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NMR study of metal-hydrogen systems for hydrogen storage

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ABSTRACT

In this contribution we report on the results of our recent ^{1}H NMR studies of different metal hydrides of interest for reversible hydrogen storage applications: Ti–V–Cr alloys of various compositions, pure and with Zr_7Ni_{10} or Hf_7Ni_{10} additives, and in additives themselves. The temperature dependences of ^{1}H spin-lattice relaxation have been treated within an exchange model.

1. Introduction

During the last decades metal hydrogen systems as hydrogen storage materials were subject of intensive studies. Despite a considerable amount of both experimental and theoretical works, a fundamental and comprehensive understanding of intrinsic mechanisms that govern the thermodynamics and hydrogen kinetics in these hydrides still merits complementary investigations. In such perspectives, deeper knowledge on local structure and hydrogen mobility is helpfully required. Appreciable enlightening of main characteristics (static and dynamics) can be provided using nuclear magnetic resonance (NMR) method which is an especially powerful tool to investigate metal hydrogen systems [1–3].

The magnesium dihydride MgH_2 is one of the most attractive materials for hydrogen storage due to its high storage capacity (7.6 wt.% of hydrogen) and low cost of magnesium. However, its rather slow hydrogen absorption and desorption kinetics as well as high dissociation temperature, which is above 673 K, essentially limit its application for hydrogen storage. Numerous attempts have been made in order to improve magnesium hydrogen absorbing–desorbing characteristics. It has been reported experimentally that mixing magnesium or magnesium hydride with small amount of transition metals (TM) [4] or their oxides [5] essentially accelerates the hydrogen kinetics. However, the nature of this improvement up to now remains unclear.

Several attempts have been undertaken to explain it using NMR techniques. In Ref. [6] it has been found from ^{1}H NMR line width measurements that in coarse-grained MgH_2 the hydrogen hopping rate remains very slow up to 400 °C, whereas in MgH_2 ball-milled with Nb_2O_5 additives the fraction of mobile hydrogen grows continuously with temperature. That indicates the acceleration of reaction kinetics in this material is not only due to the decreased diffusion distance, caused by decreasing grain size, but also due to the faster hydrogen motion.

According to ^{1}H nuclear spin-lattice relaxation data in nanoscaled MgH_2 ball-milled with 10–15% V_2O_5 [7,8], the surface layer contains paramagnetic centres which are responsible for the spin-lattice relaxation rate enhancement. The authors suppose that these paramagnetic centres result from broken bonds on the surface of MgH_2 grains (these paramagnetic centres do not originate from the ball material) and could provide high catalytical activity of the mechanically activated Mg-based alloys.

NMR has been also applied to study hydrogen dynamics in magnesium–scandium hydrides. In Ref. [9] the rates of H and D atomic hopping in $MgScH_x$ metal-hydrides has been measured. In particular, it has been found that the motion of hydrogen in $MgScH_x$ is more rapid than in the metallic ScH_2 and the ionic MgH_2, but slower than in $LaNi_5H_x$. A new double-quantum NMR method with ^{45}Sc recouping reveals two types of deuterium with and without scandium neighbours [10], which indicates that a part of hydrogen

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Table 1

Experimental structural data and calculated parameters of the exchange model of the proton spin-lattice relaxation for studied hydrides of $Ti_{0.33}V_{1.27}Cr_{1.4}$, $Ti_{0.5}V_{1.9}Cr_{0.6}$, $TiV_{0.8}Cr_{1.2}H_{5.29}$, $TiV_{0.8}Cr_{1.2}$ + 4 at.%Zr_7Ni_{10} and $TiV_{0.8}Cr_{1.2}$ + 4 at.%Hf_7Ni_{10} alloys; the values of τ_0 and $\tau_c^{300\,K}$ are given for the mobile/bounded hydrogen states.

Parameters		$Ti_{0.33}V_{1.27}Cr_{1.4}$	$Ti_{0.5}V_{1.9}Cr_{0.6}$	$TiV_{0.8}Cr_{1.2}$	$TiV_{0.8}Cr_{1.2}$ + 4 at.%Zr_7Ni_{10}	$TiV_{0.8}Cr_{1.2}$ + 4 at.%Hf_7Ni_{10}
Structure type	Alloy	bcc	bcc	bcc	bcc[a]	bcc[a]
	Hydride	bcc	fcc	fcc	fcc[a]	fcc[a]
Lattice parameter	Alloy	2.981 ± 0.002	3.028 ± 0.002	3.046 ± 0.002	3.026 ± 0.002[a]	3.041 ± 0.002[a]
	Hydride	3.036 ± 0.002	4.269 ± 0.002	4.282 ± 0.002	4.255 ± 0.004[a]	4.271 ± 0.004[a]
p_m/p_b		0.35/0.65	0.45/0.55	0.30/0.70	0.37/0.63	0.36/0.64
E_a (kJ/mol)		10.6	10.7	12.4	13.0	12.9
$\tau_0(\times 10^{-11}$ s)		3.1/420	2.4/650	2.2/520	2.2/520	2.0/550
$\tau_c^{300\,K}(\times 10^{-9}$ s)		2.2/294	1.7/474	3.2/746	3.3/759	3.5/970
$S_2(G^2)$		35	38	28	26	20
K (Ks)		53	53	53	30	33

[a] Structure type and lattice parameter are given for the main phase ($TiV_{0.8}Cr_{1.2}$).

atoms are more mobile than the rest. Moreover, NMR measurements confirm a non-statistical Mg and Sc distribution over the crystal lattice.

The Ti–V–Cr alloys belong to a class of body centred cubic systems and exhibit potentially excellent characteristics of hydrogen storage properties with maximum uptake of more than 3.5 wt.% hydrogen for the most appropriate compositions. According to the ternary phase diagram, Ti–V–Cr alloys crystallize mostly to bcc structure, except narrow region near $TiCr_2$ composition with Laves phase AB_2 structure, which forms extremely stable hydride. However, even small amounts of V promote the bcc phase formation. In the bcc structure, Cr is the element that moderates the thermal stability of the hydride. Due to the bigger covalent radius (compared to Cr and V atom), with the Ti content increasing, the lattice parameter of the bcc alloy increases. It reaches a maximum for 33.33 at.% of Ti and the atomic percentage ratio Cr/V equal to 1.5 (formula $TiV_{0.8}Cr_{1.2}$) and decrease for lower or higher ratio. Increasing the lattice parameter leads to increasing the interstitial space and likewise the number of available hydrogen sites. The stability of these sites also changes with the composition of the alloy [11].

Besides the better thermodynamic properties, these ternary alloys exhibit rather fast hydrogen sorption kinetics (compared to MgH_2) which can be improved further by alloying with Zr_7Ni_{10} or Hf_7Ni_{10} [12]. Despite numerous NMR studies of hydrides of pure Ti, V, Cr and binary Ti–V, V–Cr alloys, the ternary Ti–V–Cr systems which is interesting in terms of hydrogen storage have not been investigated by NMR before to our knowledge.

In this paper, we report on the results of our ^{1}H NMR study of hydrogen mobility in ternary Ti–V–Cr alloys of various compositions ($TiV_{0.8}Cr_{1.2}$ as a basic composition, $Ti_{0.33}V_{1.27}Cr_{1.4}$ as a Cr rich compound, and $Ti_{0.5}V_{1.9}Cr_{0.6}$ as a vanadium rich compound), $TiV_{0.8}Cr_{1.2}$ with Zr_7Ni_{10} or Hf_7Ni_{10} additives, and in additives themselves.

2. Sample preparation and experimental methods

$TiV_{0.8}Cr_{1.2}$, $Ti_{0.33}V_{1.27}Cr_{1.4}$, $Ti_{0.5}V_{1.9}Cr_{0.6}$, Zr_7Ni_{10} and Hf_7Ni_{10} samples have been prepared by induction melting of the pure elements (Treibacher Industries AG) in argon atmosphere and melted three times each. The button-type ingot obtained was about 20 g in mass. A part of each sample, obtained after melting, was hand-crushed into fine powder (200 μm), for XRD analysis, using a steel mortar in the air atmosphere.

Another part of each sample was hydrogenated in autoclave at pressure 20 bar and temperature 200 °C. The estimation of the quantities of hydrogen absorbed by the samples was made by weighting the samples before and after their hydrogenation. That resulted in the formulas $TiV_{0.8}Cr_{1.2}H_{5.29}$, $Ti_{0.33}V_{1.27}Cr_{1.4}H_{1.13}$, $Ti_{0.5}V_{1.9}Cr_{0.6}H_{5.03}$, $Zr_7Ni_{10}H_{16.76}$ and $Hf_7Ni_{10}H_{8.03}$. The grain size after hydrogenation was less than 100 μm. That is comparable to radiofrequency skin thickness in such materials.

To prepare samples with additives $TiV_{0.8}Cr_{1.2}$ has been remelted with 4 at.% of Zr_7Ni_{10} or Hf_7Ni_{10}, after that they were hydrogenated using the same techniques as it is described above.

The structural characterizations of the samples before and after hydrogenation were done using a Siemens D-5000 X-ray diffractometer operated at Co Kα radiation at room temperature. The structure type and lattice parameters for Ti–V–Cr alloys before and after their hydrogenation are listed in Table 1. It is worth noting that all compounds except Zr_7Ni_{10} remains crystalline after hydrogenation, whereas Zr_7Ni_{10} becomes partly amorphous that is in agreement with results of structural study made in Ref. [13].

The pulse ^{1}H NMR spectra were recorded within the temperature range from 180 to 380 K on home-built NMR spectrometer at 20 MHz. The temperature range was restricted by the low hydrogen release temperature of studied alloys. The temperature of the samples was controlled with the accuracy ±0.5 K. The spin-lattice relaxation times T_1 were measured using the inversion recovery techniques.

The line shapes of the samples were also tested with home-built cw NMR spectrometer (42 MHz). During the cw NMR experiment the first derivative of the absorption spectral line was recorded. However, in Fig. 1 we show the ^{1}H NMR spectrum in $TiV_{0.8}Cr_{1.2}H_{5.29}$ hydride in more usual view, after integration of the experimental signals. The ^{1}H spectra in $Ti_{0.33}V_{1.27}Cr_{1.4}H_{1.13}$ and $Ti_{0.5}V_{1.9}Cr_{0.6}H_{5.03}$ are similar to the spectrum in Fig. 1. It is worth noting, that cw NMR spectra are always distorted due to the finite amplitude of the modulation field A_m. The effect is important if the line width is comparable to the A_m value. In our case, all spectra were treated using the home-built program, which takes into account the modulation effect and provides real line intensities and widths.

As it is evident from Fig. 1, the ^{1}H NMR spectrum of studied metallic hydrides consist of two lines: narrow and broad, shifted one relative to another, that corresponds to the hydrogen existing in two states: mobile (m) and bounded to the lattice (b), respectively. And one can suppose that there is an exchange between these two states. To treat the temperature dependences of ^{1}H T_1 in Ti–V–Cr hydrides we applied the modified Bloembergen–Purcell–Pound (BPP) model [14] assuming a fast exchange between mobile and bounded to the lattice hydrogen states [15]. This model can be applied in a case when the life time of hydrogen in these states (τ_m,τ_b) is much less the spin-lattice relaxation time $\tau_{m,b} << T_1$ and the relaxation functions can be described by an average exponential function:

$$F_1(t) = \exp\left(-t\left(\frac{p_m}{T_{1,m}} + \frac{p_b}{T_{1,b}}\right)\right), \qquad (1)$$

where p_m and p_b are relative concentrations of hydrogen in mobile and bounded states ($p_m + p_b = 1$).

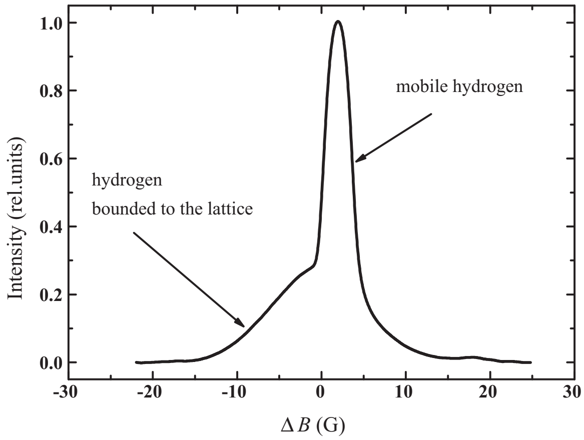

Fig. 1. ^{1}H NMR spectrum in $TiV_{0.8}Cr_{1.2}H_{5.29}$ at 42 MHz at room temperature. The spectrum is superposition of broad and narrow components.