocrystalline materials exhibiting excellent H sorption performances [6, 17]. The hydrogenation and dehydrogenation of the materials obtained by HRBM of pure Mg and its nanocomposites with a V-based BCC alloy, $\text{V}_{75}\text{Ti}_{10}\text{Zr}_{7.5}\text{Cr}_{7.5}$ (for simplicity, it further referred to in the paper as a V alloy), were experimentally studied by time resolved *in situ* synchrotron X-ray diffraction (SR XRD), in a temperature range from 20 to 400°C and at H₂ pressures up to 15 bar. In particular, the mechanism, the kinetics of the phase-structural transformations and the microstructural evolution of the samples during hydrogen uptake and release were characterized.

The main constituents of the hydrogenated by application of the RBM in hydrogen Mg and Mg-V alloy composites are two allotropic modifications of magnesium dihydride, the rutile-type $\alpha\text{-MgH}_2$ and the high-pressure $\gamma\text{-MgH}_2$ ($\alpha\text{-PbO}_2$ type) in ratio (appr. 3:1), and CaF₂-type vanadium dihydride (in Mg-V nanocomposites). The crystallite sizes of magnesium dihydrides were evaluated from the XRD peak broadening to be appr. 7 nm.

During the *in situ* SR XRD experiments the mechanochemically hydrogenated Mg and Mg-V alloy were subjected to absorption-desorption cycling at temperatures 25-300 °C and pressures 0-15 bar H₂. Evolution of SR XRD pattern of nanocrystalline MgH_2 as a function of temperature during the hydrogen desorption is shown in Fig.7. Fig.8 summarizes changes in phase abundances and allows identifying three contributing to the mechanism of decomposition

processes: (1) a metastable hydride $\gamma\text{-MgH}_2$ partially transforms into $\alpha\text{-MgH}_2$; (2) in parallel, it also directly decomposes to Mg and H_2 ; (3) $\alpha\text{-MgH}_2$ directly decomposes to Mg. These three events were observed during the hydrogen desorption from the V-containing nanocomposites. However, the decomposition temperatures appear to be substantially, by $\sim 100^\circ\text{C}$, lower than for the individual nanocrystalline MgH_2 . In addition to the $\text{MgH}_2 \rightarrow \text{Mg}$ transformation, a step-by-step transformation $\gamma\text{-VH}_2$ (FCC) $\rightarrow \beta_2\text{-VH}_{0.7}$ (BCC) $\rightarrow \beta_1\text{-VH}_{0.5}$ (BCT) $\rightarrow \text{V}$ (BCC) has been evidenced.

Peak broadening analysis of *in situ* SR XRD data showed a continuous increase in the crystallite sizes of MgH_2 hydrides during their heating in vacuum, from ~ 7 nm at room temperature up to ~ 20 nm at 350°C in the end of decomposition process. The crystallite sizes of Mg metal formed during the thermal desorption from the RBM MgH_2 exceed 150 nm. On further re-hydrogenation, large crystallites of $\alpha\text{-MgH}_2$, with sizes above 100 nm, are formed.

On subsequent isothermal re-hydrogenation/dehydrogenation cycling, the RBM materials show enhanced kinetics of the transformations. For Mg metal, its re-hydrogenation at 300°C starts from an instant formation of the MgH_x solid solution as the first stage of the H uptake process. The following hydride formation proceeds in accordance with the mechanism of nucleation and growth of $\alpha\text{-MgH}_2$ occurring in the bulk of the Mg particles via a grain boundary attack.

Presence of V-based alloy in the nanocomposite leads to dramatic improvement of hydrogenation kinetics of Mg and reduction of hydrogenation temperature from 300°C to room temperature [16]. Such improvement of hydrogenation kinetics is caused by catalytic and exothermic heat effects of hydrogen absorption by the V-based alloy.

Figure 7. *In situ* SR XRD pattern ($\lambda=0.7114(1) \text{ \AA}$) of hydrogen vacuum thermal desorption from the RBM MgH_2 .

Figure 8. Changes in phase composition of the RBM MgH_2 during hydrogen thermal desorption from Rietveld refinements of *in situ* SR-XRD data.

Present study clearly shows that synthesis of the nanostructured composites of Mg and V-based alloys dramatically facilitates the rates of H uptake by the Mg-based materials and significantly decreases the reaction temperatures; in all cases 50–80% hydrogenation of Mg was

observed already at room temperature. This facilitation has been achieved as a result of significant decrease in the particle size during the HRBM, thus decreasing diffusion lengths for hydrogen in the material, and, also by achieving synergy in hydrogenation of V and Mg. Hydrogen absorption by the Mg-V composites starts from instant formation of the V-based hydrides, which promote the hydrogenation of Mg. As can be seen from Figures 8 and 9, at the first stages of the hydrogenation process, an instant formation of the β_1 -VH_{0.5} is observed; it is followed by a fast transformation into the β_2 -VH_{0.7}. Hydrogenation of Mg leading to the formation of α -MgH₂ has slower rate and proceeds after the vanadium monohydride is formed. The rate of the transformation $V \rightarrow \beta_2$ -VH_{0.7} was found to be two orders of magnitude higher than that for the hydrogenation of Mg.

Figure 9. Evolution of the in situ SR XRD pattern ($\lambda=0.7114(1)$ Å) of Mg-V RBM composite during the hydrogenation at 80°C and 9 bar H₂.

Figure 10. Hydrogenation kinetics of the individual components of the Mg-V RBM composite from the Rietveld refinements of the *in situ* SR XRD data.

The catalytic effect of V on the hydrogenation of Mg can be identified as follows: (1) V acts as a source of atomic H, because of an easy H₂ dissociation on its surface and (2) formation of extra centers for the nucleation of MgH₂ on an interface between the Mg and V alloy, where V acts as a catalyst of the hydrogenation process.

On hydrogen desorption, the sequence of events is opposite; α -MgH₂ decomposes first followed by H release from the VH_{0.5}. Substantial decrease in desorption temperature can be explained by a facilitated nucleation of Mg phase in presence of V nanoparticles.

CONCLUSIONS

In conclusion, this work clearly demonstrates a great potential of the *in situ* diffraction techniques, neutron powder diffraction and synchrotron X-ray powder diffraction, in probing the mechanism of hydrogenation to form solid hydrogen storage materials. Neutron scattering at high pressures not only provides an insight into the metal-hydrogen bonding by establishing hydrogen neighborhood and relative population of different sites, but also shows a thermodynamic difference between the hydrogenation and hydrogen desorption processes and

changes in the behaviors of cycling of hydrogen uptake and release. When complemented by *in situ* SR XRD, extra features of the metal-hydrogen interactions become uncovered, by exploring benefits from significantly improved time resolution of the processes, high sensitivity in determining formation of the phase constituents and excellent accuracy in yielding the crystallographic data. Thus, further development of combined *in situ* NPD and SR XRD studies of the metal-hydrogen systems should be considered to be a very relevant and important task in discovery and optimization of the novel and advanced hydrogen storage materials.

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