HYDROGEN MOBILITY IN NANOSTRUCTURED C15-TYPE COMPOUND ZrTi$_2$H$_{3.9}$

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Introduction

Nanostructured hydrides prepared by mechanical activation (MA) show a number of interesting properties. In particular, MA is known to accelerate the hydrogen absorption/desorption in some hydrogen-storage materials. Laves-phase hydrides AB$_2$H$_x$ are characterized by rather high volumetric density of hydrogen and high hydrogen mobility [1]. However, little is known about microscopic mechanisms responsible for the hydrogen mobility in nanostructured hydrides. Information on hydrogen mobility in hydrides can be obtained from nuclear magnetic resonance (NMR) measurements [1, 2]. This work is aimed at the investigation of the effects of MA on hydrogen diffusion in nanostructured hydrogen-stabilized C15-type ZrTi$_2$H$_{3.9}$ compounds. In order to study the effects of mechanical activation on the properties of metal hydrides, we have measured the proton NMR spectra and spin-lattice relaxation rates in ZrTi$_2$H$_{3.9}$ compounds.

Results and discussion

The starting material for preparation of the nanostructured hydrides was the ZrTi$_2$H$_{3.9}$ compound with the cubic C15-type structure and the lattice parameter a = 8.183 Å. The mechanical activation was performed at room temperature in an argon atmosphere using a vibrating ball mill with brass vial and brass balls. Figure 1 shows the data of X-ray diffraction analysis. The evolution of the diffraction patterns with the milling time is consistent with a gradual transition from the C15-type phase having the lattice parameters a = 8.180 Å (MA for 0.5 hours), 8.178 Å (MA 1.5 hours), and 8.178 Å (MA 3 hours) to the TiH$_2$-type phase with the lattice parameter of 4.572 Å. The diffraction peaks corresponding to the C15-type phase in the ball-milled samples are considerably broader than those in the starting material. The average grain sizes estimated from the peak broadening in the samples with the milling times of 0.5, 1.5, and 3 hours are 23, 10 and 10 nm, respectively. For the TiH$_2$-type phase, the average grain size is about 10 nm. The fraction of the C15-type hydride estimated from the peak intensities is 77% (MA 0.5 hours), 16% (MA 1.5 hours), and 13% (MA 3 hours).
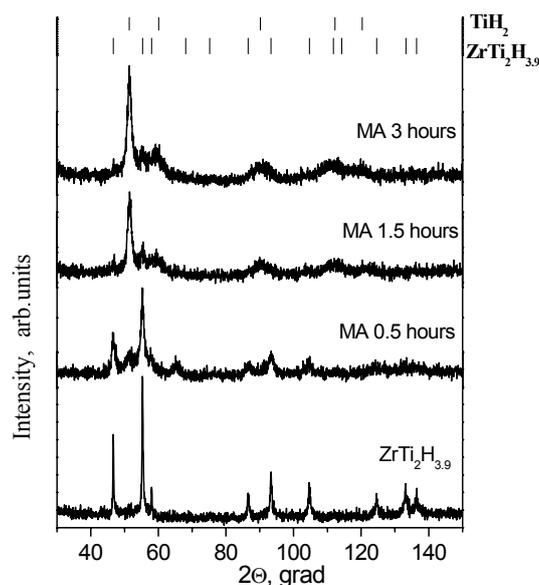

Fig. 1. X-ray diffraction patterns of ZrTi$_2$H$_{3.9}$ samples.

The proton NMR measurements have been performed at the resonance frequencies of 14.6, 23.8 and 90 MHz over the temperature range 20 − 420 K. The results of the measurements of proton spin-lattice relaxation rates T_1^{-1} at 14.6 MHz are shown in figure 2. The spin-lattice relaxation rate in metal-hydrogen systems is usually determined by the sum of two main contributions: $T_1^{-1} = T_{1e}^{-1} + T_{1m}^{-1}$, where T_{1e}^{-1} is the contribution related to the hyperfine interaction of nuclei with conduction electrons, and T_{1m}^{-1} is the contribution due to the modulation of nuclear dipole-dipole interaction by atomic motion. The T_{1m}^{-1} contribution exhibits a resonance-frequency-dependent maximum. This maximum arises at the temperature at which the atomic jump rate $\tau_d^{-1}(T)$ becomes approximately equal to the frequency of the nuclear magnetic resonance.

Fig. 2 shows that the mechanical milling results in strong changes in the behaviour of spin-lattice relaxation rates T_1^{-1}. With increasing milling time, the relaxation rate maximum gradually decreases

and shifts towards higher temperatures. For parametrization of the experimental data on T_1^{-1} in the region of the maximum, we have used the Bloembergen-Purcell-Pound (BPP) model with a Gaussian distribution of activation energies. The analysis in terms of this model has shown that the increase of the milling time leads to the growth of the average activation energy from 0.23 eV for the coarse-grained sample to 0.26 eV for $ZrTi_2H_{3.9}$ milled for 3 hours and to the increase of the activation energy distribution width.
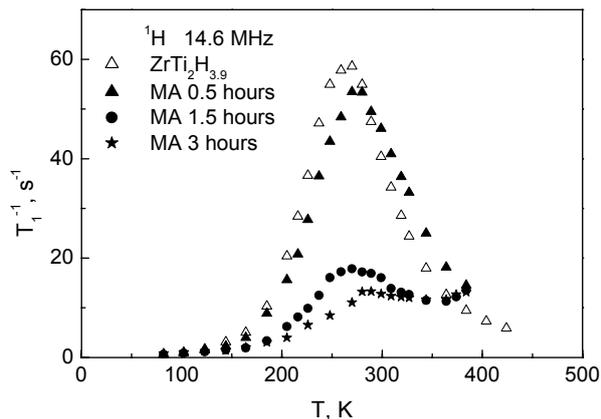

Fig. 2. Temperature dependences of the spin-lattice relaxation rate of ^1H in $ZrTi_2H_{3.9}$ at the frequency of 14.6 MHz.

The experimental data suggest that these effects are related to the growth of the fraction of the additional phase where hydrogen mobility is much lower than in the C15-type grains. The ratio of the maximum motional contributions to the relaxation rate in the starting hydride and in the nanostructured sample after 3 hours of treatment is 5.2. This suggests that the sample mechanically activated for 3 hours contains about 19% of the C15-type phase, in agreement with the X-ray diffraction data.

Figure 3 shows the spectra of the ^1H NMR for $ZrTi_2H_{3.9}$ and TiH_2 systems. The spectra were measured by continuous wave NMR (CW NMR) at 290 K. It can be seen that the spectra for the MA $ZrTi_2H_{3.9}$ samples consist of two components, and the intensity of the broad component increases with the milling time. This behavior can be attributed to the appearance and growth of the new phase with the TiH_2-type structure. In fact, the width of the broad component is close to the ^1H NMR line width for the coarse-grained TiH_2 sample.
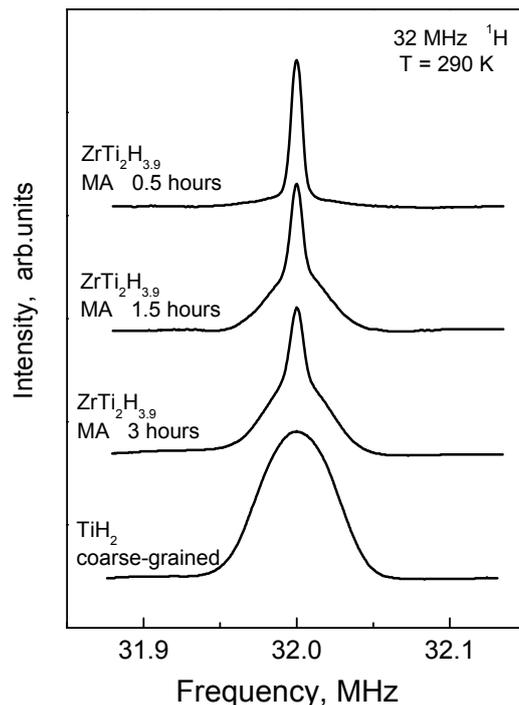

Fig. 3. Spectra of the ^1H continuous wave NMR for $ZrTi_2H_{3.9}$ and for TiH_2 systems.

Conclusions

The results of the measurements of the proton spin-lattice relaxation rates and ^1H CW NMR spectra in the ball-milled compounds $ZrTi_2H_{3.9}$ show that with increasing milling time the average activation energy for the diffusion of hydrogen atoms in the initial phase increases. Mechanical activation also leads to a phase separation resulting in the appearance of the phase with the TiH_2-type structure. The fractions of the two hydride phases are estimated from the experimental data.

References

1. Skripov A.V. Hydrogen diffusion in Laves-phase compounds. Defect and Diffusion Forum. 2004; 224-225: 75-92.

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