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**Industrial Production of Light Metal Hydrides for Hydrogen Storage**

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**Abstract**

Light metal hydrides show a high potential for reversible hydrogen storage applications. In view of the potential future storage of large amounts of hydrogen, an economic tonnage scale production will be required. This viewpoint set introduces production methods and discusses the potential for simplifying processing routes and reducing costs in view of an industrial mass production. For this purpose, sodium alanate, for which a cost-competitive production on large scale is considered to be feasible already to date, is used as an example for future promising hydrides like complex hydrides or reactive hydride composites.

**Introduction**

Reversible solid storage of kg amounts of hydrogen in tanks containing conventional transition metal alloys (e.g. TiFe$_2$, LaNi$_5$) has been demonstrated even at high charging and discharging rates, and respective prototypes are in operation today. However, the low gravimetric storage capacity of less than 2 wt% for these alloys has lead to undesirably heavy prototypes, in particular for automotive applications. This has inspired a rapid development of hydrogen storage materials based on light metal hydrides [1]. The most promising candidates today are magnesium hydrides, stabilized aluminium based hydrides like NaAlH$_4$ and combinations of borides with MgH$_2$. Although the hydrogenation of Magnesium to MgH$_2$ can take days up to weeks even at elevated temperatures [2], the development of Magnesium powder or powder compacts with submicron microstructure containing suitable catalyst facilitates the reversible storage of up to 7.0 wt.% of hydrogen at charging times of a few minutes [3-6]. Additionally, long term stability has been proven up to 2000 cycles [7]. However, the high thermodynamic stability of the hydride phase leads to a high desorption temperature of at least 300 °C for 1 bar hydrogen pressure. Thus, new materials with lower reaction enthalpy, i.e. lower desorption temperatures were developed for low temperature applications. In case of NaAlH$_4$, reversible hydrogen storage of about 4.5 wt.% of hydrogen at temperatures in the range of 80-150°C was found to be achievable by the addition of a

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suitable catalyst [8,9] and hydrogen absorption in a few minutes at 100°C and 100 bars was demonstrated [10]. A further milestone in the development of light weight storage material is the recent demonstration of reversible hydrogen storage in so-called Reactive Hydride Composites (RHC) [11-13]: For example, LiBH₄+MgH₂, reacting upon desorption to LiH and MgB₂, can store up to 11 wt.% of hydrogen, thus meeting the gravimetric storage targets defined by DOE for on-board hydrogen storage in a future zero emission vehicle. Due to the high stability of MgB₂ decomposition of the relatively stable hydrides is facilitated, and desorption at moderate temperatures is thermodynamically possible. However, these composites still suffer from slow reaction kinetics, especially at low temperatures.

Reaction kinetics of light metal hydrides depend on the surface area of the material exposed to hydrogen, the dimensions and homogeneity of the microstructure, as well as the kind and the dispersion of additives and heterogeneous catalysts. For example, fine microstructures with a high density of interfaces and phase boundaries provide short diffusion distances, fast diffusion pathways, and a high number of nucleation sites for the phase transformation in the solid state reaction [14]. To date, such novel materials with favourable morphologies and microstructures are synthesized in gram amounts, involving complicated methods and cost-intensive raw materials. The important influence of microstructure and morphology makes sorption kinetics very sensitive to the processing and imposes high demands on large scale production.

In view of the technical implementation of these materials, e. g. as mobile hydrogen storage devices in future zero emission vehicles within a comprehensive clean energy concept, economic tonnage scale production of the materials is necessary. Assuming a storage capacity of 10 wt.% on a materials level, the storage of 5 kg of hydrogen in a mid size car would require 50 kg of storage material per car. This translates to 25 million tons of storage material for the roughly 500 million cars on the road today. Such a scenario necessitates the selection of suitable cost effective large scale processing routes for the production of light metal hydride materials.
Raw Materials and Synthesis Methods

Metal hydrides have to be produced from metals due to the much weaker metal-hydrogen bonding as compared to metal-oxygen or metal-chlorine bonding, which are predominantly present in light metal ores. Although electrolysis has to be used, e.g. for the isolation of Na, Mg, Ca and Al, these metals are relatively cheap, with today’s market prices ranging typically from about 0.30 Dollar / kg Na up to 3 Dollar / kg Mg [15]. Mg and Na are highly abundant in the earth crust, and in the sea water, respectively. The situation for Li or B is more problematic. Firstly, their reserves on earth are significantly lower. Secondly, isolation contributes strongly to the today’s market price of these elements in metal form, which can be as high as 90 Dollar / kg for Li [15-17]. Here, optimisation of the processes may lead to a reduction of costs in future.

Production of the hydrides of these elements is of significant importance, not only because they can serve as potential storage materials as in the case of MgH₂, but also as precursors for the production of future complex hydrides. Na and Li can be hydrided from the metal melt at close to ambient hydrogen pressure. The process temperature has to be significantly below the equilibrium temperature, e.g. 350°C for NaH. The much higher melting point of Mg necessitates the hydrogenation in solid state, which can take days to weeks [2]. It was shown that the synthesis of MgH₂ during milling of Mg in hydrogen atmosphere is possible [18-21]. However, despite the addition of catalyst and sometimes high pressures used during milling, conversion times are quite long. This can be mainly attributed to the severe agglomeration and cold welding with the grinding tools due to the relatively high ductility of Mg. This problem may be solved by using liquid or solid milling additions, which are known to prevent cold welding during milling. Several studies using graphite, partly in combination with liquid milling agents, have shown a relatively fast absorption of hydrogen on the milled samples [2, 22-24]. However, milling necessitates a powder as precursor that has to be obtained by atomisation of the metal melt, adding additional costs for the production.

Therefore, the production of hydrides from bulk metals offers a high potential for the reduction of costs within an entire processing concept. Whereas the alkali and alkaline earth metals obtained as bulk material from the solidified melt do not take up significant amounts of hydrogen, the mechanical treatment of the bulk can facilitate its conversion to hydride. Super plastic deformation methods, such as equal channel angular pressing (ECAP) lead to the
introduction of microspores and a defect rich microstructure, which allows hydrogenation, as was demonstrated for Mg based materials [25]. Since the hydrides are brittle they can also be crushed to powder, thus serving e.g. as precursor for complex hydrides [25].

For the production of the complex metal hydrides, fine hydride powders may be preferred as precursor to the pure metals because they can be easily dispersed in other media facilitating reaction. For example, LiAlH₄ can be produced in large scale by the reaction of LiH with AlCl₃ dispersed in a suitable solvent (preferably THF):

\[ 4\text{LiH}_4 + \text{AlCl}_3 \rightarrow \text{LiAlH}_4 + 3\text{LiCl} \]  

(1)

The LiAlH₄ dissolved in THF can be mostly separated from LiCl by filtration and is subsequently precipitated by evaporation of the solvent. A further conversion to sodium alanate is possible in THF with a yield of about 90% without hydrogen pressure:

\[ \text{LiAlH}_4 + \text{NaH} \rightarrow \text{NaAlH}_4 + \text{LiH} \]  

(2)

Similar reaction pathways, using the exothermic formation of a stable chloride (e.g. LiCl in reaction 1) for the formation of the complex hydride, were also demonstrated for other complex hydride systems and can be scaled-up with the technique available today. The main drawback, however, is that a large number of production steps are necessary for recovering the educts. In particular, the chloride has to be reduced by electrolysis, which consumes a high amount of energy.

Therefore, simpler methods to produce complex hydrides have also been proposed. E.g. Dymova et al. milled AlH₃ with NaH in 1:1 ratio and succeeded in forming NaAlH₄ in relatively short times [26]. However, to date AlH₃ has to be produced by an exothermic reaction similarly to LiAlH₄, such that this production step does not significantly simplify the production route for NaAlH₄. Additionally, it was shown that the direct synthesis of alanates is possible in high pressure autoclaves, e.g. NaAlH₄ can be synthesised from Na, Al, and H₂ at 175 bar and 280°C, where Na is present in liquid state [27]. Ashby et al. showed that the direct synthesis of various alanates can be carried out at more moderate conditions by suspending the hydride or the metal and the Al in THF and applying hydrogen pressure and temperature, e.g. 140 bar at 150°C for NaAlH₄ [28]. Subsequently, the alanate present in
solution is filtered, precipitated and dried. Since the solubility of alanates is relatively low in THF, a high amount of solvent is necessary, and the still high pressure is undesirable for large scale production plants.

The discovery of reversible hydrogen sorption on NaAlH$_4$ by adding a suitable heterogeneous catalyst, like e.g. TiCl$_3$ [8] shows that the direct synthesis of complex hydrides is possible from the decomposition products in a solid state reaction. For example, it was shown for NaAlH$_4$ that the use of solvents can indeed be avoided and the pressure can be reduced, if the synthesis is carried out during milling under hydrogen pressure with the addition of catalyst [29, 30]: The formation of NaAlH$_4$ within 3 hours was demonstrated by milling NaH/Al with TiCl$_3$ under an initial hydrogen atmosphere of 83 bars [29]. The product exhibits a reversible capacity of about 4 wt.% and very fast sorption kinetics without activation. However, the pressure used during milling is too high to be applied in any industrial milling equipment. Respective experiments at lower pressure only lead to partial conversion or require very long milling times [30, 31].

A concept to avoid the use of high pressure and the associated high pressure equipment during production of hydrogen storage material is to, firstly, produce a precursor corresponding to the dehydrogenated state and subsequently activate it in the storage tank shell. The activation of the decomposed state was demonstrated in all promising reversible systems that are known today: Reversible hydrogen sorption was demonstrated on NaH/Al mixtures [32-35] and also ternary systems, like Na$_2$LiAlH$_6$, could be activated starting from the mixture of LiH/NaH/Al [8,9]. Additionally, for reactive hydride composites, the reversible formation of the metal borohydride / magnesium hydride composite from milled metal hydride / magnesium boride mixtures was achieved [13].

Since the desorbed state in complex hydrides or reactive hydride composites is a fine and homogeneous composite, the main challenge is to reproduce such a microstructure by effectively mixing the initial components. For NaAlH$_4$, it could be shown that such precursor of NaH and Al can be formed by intermixing the components in a glass reactor in pentane suspension or in a high-energy ball mill [9,34]. Due to its high vapor pressure, pentane can be easily removed by heating the material at moderate temperatures or in a technical vacuum. However, the capacity and kinetics of the material critically depend on process conditions for the synthesis of the precursor. Srinivasan et al. showed that the NaH/Al precursor synthesized
by dry milling takes up initially roughly 1 wt.% of hydrogen, while by using milling in pentane suspension 3.5 wt.% could be absorbed [34]. However, it was also shown that the milling time has substantial influence: Both kinetics and storage capacity show an optimum over the milling time [36]. Despite the high sensitivity of material properties to the process, Fig.1 shows for sodium alanate that a simplified processing route can lead to comparable product qualities: Hydrogenation of purified NaAlH₄ milled together with TiCl₃ takes about 1 h in the second absorption [37]. If Ti-nanoclusters are used instead of TiCl₃, kinetics can be significantly improved, i.e. the hydrogen can be absorbed within a few minutes [10]. However, the Ti-nanoclusters, TiCl₃ and the NaAlH₄ prepared by chemical synthesis as described above are very expensive. Since in the production today, TiCl₄ is the precursor of TiCl₃ and NaH and Al are precursors of NaAlH₄, the synthesis of nanocrystalline NaH/Al/TiCl₄ instead of the above mentioned materials shortens the production route and leads to a substantial reduction of costs.

Fast hydrogen sorption is essential, in particular in light metal hydrides used for automotive applications, where a tank has to be filled within 3-5 minutes. In view of up-scaling of the storage material production, the high sensitivity of material properties to process parameters requires therefore a deeper understanding of microstructural and morphological formation of precursors during the production process. In the case of milling for example a brittle hydride together with a soft metal, agglomerates are formed, consisting of brittle particulates embedded and dispersed in a metallic matrix [38, 39]. The formation of this morphology results from the continuous deformation of the soft phases and fracture of the hard phase [40].

Fig.1: Second absorption of NaAlH₄ based storage material with 2 mol% of Ti-based catalysts, produced by different processing routes.
Since Al is very ductile and hydrides show a low resistance to fracture, the formation of a composite of Al with predominantly sub-micron NaH inclusions is very fast. Fig. 2 shows an example of a NaH/Al agglomerate after 1 h of milling in a planetary ball mill, in which NaH particles are already refined to a submicron range. After the first hydrogenation (activation) a more porous morphology results. This further enhances kinetics, so that hydrogen is rapidly absorbed within a few minutes at 100 bar and 125 °C in the case of sodium alanate [36]. The efficient refinement mechanism of the microstructure in such light metal / light metal hydride systems does not necessitate the use of high intensity mills for the process. On the other hand, a homogeneous distribution of the main phases and the catalyst is necessary for efficient hydrogenation, imposing high demands on the ability to intermix the components during milling.

![Fig. 2: Agglomerate consisting of NaH particles (dark) in an Al-matrix (bright) after 1 h of milling in a planetary ball mill with TiCl₄ (scanning electron microscopy, back scattering mode).](image)

Therefore, the composite formation of the desorbed state in complex hydrides or reactive hydride composites may also be achieved in mixers, e.g. in pentane suspension. In view of the less deformable components like B or MgB₂ for boron based materials higher forces for deformation, as present in ball mills will probably be necessary to achieve an optimum quality of these materials. Therefore, up-scaling of the milling process is probably an important issue for the production of future light metal hydrides.

**Up-scaling of the milling process**

A future commercialization using milling as production step would necessitate the processing in tonnage batches or in continuous mode in combination with low power consumption. For this purpose, a suitable industrial scale milling equipment has to be chosen. For the synthesis
of nanocrystalline materials in kg scale a number of experiments have been carried out with horizontal attrition mills, which exhibit very high milling intensity [41, 42]. However, investment costs and power consumption are high and continuous processing is challenging. Since the refinement of light metals and composites of light metal / metal hydrides can succeed relatively easy as shown above, a high milling intensity may not be required. Gravity mills have proven to be a cost effective milling technique on an industrial scale, e.g. for processing commercial ODS alloys, however, continuous processing is also problematic. Vibratory tube mills are an alternative option for the production of light metal storage materials in continuous mode. These mills are well established for comminution and activation of minerals [43]. Therefore, mills of this type are readily available up to tonnage loads and can be run in continuous mode at high feed rates. Additionally, the kinematics and the kinetics of this kind of mills have been optimised towards low energy consumption and efficient mixing of the milled materials [44-47]. The influence of critical parameters, like milling time, shape of grinding bodies and ball to powder ratio on the efficient crystallite refinement has been studied comprehensively [14, 40, 48]. Fig. 3 shows, on the example of

NaH/Al with TiCl₄ that absorption time of a few minutes can indeed be reproduced on a kg scale in relatively short process times in a common industrial tube vibration mill (Siebtechnik, type ESM 236, modified for inert atmosphere processing). The significantly higher kinetics and capacity in the 0.5 kg batch, which was milled for an additional 0.5 h with 5 wt.% of graphite indicates a high potential for further optimisation of the process towards critical

![Fig.3: Hydrogen absorption on NaAlH₄ based storage materials, produced from a NaH/Al precursor with 2 mol.%TiCl₄ in a laboratory ball mill and on kg scale in a vibratory tube mill.](image-url)

Fig.3: Hydrogen absorption on NaAlH₄ based storage materials, produced from a NaH/Al precursor with 2 mol.%TiCl₄ in a laboratory ball mill and on kg scale in a vibratory tube mill.
application requirements. The energy consumption of the vibratory ball mill is about 1 kW, i.e. for 1 kg of NaH/Al precursor 4 kWh are necessary, translating to energy cost of less than 1 Euro per kg. Vibration mills are available up to tonnage scale, which also keeps investment costs per kg of material low.

**Tailoring material to tank design**

For the final implementation of the material into a suitable tank shell, additional properties apart from kinetics and capacity of the material will be of importance. These are in particular, high heat conductivity for fast heat transfer, high density, in order to keep the volume of the system low and the ability to accommodate to the volume changes of the material during reaction [49]. A final compaction of the powder increases density and probably also heat conductivity. However, rest porosity will be necessary to guarantee the accommodation of the compact to volume changes of the material. Using a composite in the desorbed state, i.e. deformable metals are present, facilitates the compaction at low force, which can be carried out in a simple uni-axial pressing device after milling or mixing.

A further simplification of the production might also be achieved, if after mixing the initial powders, the refinement of the microstructure is combined with the compaction in a process step, which involves plastic deformation, like cold rolling or ECAP. The main challenge, however, will be to maintain a rest porosity after the process.

**Conclusions**

The production of promising light metal hydrides based on complex hydrides or reactive hydride composites is found to be most efficient by producing a composite corresponding to the desorbed state of the material that can be activated in the final tank shell. For NaAlH₄-based materials, such a production process on the kg scale is already demonstrated today by milling the hydride and the aluminium with a catalyst, maintaining the high sorption kinetics and capacity achieved by laboratory methods. For other multi-component hydrides e.g. Reactive Hydride Composites like LiBH₄ / MgH₂ with up to 11 wt.% of hydrogen storage capacity, feasibility of the process route, is already demonstrated on the lab scale by milling. Thus, complex hydrides and reactive hydride composites based on alkali and alkaline earth metals and Al or B may be produced cost-competitive in the future.
Considering the strong differences of cost and abundance of the light metals, the end price of the hydrogen storage materials may strongly be determined by the content of less abundant elements like Li or B. Therefore, e.g. Ca(BH₄)₂ / MgH₂ systems may be preferred in the future for a high volume market application to LiBH₄ / MgH₂, despite the slightly lower storage capacity.

In a next step, the functionality of such light weight hydrides in large hydrogen storage tanks has to be proven, implying the design and testing of a suitable heat management system for fast sorption of hydrogen on a kg scale.

**Literature**


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