USE OF NEUTRON DIFFRACTION FOR THE DEVELOPMENT OF METAL HYDRIDES FOR HYDROGEN STORAGE

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Abstract

Metal hydrides are attractive solutions for hydrogen storage in a wide range of applications going from fuel cell submarine down to smart phones. In metal hydrides hydrogen is chemically bonded to other elements to form an alloy. Therefore, knowledge of the crystal structure of the metal hydride in its hydride and dehydrided state is essential. However, as hydrogen is difficult to be localized from X-ray diffraction, neutron diffraction is basically the only waynon-destructively evaluate the crystal structures of metal hydrides. In this paper we will present the use of neutron diffraction in two different metal hydrides systems. First, we will show that from neutron diffraction we were able to demonstrate the relationship between the metastable orthorhombic γ-MgH_2 and the tetragonal β-MgH_2. The second example is the two phase compound $TiV_{0.9}Mn_{1.1}$ in which the exact elemental composition and localization of the atoms in the crystal structures could only be achieved from neutron diffraction.We will end this talk with a general discussion on the benefit of using neutron techniques for the development of metal hydrides.

1. Introduction

With the growing concern about global warming, fossil fuels has to be replaced by environmentally friendly candidates. Despite manytechnological and economic problems, hydrogen is seriously considered as an energy vector, mainly because of its benefits in terms of air pollution, energy security, and renewability[1, 2]. Hydrogen is particularly attractive as an energy vector because it could be coupled to practically all types of power plants such as windmill, solar, nuclear, etc. In all cases, as energy production from renewable resources is usually not in phase with consumption, hydrogen storage of some form will be needed. The type of storage will depends on the particular application but presently three storage modes are used: gaseous, liquid, and solid (metal hydrides). However, storing hydrogen in gaseous or liquid states suffer important drawbacks such as high pressure and low volumetric capacity in the case of pressure tanks, or cryogenic temperatures (below 20 K) and important liquefaction energy in thecase of liquid [3]. The class of materials known as metal hydride seems to be a better candidate for the storage technology for mobile and portable systems [4], hydrogen storage in stationary applications, and submarine fuel cell[5].

Metalhydrides (MH) are chemical compoundsof one or many metals (M) with atomic hydrogen(H) [6]. The advantages of metal hydrides are that they havehigh volumetric storage capacity (higher than liquid hydrogen)and they could provide extremely pure hydrogen, whichis essential for utilization in fuel cells. For most practical applications theabsorptionand desorptionofhydrogen hasto be at, orclose to,room temperatureandat pressure ofaround onebar.

Themetal hydride should alsohave fastsorptionkinetics andbe resistantto poisoningby traceimpurities. Metal hydrides could furthermore be used in fast reactor cores as neutron absorbers or as transmutation target of long lived nuclear wastes [7].

Metal hydrides are intensively studied since 1970's but development is still needed in order to obtain a material that will perfectly meet the criteria for specific applications. In this respect, neutron diffraction is an important tool because it is easyay to locate the hydrogen atom in the crystal lattice. Neutron techniques are also used to study the dynamics of hydrogen in the lattice (inelastic and quasielastic)[8], study thin film (neutron reflectometry) [9] and visualize hydrogen in a storage tank (neutron imaging)[10].

In this paper we will discuss the use of neutron diffraction for the development of metal hydrides. One key fact is that because of the high incoherent scattering length of hydrogen it could actually not be used for diffraction measurements. Fortunately, deuterium does not have such high incoherent scattering. In metal hydrides, deuterium usually has the same thermodynamics and kinetics properties as hydrogen and could thus be used for neutron diffraction studies.The main disadvantage of neutron diffraction experiments are that they have to be performed in large scale facilities such as nuclear reactors or spallation sources. Each experimental pattern is compared to a simulated one from the expected crystal structure using Rietveld refinement [11]. The refinement then gives the usual crystallographic parameters such as lattice parameter, atomic position, thermal factor as well as the crystallite size and microstrain. In this paper we will review the use of neutron diffraction in the investigation of two well-known classes of metal hydrides: magnesium and Body Cubic Centered (BCC) alloys.

2. Magnesium hydride

The high hydrogen storage capacity of magnesium (7.6 wt.%) and its relatively low cost could make this material a good candidate for hydrogen storage applications. However, its high temperature of operation and the slow sorption kinetics have seriously limited the number of commercial uses. Improvement of the sorption kinetics in magnesium-based alloys could be achieved in various ways such as by the adding a catalyst [12, 13], forming a composite with a low temperature hydride[14, 15], using multiphase systems[16], chemical modifications using organic materials [17] or by developing magnesium-graphite composites [18]. Nevertheless, these techniques have the drawback of cost increase, reduction of hydrogen capacity and cycling degradation.

2.1 Milling of magnesium hydride

Milling is a powerful and scalable technique that is intensively investigated for the synthesis of numerous systems[19-24]. It is broadly used to improve hydrogen storage properties of metal hydrides. In the milling process, the powder or powder mixture is loaded in the mill along with the grinding medium (usually steel balls) and shaken for the desired length of time. During milling, the powder particles are repeatedly fractured and cold welded. Depending on the nature of the powder and the process variables, the milled materials could be crystalline (metastable, high pressure or equilibrium), quasicrystalline, amorphous, or nanocrystalline[24].

Many studies have been performed on milling magnesium hydride. The phase diagram of Mg-H system consists of an interstitial solid solution of hydrogen in magnesium (hcpα phase) and a stoichiometric tetragonal β-MgH_2 phase[25, 26]. These are the stable phases. However, it has been shown that under high pressure and temperature metastable phases are synthesized. Amongst them we should mention the orthorhombic high-pressure (γ-MgH_2) phase found by Bastide et al [27]. The structure of β- and γ-MgH_2 are closely related and are shown in Figure1. In both structures, Mg is in an octahedral coordination of 6H. The octahedra in γ-MgH_2 are strongly distorted compared to those in β-MgH_2.

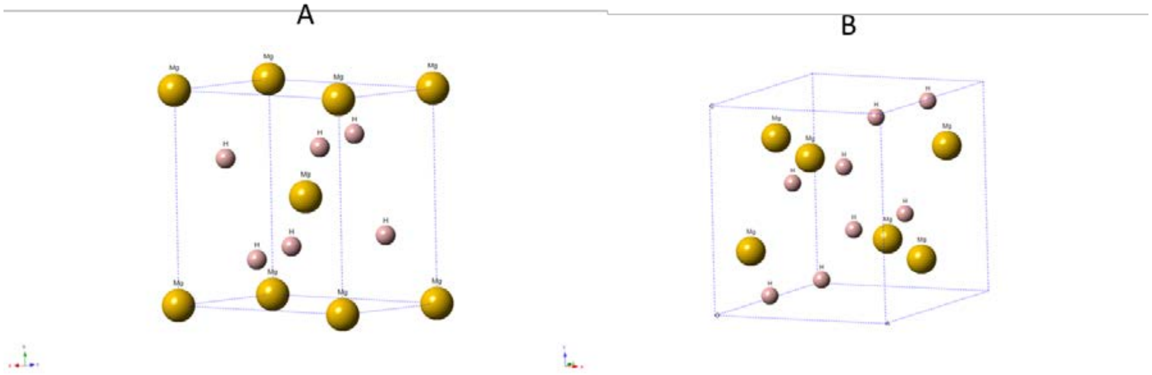

Figure 1.Crystal structure of β-MgH_2(A) and γ-MgH_2(B).

It has been found that, upon milling β-MgH_2, the metastable phase γ-MgH_2 is formed but its abundance reach a steady-state value after two hours of milling and do not increases with further milling[28, 29].In figure 2 we present the morphology of commercial MgH_2 (Th. Goldschmidt powder, 99.95% pure) before and after ball milling. The ball to powder ratio was 10:1 and milling was performed on a high-energy mill Spex 8000. We see that particle size is drastically reduced going from a few tens of microns to a few microns.

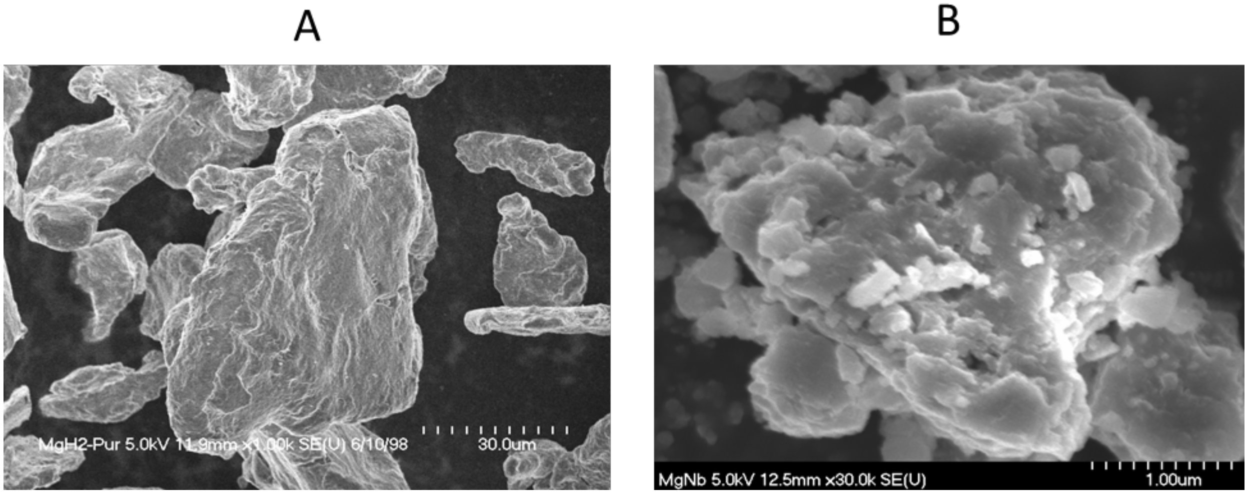

Figure 2.Morphology of MgH_2before and after ball milling.

In order to understand the formation mechanism of γ-MgH_2 and the reason why its abundance do not increases with milling time we used neutron diffraction. Figure 3 shows the neutron powder diffraction of MgD_2 milled for 20 hours. In this figure the measured, calculated and difference neutron diffraction patterns as calculated by Rietveld refinement are presented. The broadness of the peaks is mainly due to the nanocrystalline nature of the sample. Moreover, we see the presence of $Mg(OH)_2$ which is due to air exposure during neutron diffraction. The incoherent diffraction of hydrogen contained in $Mg(OH)_2$ is responsible for the high background seen in this pattern. The presence of magnesium oxide and hydroxides were confirmed by the Rietveld analysis. The phase abundance of MgO and $Mg(OH)_2$ was respectively 36wt.% and 18 wt.%.

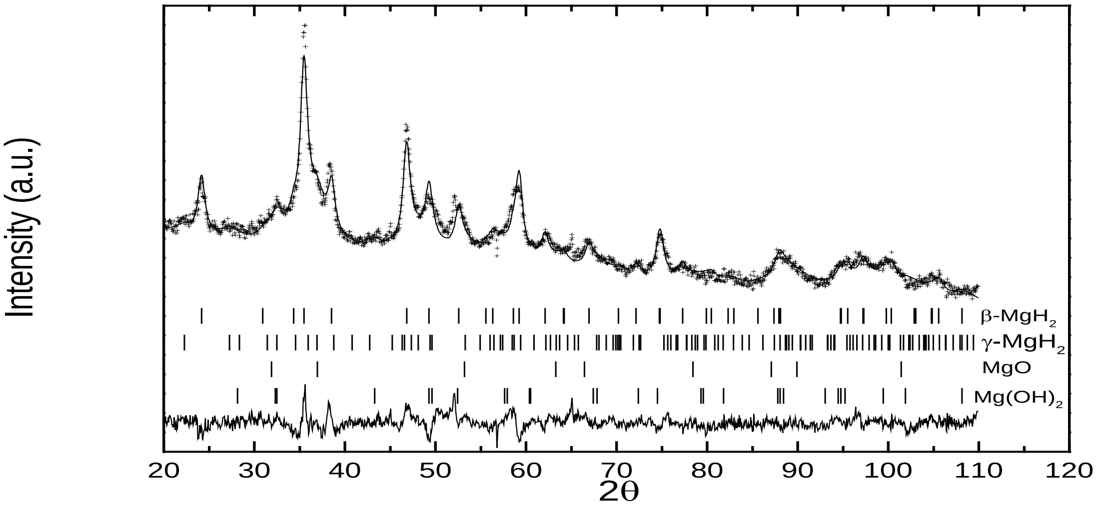

Figure 3Neutron powder diffraction of 20 hours milled nanocrystalline MgD_2. (crosses: experimental intensity, upper solid line: calculated intensity, lower line: residue). From ref [30]

Using FULLPROFRitveld refinement we were able to locate the hydrogen (deuterium) atoms in the milling β-MgH_2 and γ-MgH_2 phases and to compute the metal-hydrogen bond length in each of these phases[31]. Localisation of hydrogen (deuterium) could only be done using neutron diffraction because the X-ray scattering power of hydrogen is too small. From atom localisation and lattice parameters the bond lengths could be computed. Table 1 report the bond lengths compared to the literature values.For the β phase, one bond length is stretched while the other one is compressed by the same amount with respect to the literature values. In the γ structure, two bond lengths are very similar while one is highly stretched compared to the γ-phase synthesised at high temperature and pressure.

Phase	Literature	This work	Variation (%)
β-MgD_2	1.9351(9)	1.915(4)	-1.0
	1.9549(6)	1.976(5)	1.1
γ-MgD_2	1.915(3)	1.92(2)	0.3
	1.943(3)	1.93(2)	-0.7
	2.004(3)	2.04(2)	1.8

Table 1. Deuterium-magnesium distances (in Å) in MgD_2.Number in parenthesis is the error on the last significant digit. Literature values are from ref. [32]

In reference [32], the authors pointed out that for the pressure induced β⇒γ phase transition, bonds are broken and re-established. In our ball milled sample, the bond length in β phaseare symmetrically stretched and compressed by about 1% with respect to the literature values. This could be the limit where bonds break and where the structural transformation into γ phase takes place. Stress relaxation associated with the phase transition could therefore be the explanation for the appearance of γ phase in ball-milled samples. The stress field may act as the driving force for the β⇒γ phase transition.

3. Ti-V-Mnalloy

Solid solution BCC alloys (mainly Ti-V-Cr and Ti-V-Cr based) are promising hydrogen storage materials because of their relatively high storage capacity and their ability to absorb and desorb hydrogen in ambient conditions[33]. This type of hydride is also considered by Toyota Motor Corporation in hybrid high-pressure/metal hydride storage tanks for vehicular applications[34]. In almost all compositions, the highest hydrogen storage capacity is reached when the alloy is single phase BCC solid solution. However, some authors claims that a lamellar structure may help the hydrogenation by interactions of nano-composite phases through a coherent interface[35].We report here the crystal structure of the multiphase alloy $TiMn_{1.1}V_{0.9}$. This alloy crystallizes in a two phase compound. One phase is body-centered-cubic (BCC) the other one the hexagonal Laves phase C14. For this alloy we have the complication that the scattering cross section of Ti and Mn are almost the same (respectively -3.44 and -3.73 barn) and vanadium is practically transparent to neutron (-0.38 barn). Despite these disadvantages, a good quality neutron diffraction pattern could give precise information about the crystal structure. The neutron diffraction pattern along with Rietveld refinement of as-cast alloy is shown in Figure 4. The residue curve is small, indicating a good fit of the pattern.

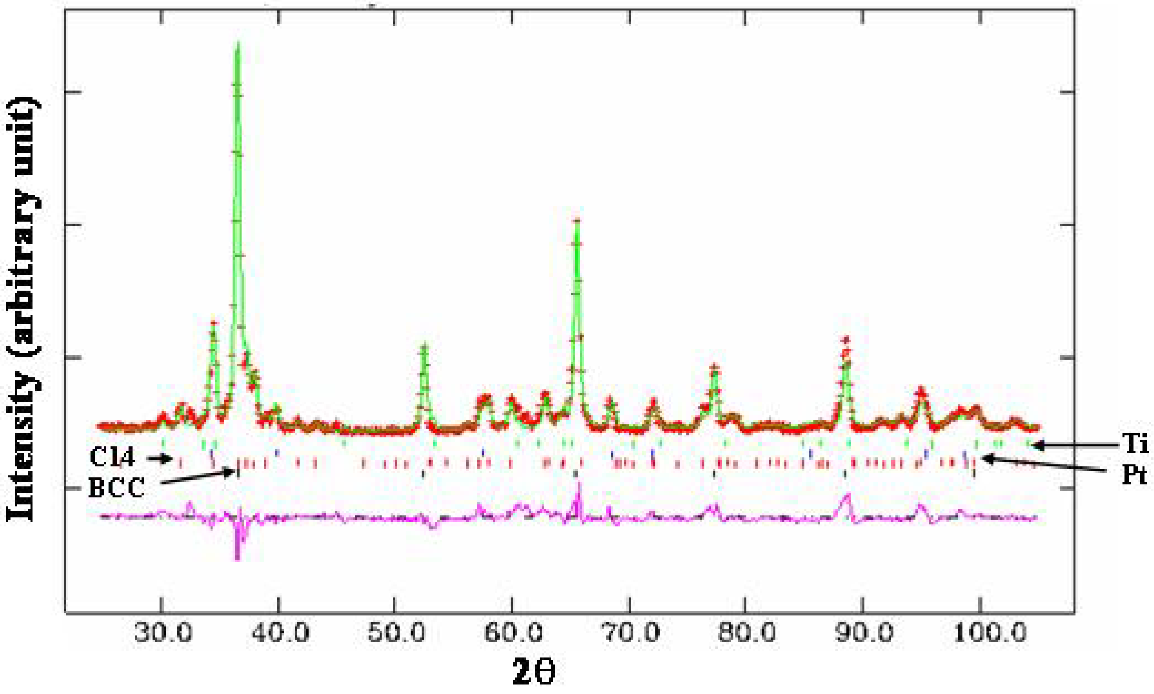

Fig. 4. Neutron diffraction pattern and Rietveld refinement of $TiV_{0.9}Mn_{1.1}$. The short vertical bars indicate the position of Bragg peaks: the upper row is for titanium, second row is platinum, third row is C14 phase, and fourth row is the BCC phase. The bottom curve is the difference between experimental and calculated pattern. From ref. [36]

In our Rietveld analysis the atomic occupancy and position in the C14 phase were refined. Atomic positions are noted by using the Wyckoff notation. The Wyckoff symbol describe the special positions of the space group, beginning with *a* for the highest symmetry. For the C14 structure, position 2*a* is (0,0,0), 4*f* is (1/3,2/3,z), and 6*h* is (x,2x,1/4). In the refinement we assumed that all atoms (Ti, V, and Mn) could be located on each site and we varied the occupancy factor searching for the solution giving the best fit. In Table 2 the refined parameters for the C14 phase are shown. We see that titanium is only located on one site (4*f*) while manganese and vanadium are unevenly distributed on2*a* and6*h* sites. These abundances give a stoichiometry of $TiV_{0.8}Mn_{1.2}$ for the C14 phase. This is an example of the use of neutron as a technique for structure determination and characterization. The hydrogen storage properties of this alloys is reported in ref. [37].

Site (Wickoff symbol)	Refined Coordinates	Atoms	Occupancy
2*a*	--	Mn V	0.65 0.35
4*f*	z = 0.065	Ti	1.0
6*h*	x = 0.82356	Mn V	0.58 0.42

Table 2. Crystallographic parameters of the C14 phase in $TiV_{0.9}Mn_{1.1}$ as determined from Rietveld refinement of neutron diffraction pattern.

4. Conclusion

Neutron diffraction is a unique and powerful tool for the development of metal hydrides. It can be used for structure characterization and the localisation of hydrogen (deuterium) atoms.In the case of ball milled magnesium hydride, powder neutron diffraction showed that strain relaxation during milling could be a possible explanation for the β-$MgD_2 \Rightarrow \gamma$-MgD_2 transition.A complete discussion of this is in ref [30]. This explanation was possible only because hydrogen atoms could be located in the lattice and hydrogen bonds be computed. Therefore, neutron diffraction was essential for finding the β-$MgD_2 \Rightarrow \gamma$-MgD_2transition during ball milling. Neutron diffraction of $TiV_{0.9}Mn_{1.1}$ alloy confirmed that the arc melted alloy was formed by a C14 and a BCC phases.In the case of C14, titanium atoms occupy the 4*f* site while on the two other sites there is a higher proportion of manganese than vanadium. Neutron diffraction is an essential technique for the development of metal hydrides. We wish the international facilities where this technique is available will continue to be supported in order to be available to the scientific community

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