Influence of nickel and silicon addition on the deuterium siting and mobility in fcc Mg-Ti hydride studied with 2H MAS NMR.
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Hydrogen is considered to be a promising energy carrier for our future society as it is lightweight and has a high energy density (142 MJ kg⁻¹), almost three times higher than that of natural gas (55 MJ kg⁻¹). However, storing hydrogen in a safe and energy dense way is one of the remaining challenges. The volumetric density of hydrogen in metal hydrides is higher than that in alternative storing methods, such as liquid and compressed hydrogen. In addition, metal hydrides offer a relatively safe storage environment.[1–5] Compared to conventional metal hydrides, such as LaNi₅Hₓ, MgH₂ is a potentially attractive hydrogen-storage material because of its high gravimetric storage capacity amounting to 7.6 wt% of hydrogen.[2,4,6] However, in its common rutile crystal structure MgH₂ suffers from a poor (de)hydrogenation kinetics. In order to improve the thermodynamics and (de)sorption kinetics MgH₂ can be modified in different ways, i.e., by forming nanoparticles, alloying Mg with transition metals and adding catalysts.[7–9]

Alloying Mg with a transition metal (TM), such as Sc, Ti, V, or Cr has a remarkable positive effect on the (de)hydrogenation kinetics.[9] Well-mixed MgTM alloys with >20 at% TM tend to adopt the fluorite structure after hydrogenation,[10–12] which increases the hydrogen mobility significantly compared to that in rutile MgH₂.[13] Due to its relatively high abundance and low atomic weight, Ti is particularly interesting as alloying element for large-scale applications. Mg and Ti have a positive mixing enthalpy and thus no thermodynamically stable alloys are formed.[14,15] However, metastable alloys composed of Mg and Ti have been successfully synthesized in thin films by making use of advanced deposition techniques, such as co-sputtering, physical vapor- and electron-beam (e-beam) deposition.[9,16,17]

Although the results for thin films[18,19] are scientifically interesting as a proof of principle, for large-scale applications bulk powders are much more expedient because of the readily available synthesis and processing routes. For economically feasible large-scale production of powders mechanical alloying is a proven method. Ball-milling has been successfully employed for the preparation of metastable Mg-Ti powders.[20–22] Hydrogenation of Mg-Ti alloys can be achieved either via the gas phase at elevated temperatures or via electrochemical reduction in hydrogen/deuterium donating electrolytes at room temperature. Disadvantageously, the elevated temperatures required for H₂ gas ab- and desorption induce phase segregation in these metastable alloys.[23,24] In contrast, electrochemical hydrogenation of thin Mg₁ₓTiₓ films can be achieved at room temperature without phase segregation and yields a single-phase fluorite-structured compound with favorable materials properties.[25] However, the phase stability of the mechanically prepared Mg₁ₓTiₓ powders during low temperature electrochemical (de) hydrogenation is yet unclear. To the best of our knowledge, this is the first report which shows that the phase segregation of ball-milled powders can be prevented by electrochemical deutronation instead of gas-phase deuteration.

Here we report a magic-angle spinning (MAS) ¹H NMR study on electrochemically deuterated Mg-Ti electrodes at room temperature, leading to the conclusion that phase segregation does not occur under these low temperature conditions. The chemical resolution in ¹H NMR spectra of metal deuterides tends to be higher than in ¹H NMR spectra of the corresponding metal hydrides.[13,26,27] In the present study Mg₀.₆₅Ti₀.₃₅ was prepared by means of 28 h ball-milling. Subsequently, Pd was added to the homogenous alloy and ball-milling was continued for 90 min in order to create a 5 at% Pd coating at the surface of the Mg₀.₆₅Ti₀.₃₅ particles. Pd is an essential catalyst to provide excellent electrochemical hydrogenation properties.[28,29] It also protects the underlying alloy from oxidation.

Electrochemical deuterium loading, also denoted here as charging, was carried out in a conventional three-electrode electrochemical cell, which was thermostated at 25 °C, using alkaline D₂O as electrolyte (Figure 1a). The cell consisted of a metal deuteride (MD) working electrode containing the Mg₀.₆₅Ti₀.₃₅Dₓ alloy along with silver or carbon black as additive, a Pd counter electrode and a Hg/HgO reference electrode. All electrode potentials are referring to this reference electrode. Charging of the working electrode is initiated by electrochemical reduction of D₂O according to

$$\text{M} + \text{D}_2 \text{O} + e^- \leftrightarrow \text{MD}_{\text{ad}} + \text{OD}^- \quad (1)$$

resulting in the adsorption of deuterium atoms (MD_{ad}) at the electrode surface. Subsequently, the adsorbed deuterium atoms diffuse into the bulk of the electrode, forming a metal deuteride. Two neighboring deuterium atoms adsorbed at the electrode surface can also recombine to D₂, which is released from the electrode surface as a gas. Obviously, this parasitic
where \( F \) is Faraday’s constant (\( 9.65 \times 10^4 \) C mol\(^{-1}\)) and \( M_D \) is the molar mass of deuterium (2.01 g mol\(^{-1}\)). Thus, the deuterium storage capacity of \( \text{Mg}_{0.65}\text{Ti}_{0.35} \) in the present study corresponds to 6.2 wt\% D. This is equivalent to overall composition \( \text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.12} \). Curve b of Figure 2A shows the result of the same experiment but now with a \( \text{Mg}_{0.65}\text{Ti}_{0.35}/\text{CB} \) electrode. Since the electrode voltages are more negative in this case, the charge transfer kinetics is poorer than for the electrode with Ag. As a result of the higher overpotentials the distinction between the plateaus has vanished. However, the purpose of this experiment is not to investigate the electrochemistry of the deuteration reaction in detail, but to electrochemically deuterate the metastable \( \text{Mg}_{0.65}\text{Ti}_{0.35} \) alloy, and characterize its nanostructure and deuteron mobility with NMR afterwards. To check whether the \( \text{Mg}_{0.65}\text{Ti}_{0.35}/\text{CB} \) has indeed absorbed deuterium, the electrode was discharged in two current steps, i.e. with a high and low current (curves c and d, respectively in Figure 2A), until the cut-off voltage of 0 V vs the Hg/HgO reference electrode had been reached. The total charge extracted from the electrode was 630 mAh g\(^{-1}\). This is in good agreement with the extracted charge (600 mAh g\(^{-1}\)) measured for the Ag electrode. The extracted charge is smaller than the loaded charge which is likely due to the stronger fixation of deuterium in TiD\(_2\) nanodomains than the MgD\(_2\) nanodomains. The non-extracted deuterium is strongly bound in TiD\(_2\) nanodomains. Evidence for this is that the formation enthalpy of TiD\(_2\) (144 kJ mol\(^{-1}\)) is much higher than that of MgH\(_2\) (77 kJ mol\(^{-1}\)).

Selected area electron diffraction (SAED) of electrochemically deutered \( \text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.12} \) (Figure 2C) shows three reflections corresponding to d-spacing values of 4.78, 2.75 and 2.38 Å. This suggests close similarity to the Ca\(_3\)Ge-type fcc superstructure reported for the high-pressure phase of Mg\(_7\)TH\(_2\)\(^{[30]}\). These corresponding reflections have been labeled 200, 222, and 400. The d-spacing derived from the strongest 222 reflection (2.38 Å) is close to the reported value from the 111 reflection observed for \( \text{Mg}_{0.70}\text{Ti}_{0.30}\text{H}_4 \) thin films, for which a simple fcc structure was assumed\(^{[31]}\).

The nanostructure of \( \text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.12} \) was further investigated with \(^2\)H NMR (Figure 3). In order to fully understand the NMR spectra of this complex material also NMR spectra of the separate elemental metal hydrides have been investigated. Moreover, spectra were recorded for both electrochemical or gas-phase deutered samples, which will be distinguished below by the superscripts (e) or (g), respectively. Magic angle spinning (MAS) increases the chemical resolution in the \(^2\)H NMR spectra by removing the quadrupolar line broadening. The spinning sideband patterns, which are visible at moderate sample rotation rates, reflect the deuteron-coordination symmetry in the respective crystal structures. The \(^2\)H NMR spectrum of MgD\(_2\)\(^{[40]}\) exhibits an extensive sideband pattern over a wide frequency range (Figure 3a). This is consistent with the threefold coordination of deuterium by Mg atoms in rutile MgD\(_2\)\(^{[31]}\). In contrast, TiD\(_2\) has a fluorite structure with deuterium atoms located at tetrahedral interstitial sites. The high coordination symmetry results in weak sidebands surrounding the centerband at ~150 ppm for gas-phase deutered TiD\(_2\)\(^{[40]}\) (Figure 3d). The large, negative Knight shift for TiD\(_2\)\(^{[40]}\) is typical for the conductive bulk material.
similar to that of the melt-cast Mg$_{0.65}$Sc$_{0.35}$D$_{2.2}$ and co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.1}$ reported before. The latter two materials were shown to have a single-phase fluorite structure with the deuterium atoms at tetrahedral positions. Indeed, the tetrahedral coordination of deuterium in the fluorite structure leads to weaker spinning sidebands than the threefold coordination in rutile MgD$_2$. Unlike in fcc TiD$_2$, however, deuterium atoms in fcc Mg$_{0.65}$Ti$_{0.35}$ may well have mixed (Mg, Ti) coordination, or the fcc crystal structure may be otherwise distorted by the co-presence of Mg and Ti. The resulting symmetry distortion is reflected by the spinning sidebands stronger than those for TiD$_2$ (g) (Figure 3 d).

In contrast to the Mg$_{0.65}$Ti$_{0.35}$D$_{1.12}$ (e), the sideband pattern of Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$ (g) (Figure 3 c) is similar to that of rutile MgD$_2$. Unlike in fcc TiD$_2$, however, deuterium atoms in fcc Mg$_{0.65}$Ti$_{0.35}$ may well have mixed (Mg, Ti) coordination, or the fcc crystal structure may be otherwise distorted by the co-presence of Mg and Ti. The resulting symmetry distortion is reflected by the spinning sidebands stronger than those for TiD$_2$ (g) (Figure 3 d).

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The $^2$H NMR spectrum of M$_{0.65}$Ti$_{0.35}$D$_{1.12}$ (e) can be decomposed into four overlapping line shape components, positioned at 7, 4, –30 and –73 ppm (Figure 3 a). Only the 4 ppm component has spinning sidebands, which helps to define

![Figure 3](image-url)

Figure 3. $^2$H NMR spectra of a) MgD$_2$, b) Mg$_{0.65}$Ti$_{0.35}$D$_{1.12}$, c) Mg$_{0.65}$Ti$_{0.35}$D$_{0.65}$ and d) TiD$_2$. Samples indexed with (e) were electrochemically deuterated with a current density of 50 mA g$^{-1}$ at 25 °C. Samples indexed with (g) were deuterated via the gas phase at 175 °C under 75 bar. Spinning sidebands are marked with $^*$. Sample rotation rates were between 8 and 12.5 kHz.
its lineshape in the centerband as well. Both signals at 4 and 7 ppm are assigned to deuterium with tetrahedral Mg_{n}Ti_{4-n} coordination in Mg-rich nanodomains. The components at −30 and −73 ppm are comparable to those attributed to the Ti-rich nanodomains found in co-sputtered Mg_{0.65}Ti_{0.35}D_{1.1}. Electrochemically discharging has a remarkable effect on the component distribution as Figure 4b shows. The intense 4 ppm component and its accompanying side-bands are now completely absent whereas the 7, −30 and −73 ppm components are more or less unaffected. Apparently, the intense 4 ppm component with its side-bands can be entirely correlated to the reversible deuterium stored in Mg_{0.65}Ti_{0.35}D_{1.12}. The other, less intense, components must then be related to the strongly bound deuterium staying behind in the discharged material.

Using 2D exchange NMR spectroscopy we have studied the deuterium mobility between Mg-rich and Ti-rich sites. More precisely, 2D Exsy correlates the chemical shift of deuterium atoms before and after a selected mixing time interval \( t_{mix} \), during which the deuterium atoms have the chance to move between different sites. Deuterium atoms which are stably bound or deeply buried within a separate phase do not undergo a chemical-shift change during \( t_{mix} \) and will give rise to peaks at the spectral diagonal only. In contrast, deuterium atoms which exchange between, e.g. Mg-rich and Ti-rich sites during \( t_{mix} \) will change their chemical shift, which shows up as off-diagonal “cross-peaks” in the 2D spectrum. For \( t_{mix} = 0.01 \) s (Figure 5a) only peak intensity along the diagonal appears, indicating that no deuterium exchange occurs at this timescale. For \( t_{mix} = 2 \) s, cross-peaks are observed (Figure 5b), indicating extensive deuterium exchange between Mg-rich and Ti-rich sites. A measure for the “unrestrictedness” of the exchange is the similarity between projections \( P \) and cross-sections \( S \) as plotted above the 2D spectra in Figure 5a,b. The projections reflect the deuterium distribution over the various sites, while the particular cross-sections shown in Figure 5 indicate how deuterium atoms, which were initially located in Mg-rich domains, become redistributed during the mixing time. For \( t_{mix} = 2 \) s the cross-section is similar to the projection. Thus, at this timescale deuterium has become evenly redistributed over all sites. The fact that this occurs in seconds proves that no macrophase segregation occurs in the electrochemically deuterated alloy.

The exchange between Mg-rich and Ti-rich sites was studied systematically as a function of mixing time with one-dimensional

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**Figure 4.** \(^2\text{H} \) NMR spectra of Mg_{0.65}Ti_{0.35}D_{1.1} (a) ball-milled and electrochemically charged (a) and after electrochemical low current discharging (b).

**Figure 5.** 2D exchange spectra with mixing time \( t_{mix} \) of a) 0.01 s and b) 2 s. Projections \( P \) and cross-sections \( S \) for \( \delta_1 = 4 \) ppm are shown above the 2D spectra. \( P \) illustrates the overall deuterium distribution, while \( S \) the redistribution of deuterium initially at Mg-rich sites.
exchange spectroscopy. Our 1D exchange experiments involve selective polarization inversion of deuterium spins at the Mg-rich sites followed by a varied mixing time \( t_{\text{mix}} \). Deuterium atoms with perturbed polarization initially at Mg-rich sites will replace unperturbed deuterium at the Ti-rich sites and vice versa. As a result, the signal intensity of the originally non-perturbed sites will decrease, and that of the initially perturbed sites will increase as function of \( t_{\text{mix}} \) (see Figure 6a,b). Figure 6c illustrates the development of the intensity \( I_{\text{Bg}} \) of the 4 ppm component combined with its sidebands, and \( I_{\text{Tg}} \) of the combined \(-30\) and \(-73\) ppm components versus \( t_{\text{mix}} \) at 280 K. \( I_{\text{Bg}} \) shows a two-step increase, whereas \( I_{\text{Tg}} \) initially decreases and then increases. The combined behavior of \( I_{\text{Bg}}(t_{\text{mix}}) \) and \( I_{\text{Tg}}(t_{\text{mix}}) \) is well described by a coupled bi-exponential model \([\text{31}]\)

\[
I_{\text{Bg}}(t_{\text{mix}}) = \left\{ I_{\text{Bg}}(0) - I_{\infty}^{\text{Bg}} \right\} \exp\left(-t_{\text{mix}}/\tau_{\text{ex}}\right) + \left( I_{\infty}^{\text{Tg}} - I_{\text{eq}}^{\text{Bg}} \right) \exp\left(-t_{\text{mix}}/T_1\right) + I_{\text{eq}}^{\text{Bg}} \\
I_{\text{Tg}}(t_{\text{mix}}) = \left\{ I_{\text{Tg}}(0) - I_{\infty}^{\text{Tg}} \right\} \exp\left(-t_{\text{mix}}/\tau_{\text{ex}}\right) + \left( I_{\text{eq}}^{\text{Tg}} - I_{\text{Tg}}(0) \right) \exp\left(-t_{\text{mix}}/T_1\right) + I_{\text{eq}}^{\text{Tg}}
\]

where the thermal-equilibrium intensities \( I_{\text{eq}}^{\text{Tg}} \) and \( I_{\text{eq}}^{\text{Bg}} \) are proportional to the respective densities of Mg- and Ti-rich sites, and \( I_{\infty}^{\text{Tg}} = \left\{ I_{\text{Tg}}(0) + I_{\text{Tg}}(0) \right\} I_{\text{eq}}^{\text{Tg}}/(I_{\text{eq}}^{\text{Tg}} + I_{\text{eq}}^{\text{Bg}}) \) and \( I_{\infty}^{\text{Bg}} = \left\{ I_{\text{Bg}}(0) + I_{\text{Bg}}(0) \right\} I_{\text{eq}}^{\text{Bg}}/(I_{\text{eq}}^{\text{Tg}} + I_{\text{eq}}^{\text{Bg}}) \) are the signal intensities in the intermediate state, when the combined initial polarization \( I_{\text{Tg}}(0) + I_{\text{Tg}}(0) \) is homogeneously distributed over the Mg- and Ti-rich sites by deuterium exchange. Herewith it is assumed that the deuterium exchange is fast compared to the spin-lattice relaxation \( (\tau_{\text{ex}} < T_1) \) and averages out any intrinsic \( T_1 \) differences between deuteriums at Mg- and Ti-rich sites. The spin-lattice relaxation times \( (T_1) \) can also be independently determined by making use of inversion-recovery relaxometry. The obtained relaxation times nicely match the \( T_{1Z} \) values extracted from the 1D ExSY curves at the corresponding temperatures.

Figure 6. a,b) 1D ExSY spectra of electrochemically deuterated \( \text{Mg}_{0.65}\text{Ti}_{0.35}\text{D}_{1.12} \) at various mixing times: 0.001, 0.3, 1, 10 s. For comparison, the fully relaxed spectrum after 10 s mixing time is also shown (grey curves) at 280 K (a) and 355 K (b). c) Peak areas \( I_{\text{Bg}} \) (squares) and \( I_{\text{Tg}} \) (circles) as a function of mixing time \( t_{\text{mix}} \) together with the total intensity \( I_{\text{BG}} \) (triangles). The continuous curves are based on a least-square fit of the coupled bi-exponential model described by Equation 2. d) Arrhenius plot of the effective deuterium exchange rate \( \tau_{\text{ex}}^{-1} \) extracted from the coupled bi-exponential fit of \( I_{\text{Bg}}(t_{\text{mix}}) \) and \( I_{\text{Tg}}(t_{\text{mix}}) \) at various temperature (squares) and \( 1/T_1 \) extracted from the inversion recovery experiments (inverted triangles).
To estimate the activation barrier for deuterium mobility in Mg$_{0.65}$Ti$_{0.35}$D$_{1.12}$, 1D Exsy was carried out at various temperatures. The observed deuterium exchange becomes faster with increasing temperature. For instance, the zero crossing of the initially inverted 4-ppm signal during the recovery process occurs earlier at 355 K (Figure 6b) than at 280 K (Figure 6a). Such temperature trend is indeed to be expected for chemical exchange of deuterons between different sites. In principle, polarization exchange between deuterium spins could also give rise to cross-correlation in 1D and 2D Exsy. However, such $^2$H-$^2$H spin diffusion would essentially be temperature independent. The observed exchange in 1D and 2D Exsy is indeed dominated by deuterium mobility. From 280 to 355 K, the effective deuterium residence time $\tau_{ex}$ in Mg- and Ti-rich nanodomain decreases from 0.48 to 0.10 s (Figure 6d), which corresponds to an activation energy of 16.8 kJ mol$^{-1}$, comparable to the barrier energy estimated from the 1D Exsy of co-sputtered Mg$_{0.65}$Ti$_{0.35}$D$_{1.12}$.

The $T_1$ values extracted from the 1D Exsy curves also contain information about deuterium mobility. In contrast to $\tau_{ex}$, directly reflecting deuterium exchange between the NMR-distinguishable Mg- and Ti-rich sites, $T_1$ is an indirect measure for the correlation time $\tau_c$, $T_1$ of deuterium exchange between any neighboring sites. The overall $T_1$ relaxation in the weighted average between the intrinsic relaxation at the Mg-rich sites controlled by quadrupolar-coupling fluctuations, and the intrinsic relaxation at the Ti-rich sites controlled by Knight-shift fluctuations.

\[
\frac{1}{T_1^M} = \frac{2}{3} \frac{\Delta \omega Q^2}{\Delta \omega_0^2} \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega_0^2 \tau_c^2} \right) \quad (4a)
\]

\[
\frac{1}{T_1^T} = \frac{1}{15} \frac{\Delta \omega Q^2}{\Delta \omega_0^2} \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \right) \quad (4b)
\]

where $\langle \Delta \omega Q^2 \rangle$ and $\langle \Delta \omega_0^2 \rangle$ represent the average size of the quadrupolar-coupling and Knight-shift fluctuations, respectively, $\omega_0$ the $^1$H NMR frequency and $\tau_c$ the motion correlation time. For very fast deuterium mobility ($\omega_0 \tau_c << 1$), $T_1$ is inversely proportional to $\tau_c$, whereas for less fast mobility ($\omega_0 \tau_c >> 1$), $T_1$ is directly proportional to $\tau_c$. The spin lattice relaxation time $T_1$ of deuterium in Mg$_{0.65}$Ti$_{0.35}$D$_{1.12}$ decreases from 6.2 s at 280 K to 2.0 s at 355 K (Figure 6d) showing an Arrhenius temperature dependence with an activation energy of 13.6 kJ mol$^{-1}$. This indicates that the deuterium mobility is relatively slow on the NMR frequency scale ($\omega_0 \tau_c >> 1$) as is consistent with the timescale of the hydrogen ($^1$H) mobility in the related Mg$_{0.65}$Sc$_{0.35}$H$_{1.13}$. The comparable temperature dependence of $\tau_c$ and $\tau_{ex}$ in our present study of Mg$_{0.65}$Ti$_{0.35}$D$_{1.12}$ suggests that the mobility underlying the $T_1$ relaxation and the Exsy correlation are related. A possible explanation is that $\tau_c$ reflects the hopping of the deuterium atoms between neighboring sites within the Mg-rich and Ti-rich nanodomains, whereas $\tau_{ex}$ reflects the (longer) average time it takes for deuterium to diffuse in multiple steps from sites within Mg-rich nanodomains across the Mg-Ti interphase to sites within Ti-rich nanodomains, and vice versa.

In summary, although thin-film electrodes are scientifically interesting, bulk powders are more favorable for large-scale practical applications. Ball-milled Mg-Ti alloy powders do not undergo phase segregation during electrochemical loading at low temperatures, whereas gas-phase loading at the required elevated temperatures induces the alloys to phase segregate. 2D and 1D Exsy shows that Mg-rich and Ti-rich nanodomains in Mg$_{0.65}$Ti$_{0.35}$D$_{1.12}$ are closely connected. Therefore electrochemical hydrogenation at room temperature is an excellent alternative to hydrogenate metastable alloys, which phase segregate at the elevated temperatures required for gas-phase hydrogenation. These economically feasible ball-milled metastable Mg-Ti alloy powders are therefore interesting to be applied in next generation of light-weight rechargeable Nickel Metal Hydride batteries.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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