Deuterium NMR Studies of $Mg_{2-x}Mn_xNiD_z$ ($0 < x < 1$)

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Metal hydrides are extensively investigated due to their potential application as hydrogen storage materials. Among them magnesium based alloys are considered to be one of the most promising systems. Mg_2Ni crystallizes in the hexagonal structure and reacts with hydrogen to form a stable hydride with one of the highest hydrogen storage capacity, about 3.6 wt.%. However, the most serious drawbacks arise from the slow hydriding/dehydriding kinetics. Moreover, the hydriding reaction requires high temperature and pressure, which seriously hinders the practical application.

Recently, it has been shown that materials obtained by processing techniques such as mechanical alloying (MA), or materials in which nickel has been substituted to some extent by manganese or aluminum, exhibit enhanced hydrogen absorption and desorption kinetics, even at relatively low temperatures. These materials posses also higher discharge capacity than the pure Mg_2Ni.

In this work we present results of structural and microstructural studies ^2H NMR of $Mg_{2-x}Mn_xNiD_z$ ($z \approx 4$) system obtained by MA. The starting materials used for MA were metallic powders of Mg (≤300 μm, 99.9%), Ni (3–7μm, 99.9%) and Mn (≤45 μm, 99%). The powders were put into a steel vial together with stainless steel balls. Mechanical alloying was carried out using the SPEX 8000 Mixer Mill. The milled powders were heated at 450^0C for 0.5 h under high purity argon in order to form the desired phase. The structure of the $Mg_{2-x}Mn_xNi$ ($0 < x < 1$) was characterized by the X-ray diffraction using CuKα radiation. Microstructural studies were performed by scanning electron microscopy (SEM). Mg_2Ni and $Mg_{1.75}Mn_{0.25}Ni$ compounds were found to be single phase with hexagonal structure. The further increase of manganese concentration leads to a multi phase system with major phase being close to $Mg_{1.75}Mn_{0.25}Ni$, and residual phases of Mn and Ni. SEM studies revealed similar microstructure of all compounds with agglomerate sizes in the 0.5–1μm, which consisted of much smaller, highly sintered crystallites.

Before deuterating, the samples placed in the high pressure apparatus were annealed at 100^oC in vacuum. The hydrogenation was performed at 0.3 kbar pressure at 200^oC for 15 min and at 10 kbar pressure at 200^0C for 3 days. In order to avoid possible hydrogen desorption, the samples were quenched and immediately transferred into liquid nitrogen.

Fig. 1 shows the ^2H MAS NMR spectra of $Mg_{2-x}Mn_xNi$ referring to 0.3 and 10 kbar pressures, measured at 7 kHz spinning at room temperature. The linewidth of the samples prepared at 0.3 kbar is much smaller than for the samples of 10 kbar. It can be seen that deuterium is in the same chemical lattice position for both series of samples. The $Mg_{1.75}Mn_{0.25}Ni$ sample contained about 40% more deuterium than Mg_2Ni. However, for samples with higher Mn amount, the concentration of deuterium decreased. In Fig. 2 the ^2H spin–lattice relaxation rates of $Mg_{1.75}Mn_{0.25}NiD_z$ as a function of temperature are presented. Two relaxation rates can be seen and both of them increase with temperature. The presence of

two relaxation times most probably can be related to the appearance of defected crystal structure after hydriding. Due to defects in crystal structure some deuteriums are mobile, while the rest of them exhibits much lower mobility. However, more studies are needed to clarify this assumption.

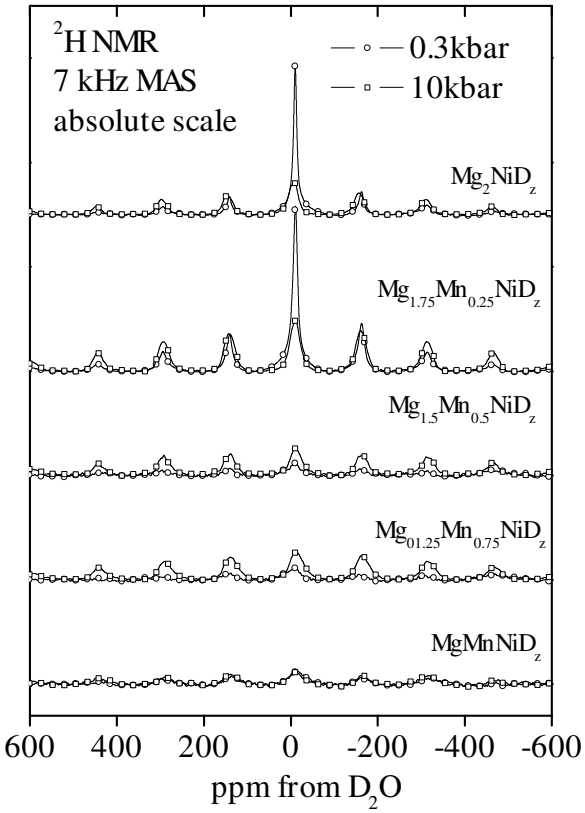

Fig. 1. ^{2}H MAS NMR spectra of $Mg_{2-x}Mn_xNi$ for 0.3 and 10 kbar samples, measured at 7 kHz spinning at room temperature.

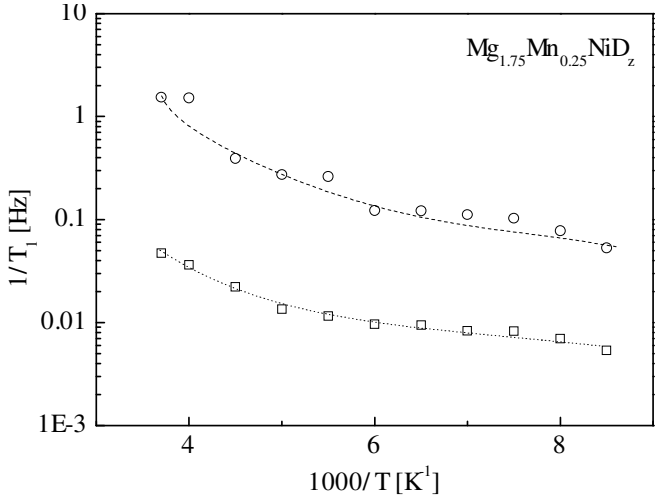

Fig. 2. ^{2}H spin–lattice relaxation rate as a function temperature for $Mg_{1.75}Mn_{0.25}NiD_z$.