6. CASE STUDIES OF SELECTED HYDRIDES FOR NON-AUTOMOTIVE HYDROGEN ENERGY STORAGE (ALANATES) <u>Case 1-LiAlH4</u>

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2.18.2. Background

Unfortunately, no solid hydride system that could meet all those (**automotive**) requirements has been discovered yet. Despite a very extensive research on solid hydrides in the past decade, a breakthrough has not been achieved yet and there is not even one hydride system that is close to commercialization for application as a storage medium for the most important automotive market. However, there is a number of other potential market applications for simple H_2 generation systems rather than "on board" reversible storage systems, where some of them could be even recharged "off board", supplying H_2 at the ambient and slightly elevated temperatures, in the commercial, non-automotive sectors of the economy. For example, they could be utilized for supplying fuel cells in such applications as stationary auxiliary power systems, off-road vehicles (forklifts, street sweepers etc.), locomotives, submarines, drones, coastal and international shipping, auxiliary devices in air transportation, lawn mowers, disposable cartridges for long duration, low power military devices, civilian portable electronic devices, bulk hydrogen storage and many others [10-18].

A screening of various hydrides from the standpoint of their suitability of desorbing H₂ in 1 bar pressure and at temperatures, not exceeding 100°C, is very important. This can be achieved by knowing a thermodynamic property of hydrides such as the enthalpy of decomposition/formation change, Δ H. If the natural logarithm of desorption/absorption H₂ pressure is plotted vs. wt.% H₂ desorbed/absorbed at constant temperature then so-called *pressure-composition-temperature* (PCT) curve is obtained which usually exhibits plateau [19]. Then the equilibrium mid-plateau H₂ pressure for the hydrogen desorption/absorption plateau is related to temperature through the Van't Hoff equation [19]:

 $\ln (P/P_0) = -\Delta H/RT + \Delta S/R$

where P is the recorded pressure (atm/bar), P_0 is the atmospheric pressure (1 atm/1 bar), ΔH and ΔS are the enthalpy and entropy changes in kJ/molH₂ and J/molH₂K, respectively, R is the gas constant (8.314472 J/molK) and T is absolute temperature (K). This approach requires time

(1)

consuming measurements of pressure and corresponding H_2 capacity for one PCT and at least for three selected temperatures. More recently, we simplified this approach by using step-wise desorption curves (pseudo-PCT curves), where we measure pressure vs. desorption time at a constant temperature and then after obtaining satisfactory equilibrium plateau, temperature is rapidly ramped to a higher value until equilibrium plateau is achieved and again temperature is ramped to yet higher value and equilibrium plateau pressure recorded. Then the term ln (P/P₀), where p is the equilibrium plateau pressure for each temperature, is plotted vs. 1000/T according to Eq. (1). This method is shown in Fig. 1a,b as applied to a ball milled mixture of lithium amide (LiNH₂) and lithium hydride (LiH) in the molar ratio (LiNH₂+1.2LiH) [20]. A value of the dehydrogenation enthalpy obtained in Fig. 1b agrees well with the values quoted in the literature [21].



Fig. 1. a) Step-wise pseudo-PCT curves at varying temperatures and b) corresponding Van't Hoff plot (Eq.(1)) for the (LiNH₂+1.2LiH) mixture milled for 25 h under a high energy milling mode. Reproduced from [20].

Furthermore, according to the Van't Hoff equation (1) a certain hydride (or a hydride composite system) would be thermodynamically capable of desorbing H_2 only if **desorption pressure (e.g.** 1 bar) is *lower* than its equilibrium plateau pressure at experimental desorption temperature (T=const.). The larger the difference between the desorption pressure and the PCT equilibrium pressure, the larger the driving force for dehydrogenation. However, these thermodynamic considerations do not tell us about the rapidity of H_2 release during dehydrogenation which is a kinetic property.

The earlier status of solid state hydrides and their H_2 storage behavior has been reported in our book "Nanomaterials for Solid State Hydrogen Storage", that was published in 2009 [19] and a book chapter that appeared in 2013 [22]. The aim of the present chapter is to review the progress

made in the past few years in the research on complex, metal-nonmetal hydrides and their composites which have the greatest potential as a viable source of generation/storage H_2 for non-automotive applications, particularly, for being applied in disposable containers/cartridges. In this respect a system based on LiAlH₄ with nanometric additives, may be close to near-commercialization for applications for disposable H_2 storage cartridges for long-duration, low power demand devices that use H_2 .

2. 18. 3. Selected complex hydrides

In the broadest sense complex hydrides are composed of an anionic metal-hydrogen complex or non metal-hydrogen complex bonded to a cationic alkali or transition metal [19, 23, 24]. Thus complex hydrides can be roughly subdivided into two categories: group I and II salts of [AlH₄]⁻, [NH₂]⁻, [BH₄]⁻, i.e. alanates, amides, and borohydrides [19, 23, 24], and transition metal (TM) complex hydrides that have anionic (TMH_x)⁻ complexes such as [FeH₆]⁴⁻ attached to a cationic light metal, e.g. Mg²⁺, in Mg₂FeH₆ [18, 19]. Their bonding is usually an ionic-covalent mix [24]. Similar transition metal ternary complex hydrides exist in the Mg-Co, Mg-Ni and Mg-Mn systems forming Mg₂CoH₅, Mg₂NiH₄ and Mg₃MnH₇ (the latter was synthesized under 20 kbarH₂ at ~800°C [19, 25]). Some references classify certain complex hydrides, e.g. NaBH₄, as "chemical hydrides" because they can easily react with water solution of KOH or NaOH (or water steam) releasing hydrogen [19].

2. 18. 3. 1. LiAlH₄ with nano-additives

One of the most interesting hydrides for solid state hydrogen generation/storage, for nonautomotive applications, is a complex metal hydride LiAlH₄ (lithium alanate), since it can liberate a relatively large theoretical quantity of 7.9 wt.% H₂ much below 250°C [**19**]. Graetz and Reilly [**26**] classified LiAlH₄ as belonging to a group of hydrides called "kinetically stabilized metal hydrides" which also include AlH₃, Mg(AlH₄)₂ and Ca(AlH₄)₂, among others. All these hydrides are characterized by an equilibrium H₂ pressure of their respective PCT curves at room temperature (298K), much higher than 1 bar. This feature alone creates a large driving force for decomposition. However, they are quite stable at near room temperature, most likely, due to kinetic limitations as their name indicates. The mechanisms responsible for their stable behavior are not well understood although slow/hydrogen metal diffusion and surface barriers that hinder the easy formation of molecular H₂ are quite likely [26].

It is well established [19, 27] that pure (additive free) LiAlH₄ decomposes releasing H₂ according to the following steps:

$LiAlH_4(s) \rightarrow LiAlH_4(l)$	(2a)
$LiAlH_4(l) \rightarrow 1/3Li_3AlH_6(s) + 2/3Al(s) + H_2(g)$	(2'b)
$1/3Li_3AlH_6(s) \rightarrow LiH + 1/3Al + 0.5H_2$	(2c)
LiH→Li+0.5H ₂ or LiH+Al→LiAl+0.5H ₂	(2'd) (2"d)

where s-solid, l-liquid and g-gas. In Differential Scanning Calorimetry (DSC), reaction (2a) is endothermic, (2'b) is exothermic, and (2c) and (2d) are both endothermic reactions. Reactions (2'b), (2c) and (2d) proceeds with a theoretical hydrogen release of 5.3, 2.6 and 2.6 wt.%, respectively [19]. Obviously, these values will be lower for purity-corrected capacity of LiAlH₄.

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In contrast to NaAlH₄, the **enthalpies of each step in reactions (2) are not so well established** as those for NaAlH₄. The experimentally observed enthalpy of reaction (2'b) was reported as being equal to -14 kJ/mol H₂ (exothermic)[**45**] and -10 kJ/mol H₂ (exothermic)[**19**, **37**]. The calculated values of 9.79 and 15.72 kJ/mol H₂, both endothermic, were reported for reaction (2'b) and (2c), respectively [**46**].

The PCT equilibrium plateau pressure for the decomposition of LiAlH₄ has been reported to be very high which could make LiAlH₄ irreversible under practical conditions of temperature/pressure. The plateau pressure for Stage I dehydrogenation reaction of LiAlD₄, containing a catalytic precursor TiF₃, into Li₃AlD₆, Al and H₂ ((2'b) or (2''b)) was reported by

Brinks et al. [47] to be higher than 99 and 87 bar at 53 and 80°C, respectively. Furthermore, Mulana and Nishimiya [48] estimated the enthalpy (Δ H) and entropy (Δ S) for Stage I dehydrogenation ((2'b) or (2"b)) and the second stage dehydrogenation reaction (2c) (Stage II) as being equal to Δ H=17.5 kJ/molH₂ and Δ S=121.6 J/molH₂ K, and Δ H=11.1 kJ/molH₂ and Δ S=62.6 J/molH₂ K, respectively. Assuming Δ H=17.5 kJ/molH₂ and Δ S=121.6 J/molH₂K, the equilibrium pressure for Stage I dehydrogenation calculated from Eq. (1) would amount to 1.88×10³ and 19.6×10³ atm at room temperature (24°C=297 K) and 170°C (443 K), respectively. Apparently, the first dehydrogenation reaction (2'b) appears to be completely irreversible due to extremely high pressures required for rehydrogenation. Assuming Δ H=11.5 kJ/molH₂ and Δ S=62.6 J/molH₂ K for Stage II in Eq. (1), it is calculated that at 170°C the equilibrium H₂ pressure is around 82 atm. This pressure level although still relatively high can be achieved for realizing reversibility under more practical conditions. On the other hand, the computed stability diagrams for LiAlH4/Li₃AlH₆/LiH show very high pressures on the order of 10³ atm at 170°C needed for the rehydrogenation of LiH/Al into Li₃AlH₆ (Fig. 3.12 in [15, 49, 50]).

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Decomposition of additive-free LiAlH₄ always occurs from a molten state through reaction (2'b). The DSC thermal peak maxima for the above reactions are not affected by ball milling as shown for a DSC curve in Fig. 2a [27]. The first exothermic peak at 143.8°C in Fig. 2a, before the peak (2a) was assigned by Block and Gray [28] to the reaction of the surface aluminum-hydroxyl groups owing to the presence of impurities.



Fig. 2. DSC curves for (a) additive-free, ball milled LiAlH₄, (b) (LiAlH₄+5 wt.% n-Ni) mixed without ball milling, (c) (LiAlH₄+5 wt.% n-Ni) balled milled under a high energy mode and (d) (LiAlH₄+5 wt.% n-Fe) balled milled under a high energy mode. IMP68-a high impact energy mode of milling, R40 and R132 means ball-to-powder-weight ratio=40 and 132, respectively. n-Ni: nano-nickel additive. Reproduced from [27, 29, 30].

We reported in [29-31] that the nano-additives substantially modified the thermal DSC response of LiAlH₄. Adding 5 wt.% of the nano-nickel (n-Ni) additive [29] by a simple mixing with LiAlH₄, using mortar and pestle, does not change the DSC curve as compared to that for ball

milled LiAlH₄ without additives and LiAlH₄ still decomposes in a molten state (Fig. 2b) through reaction (2'b) forming Li_3AlH_6 (s). In contrast, a highly energetic ball milling of LiAlH₄ with either 5wt.% of the n-Ni or n-Fe additive, completely eliminates melting of LiAlH₄ and the LiAlH₄ decomposition peak (2'b) in Fig. 2a, b merges with the first peak for reaction of the surface aluminum-hydroxyl groups [28] and becomes now a single peak corresponding to reaction (2''b):

 $LiAlH_4(s) \rightarrow 1/3Li_3AlH_6(s) + 2/3Al(s) + H_2(g)$ (2''b)

The (2"b) peak is now shifted to slightly lower temperatures (Fig. 2c, d). Remarkably, this behavior is identical for both types of nanometric metallic additive, either n-Ni or n-Fe. The other two peaks corresponding to reaction (2c) and (1d) appear unaffected except that they are shifted to slightly lower temperatures after high energy ball milling with a nanometric metal additive (Fig. 2c, d). The merging of peaks attributed to surface hydroxyl reaction and the decomposition of LiAlH₄ in reaction (2'b) into one peak (2''b) for solid state decomposition is a very peculiar phenomenon which we reported for the first time [22, 29]. As pointed out in [22], it is still unclear if this is just a coincidence or indeed, a new physical phenomenon. We hypothesized in [22, 29, 30] that reaction of the surface aluminum-hydroxyl groups may trigger a spontaneous decomposition of ball milled LiAlH₄ containing nanometric metallic additives at temperatures much lower than the melting point of either unmilled or ball milled LiAlH₄ without additives. However, it is unknown if the origin of the exothermic nature of the first exothermic peak in Fig. 1a, b is related to the inherent exothermic nature of reaction of the surface aluminum-hydroxyl groups or, indeed, reaction (2"b) is simply exothermic in nature, despite the fact that melting has been eliminated. It should also be pointed out that in **contrast to the nanometric Fe additive**, the DSC curves for LiAlH₄ ball milled with the 5 wt.% micrometric size Fe additive were exactly the same as those for additive-free LiAlH4 in Fig. 2a, in the sense, that the decomposition of LiAlH₄ occurred after melting (reaction (2'b)) [30]. The DSC observations clearly show that the elimination of the melting stage of LiAlH4 and its decomposition from solid state can only occur if two conditions are met: (i) the metallic additive must be nanometric and (ii) high energy ball milling is employed for processing of LiAlH4 with a nanometric additive. It seems that an important condition is that the n-Ni and n-Fe additives must be very intimately embedded within the LiAlH₄ particles in contrast to mixing where metal nano-particles are just loosely distributed at the surfaces of LiAlH₄ powder particles. In addition, (LiAlH₄+5 wt.% n-Fe) nanocomposite powder was subjected to a thermal sectioning in DSC by stopping the test at varying pre-determined temperatures and after stopping the test at selected temperature, the powder sample was immediately extracted from a crucible for an XRD test [22, 30]. At 415 and 500°C just before and after peak (2d), an intermetallic compound LiAl appeared in the microstructure which confirmed the occurrence of reaction (2"d).

Another phenomenon that we discovered during our studies on the effect of additives in LiAlH₄, which has never been before reported in the literature, is that some nanometallic [22, 30] and nano-carbide [31] additives trigger a profound mechanical dehydrogenation phenomenon.

We have found that LiAlH₄ ball milled together with the n-Fe additive, under a high energy milling mode, starts decomposing rapidly during milling releasing large quantities of H₂ (Fig. 3a)[**30**]. Interestingly, no H₂ desorption was observed during *low energy* milling of LiAlH₄ containing n-Fe, for example, under a low energy shearing mode (Fig. 3a). Similarly, no H₂ desorption occurred during high energy ball milling for LiAlH₄ containing micrometric Fe (μ -Fe) and, for comparison, containing the micrometric and nanometric Ni (μ -Ni and n-Ni) additive. In order to identify reactions occurring as the milling progresses, the XRD patterns were obtained from the powders milled for 15 min, 1 h and 5 h, which are compared to the XRD pattern for a just mixed powder in Fig. 3b. After barely 15 min of milling, the diffraction peaks of Li₃AlH₆ are clearly seen as opposed to the LiAlH₄ peaks observed for the mixed powders. The intensity of the Li₃AlH₆ peaks increases after 1 and 5 h (300 min) of milling while the intensity of LiAlH₄ peaks gradually decreases and they eventually disappear (Fig. 3b). Simultaneously, more H₂ is desorbed as can be seen in Fig. 3a. It is obvious that during high energy milling, there is a gradual decomposition of LiAlH₄ in *solid state* according to reaction (1"b).



Fig. 3. (a) The quantity of H_2 desorbed during ball milling under the high impact energy (IMP68; 4B: 4 balls [19]) mode and the low shearing energy (LES6) mode as a function of milling time. (b) XRD patterns after milling under high energy (IMP68) for various times. Milling under high energy mode (IMP68) was repeated twice (solid circles and triangles). ICDD file numbers are shown for peak identification. 4B- four balls in the milling vial. Ball-to-powder weight ratio R=132. Reproduced from [22, 30].

Furthermore, XRD studies have shown that ball milling resulted in a varying degree of the lattice expansion of LiAlH4 for both the n-Fe and n-Ni additives [22, 30]. It seems that a volumetric lattice expansion larger than 1% can trigger the accelerated decomposition of LiAlH4 accompanied by continuous H₂ desorption during milling according to reaction (2"b).

It was hypothesized [8, 22, 30] that the Fe and Ni ions are able to dissolve in the lattice of LiAlH₄ by the action of mechanical energy, replacing the Al ions and forming a substitutional solid solution of either the LiAl_{1-x}Fe_xH₄ or LiAl_{1-x}Ni_xH₄ type [8, 22, 30]. This is similar to a well-known **mechanical alloying phenomenon**. The ionic radius of 77 pm for Fe²⁺ is much larger than 53 pm for Al³⁺ [32] and the LiAlH₄ lattice expansion increases. In contrast, the ionic radius of Ni²⁺ is 69 pm [32] and the volumetric lattice expansion is smaller. It is interesting that the profound dissolution of the Fe²⁺ ions in the LiAlH₄ matrix can only occur when the Fe additive is *nanometric* (n-Fe) while it does not occur if the additive is micrometric in size [8, 22, 30]. Furthermore, the experimental results in [8, 22, 30] showed that n-Fe is more efficient in enhancing the mechanical dehydrogenation of LiAlH₄ during ball milling than n-Ni. This is a puzzling finding because the Ni²⁺ ionic radius is smaller than that of the Fe²⁺ ion and thus, one would expect more Ni²⁺ ions dissolved in the LiAlH₄ lattice. Apparently, for the same milling



Fig. 10. The correlation of the volumetric lattice expansion for LiAlH₄ with the type of Fe additive (μ -Fe n-and Fe), milling mode and observed hydrogen desorption event during milling. For comparison, the results for μ -Ni and n-Ni are also shown. Milling conducted with four balls (4B) in the milling vial except where two balls (2B) are indicated; milling time duration is shown. Ball-to-powder weight ratio R=132. IMP68-impact mode with two magnets, LES6-low energy shearing mode with one magnet (for more details on ball milling in a magneto-mill reader is referred to [15]). SSA - specific surface area. μ -Fe - micrometric Fe additive: 1h, 3h and 10h-indicate the length of pre-milling time for the micrometric Fe additive. Reproduced from *R.A. Varin, R. Parviz. The effects of the micrometric and nanometric iron (Fe) additives on the mechanical and thermal dehydrogenation of lithium alanate (LiAlH₄), its self-discharge at low temperatures and rehydrogenation. Int J Hydrogen Energy 37 (2012) 9088-9102.*

conditions, the incorporation of Ni^{2+} ions into the ionic-covalent crystal of LiAlH4 is less efficient than the Fe²⁺ ions. Therefore, we suggested [33] that an efficient incorporation of metal ions in an ionic-covalent lattice, like that for LiAlH4, could be driven by chemical reactions with oxide forming on the additive metal nanoparticles, instead of the metal itself. Indeed, the n-Fe particles of received n-Fe (NANOFER 25S from the Nano Iron, s.r.o., The Czech Republic) had a high surface content of Fe₃O₄ (about 15 wt. %) [30] that was much higher than that for n-Ni [34]. The NANOFER 25S n-Fe containing Fe₃O₄, could be more efficient in enhancing the dehydrogenation reaction during ball milling. Since the iron oxide associated with n-Fe is Fe₃O₄ [30] which, in essence is a partly reduced form of Fe₂O₃ such as $Fe^{2+}O \cdot Fe^{3+}_{2}O_{3}$, we postulated the following reaction sequence [33]:

$$(1+2x)LiAl^{3+}H_4 + xFe^{2+}O \cdot Fe^{3+}_2O_3 \rightarrow LiAl^{3+}Fe^{3+}_xH_4 + [2xFe^{2+}O + 2xLiOH + (1+2x)AlH_3]$$
(3a)

$$LiAl^{3+}Fe^{3+}_{x}H_{4} \rightarrow 1/3 Li_{3}AlFe_{x}H_{6}+2/3Al(Fe_{x})+H_{2}$$
(3b)

(3c)

$$Li_3AlFe_xH_6\leftrightarrow 3LiH+Al(Fe_x)+3/2H_2$$

In reaction (3a) the additive is metal oxide Fe_3O_4 . A fraction of ions in Fe_3O_4 exhibit valence Fe^{3+} the same as the valence of Al^{3+} . The ionic radius of Fe^{+3} is smaller than that of Fe^{2+} (63 pm vs. 77pm [32]) and the charge is the same as Al. So, the substitution of Fe^{3+} for Al^{3+} (53 pm [32]) in the LiAlH4 alanate lattice sites is more favorable. Both the substituted LiAlFe_xH4 and Li₃AlFe_xH₆ might be easier to dehydrogenate through (3b) and (3c). Finally, it must be pointed out that the mechanism of accelerated mechanical dehydrogenation of LiAlH4, containing n-Fe additive, seems not to be a typical catalytic mechanism in which a catalyst is supposed to accelerate the surface formation of molecular H₂ from the atomic hydrogen escaping from the bulk.

A similar mechanical dehydrogenation phenomenon was observed for LiAlH₄ containing nanometric interstitial compounds, such as nanocarbides n-TiC and n-ZrC and nanonitride n-TiN [**31**]. Fig. 4a shows a trend of increasing amount of H₂ desorbed during ball milling under milling energy intensity of Q_{TR132} =72.8 kJ/gh (the methodology of milling energy intensity for a certain milling mode is described in [**35**]) with increasing milling time (h). After about 18 h of milling (total injected milling energy Q_{TR} =1310 kJ/g [**35**]) the amount of mechanical dehydrogenation for the n-TiN additive reaches ~6.6 wt.% H₂. Finally, after 25 h of milling (Q_{TR} =1820 kJ/g [**35**]) the amount of mechanical dehydrogenation reaches ~7 wt.% H₂ for the n-TiC additive, and ~3 wt.% H₂ for the n-ZrC additive. Therefore, the mechanical dehydrogenation curves in Fig. 4 confirm that the mechanical dehydrogenation rate of the samples containing the nanometric interstitial compound additives increases noticeably during high energy ball milling, with increasing quantity of injected energy, in the order of n-TiN>n-TiC>n-ZrC, while no mechanical dehydrogenation occurs during milling when the quantity of total injected energy is very small, Q_{TR} =18.2 kJ/g [**31**].



Fig. 4. (a) The quantity of H₂ desorbed during ball milling (mechanical dehydrogenation) under the high impact energy mode IMP68-4B-R132 (Q_{TR132} =72.8 kJ/gh [**35**]) as a function of milling time for LiAlH₄ containing 5 wt.% n-TiC, n-TiN and n-ZrC. Reproduced from [**31**]. (b) XRD patterns after milling of (LiAlH₄+5 wt.% n-TiC) under high energy milling mode IMP68-4B-R132 (Q_{TR132} =72.8 kJ/gh [**35**]) for various milling times. ICDD file numbers are shown for peak identification. AR-as received, BM-ball milled. Reproduced from [**31**].

The XRD patterns in Fig. 4b were taken for (LiAlH₄+5 wt.% n-TiC), milled for 15 min, 5 h and 25 h [31]. For comparison, an XRD pattern for as-received (AR) LiAlH₄ is also included. As can be seen, after 15 min of ball milling of a nanocomposite (LiAlH₄+5 wt.% n- TiC) (Q_{TR} =18.2 kJ/g) no peaks of Li₃AlH₆ are observed. The diffraction peaks of Li₃AlH₆ appear after 5 h of milling (Q_{TR} =364 kJ/g) accompanied by decreasing intensity of the LiAlH₄ peaks and more H₂ desorption (Fig. 4a). This trend continues until a complete disappearance of the LiAlH₄ and Li₃AlH₆ peaks after 25 h ball milling (Q_{TR} =1820 kJ/g) occurs. Only diffraction peaks of elemental Al and the n-TiC additive are visible on the XRD pattern after 25 h of ball milling (Fig. 4b). It is obvious that during high energy ball milling with intensity Q_{TR132} =72.8 kJ/gh [35] there is a gradual decomposition of LiAlH₄ in solid state according to reactions (2'b) and (2c).

It was found that there was **no measurable change in a unit cell volume of LiAlH4 containing nanointerstitial compounds after ball milling** [**31**]. **That means that accelerated mechanical dehydrogenation for LiAlH4 containing nanometric interstitial compounds in Fig. 4a is unrelated to the lattice expansion** that might have been induced by, for example, diffusion of the Ti or Zr ions from the nanometric interstitial compounds into the LiAlH4 crystal lattice. The absence of a measurable lattice expansion is in agreement with the experimental fact that the nanometric interstitial compounds are very stable during high energy ball milling and do not decompose releasing the Ti or Zr ions.

The crystal structures of interstitial compounds like TiC and TiN belong to the general family of electron compounds whose crystallographic structures depend on the average number of valence electrons per atom (valence electron concentration, VEC) [36]. However, for both TiC and ZrC VEC=8 and TiN has VEC=9 [36] but the n-ZrC additive is the weakest one then their catalytic activity for mechanical dehydrogenation seems not to be related to their VEC number. We postulated in [31] that the primary factor responsible for a strong catalytic effect of the nanometric interstitial compounds during mechanical dehydrogenation is a very small particle size on the order of 20 nm or less. The secondary factor, at an equal particle size, seems to be a stronger catalytic effect for Ti than that for Zr in an interstitial compound. This hypothesis is in agreement with the work of Rafi-ud-din et al. [37] who suggested that the very stable nanometric TiC particles, strongly embedded in the LiAlH₄ matrix during ball milling, produced deformed interfacial regions surrounding them which exhibited an increased density of lattice defects which, in turn, enhanced dehydrogenation capability. Since, the n-TiN had the smallest average particle size of 20 nm [31] work, most likely, it produced the highest density of lattice defects in the surrounding deformed matrix leading to considerably enhanced mechanical dehydrogenation, compared to the other two additives, n-TiC and n-ZrC, exhibiting larger particle sizes.

Table 1 summarizes the propensity to mechanical dehydrogenation for LiAlH₄ with metallic and nonmetallic nano-additives.

LiAlH₄ system	LiAlH₄ lattice parameter change	Reaction between additive and the LiAlH4 matrix and formation of metal/intermetallic product	H ₂ desorption during ball milling	Reference
(LiAlH ₄ +5 wt.% n-Ni)	Small	No	No	[29]
(LiAlH ₄ +5 wt.% n-Fe)	Excessive	No	Yes	[30]
(LiNH ₄ +5 wt.% n-	None	No	Yes	[31]
TiC/n-TiN/n-ZrC)				

Table 1. Summary of the high energy ball milling behavior of the LiAlH₄ systems with nano-additives.



Fig. 5. (a) Thermal H₂ desorption curves at 100°C under 1 bar H₂ pressure for LiAlH₄ BM with 5 wt.% of nano additives. Slow desorption of LiAlH₄ BM with 5 wt.% (b) nanometallic and (c) nano interstitial compound additives at 40°C. Reproduced from [27, 29-31]. (BM-ball milled).

As shown in Fig. 5a the reduction of thermal dehydrogenation temperature for LiAlH₄, which is accompanied by increasing dehydrogenation rate, can be achieved by incorporating nano additives. In general, **isothermal decomposition of LiAlH₄ occurs in two stages: quite fast Stage I and much slower Stage II (Fig. 5a)** which corresponds to reaction (2''b) and (2c), respectively. Those stages were confirmed by X-ray diffraction after completion of desorption at each temperature [27, 29-31]. It was found [29-31] that for thermal dehydrogenation in Stage I the average apparent activation energy, E_A , for the nano interstitial compound additives, n-TiC/n-TiN/n-ZrC, was within the range of 87-96 kJ/mol whereas, for comparison, the nanometric metallic additives, n-Fe and n-Ni, exhibited drastically smaller apparent activation energy on the order of 55-70 kJ/mol. The average apparent activation energy for thermal dehydrogenation in Stage II was in the range of 63-80 kJ/mol in the order of $E_A(n-ZrC) < E_A(n-Ti=n-TiC)$ and was lower than that for the nanometric metal additives n-Ni and n-Fe. In summary, the nanometric interstitial compounds did not substantially affect the apparent activation energy of Stage I but were able to reduce the apparent activation energy of thermal dehydrogenation in Stage II.

Fig. 5b shows that **ball milled nano-additive bearing LiAlH**⁴ is capable of slowly desorbing H₂ at **a low temperature of barely 40°C**. The nano-interstitial additives (n-TiN, n-TiC and n-ZrC) seem to be slightly more effective in inducing low-temperature H₂ desorption because **after 20** days the desorbed H₂ quantity is about 6 wt.%, as compared to about 5 wt.% H₂, desorbed after the same number of days from LiAlH₄ containing nano-metal (n-Ni and n-Fe)

additives. The slow desorption phenomenon at such a low temperature makes LiAlH₄ with nano-additives a nearly ideal hydride for filling in disposable cartridges for long-term, low-volume applications.

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Case 2-NaAlH₄

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Letter

Reversible hydrogen storage in Ti–Zr-codoped NaAlH₄ under realistic operation conditions

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1. Introduction

Since the discovery of the catalytic effect of Ti halide precursors [1], NaAlH₄ has become a promising candidate for the solid-state storage of hydrogen. This finding was followed by several papers dealing with different approaches to improve the activity of Ti catalysts [2]. Several Ti-containing compounds, such as organic precursors [3], TiH₂ [4] and Ti nanoparticles [5] have been proven to catalyze hydrogen desorption of NaAlH₄ efficiently. In this respect, recent findings indicate that Ti(0) is the actual catalyst [6,7].

Zr is in the same group in the periodic table as Ti, thus, a similar catalytic effect can be anticipated. However, there are only few publications dealing with Zr catalysts for dehydrogenation and rehydrogenation of NaAlH₄. From a systematic screening of a multitude of transition metal chlorides for dehydrogenation of NaAlH₄ it turned out that ZrCl₄ is less efficient than different Ti chlorides but much more efficient than all other catalyst precursors tested [8]. In addition, organometallic Zr additives were successfully used for the dehydrogenation of NaAlH₄. Furthermore, it was demonstrated that the combination of Zr and Ti catalyst precursors helps to improve the desorption kinetics [9]. X-ray diffraction studies were carried out in order to investigate the influence of the dopants Ti and Zr on the lattice parameters of NaAlH₄ [10]. A synergistic effect

ABSTRACT

Ti-Zr-codoped NaAlH₄ exhibits improved hydrogen desorption and reabsorption properties compared with sole Ti- or Zr-doped alanate. This contribution aims on reversible hydrogen storage in such material under realistic operation conditions. Results on isothermal dehydrogenation-rehydrogenation cycles at 125°C and desorption at 4 bar hydrogen back-pressure are presented, proving NaAlH₄ to be a suitable hydrogen material in combination with proton exchange membrane fuel cells.

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AND COMPOUNDS

was observed both for desorption and reabsorption of hydrogen by different authors [11,12].

Doped NaAlH₄ has several promising properties as reversible hydrogen storage material for technical use, such as cycle stability, rather low absorption and desorption temperatures from 100 to 150°C [2] and the possibility of its direct synthesis starting from NaH and Al via reactive milling [13]. More importantly, the dehydrogenation of NaAlH₄ exploiting the exhaust heat of a high-temperature proton exchange membrane (HT-PEM) fuel cell, working at 1.2 bar has been tested [14]. However, for practical applications a fuel cell back-pressure of several bar is required in order to reach a sufficient performance, in particular for mobile applications [17].

In this contribution, dehydrogenation of doped NaAlH₄ is presented for the first time at a constant *hydrogen back-pressure of 4 bar* and a temperature of 150 °C in order to mimic realistic operation conditions in combination with a HT-PEM fuel cell. For this purpose, NaAlH₄ was ball-milled with Zr, TiCl₄ and both in combination (codoping). In addition, dehydrogenation and rehydrogenation of hydrogen storage material were studied under *isothermal conditions*, being favourable for technical processes.

2. Experimental

2.1. Powder preparation

All samples were prepared and handled in a glovebox (MBraun) under Ar to prevent unwanted oxidation. For Zr-doping, 5 mol% Zr powder (Chemetall, 97.8% purity) with a particle size of 2–3 µm was intermixed with NaAlH₄ powder (Aldrich,

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Fig. 4. Dehydrogenation of NaAlH₄ at 4 bar in dependence of the catalytic system in comparison with the dehydrogenation of Zr–TiCl₄-codoped NaAlH₄ at 1 bar.

tion temperature, respectively). The codoped NaAlH₄ reversibly stored about 4 wt% hydrogen at a constant temperature of 125 °C with a total catalyst amount of only 2 mol%. Values of >4 wt% reversible hydrogen release were achieved after 5 h of dehydrogenation, and hydrogen uptake of 4 wt% after 1 h was demonstrated for this sample. Within the investigated range the catalyst concentration in the codoped system has only a minor effect on the sorption kinetics of NaAlH₄. However, the storage system with 2 mol% catalyst stored 0.4 wt% hydrogen more than the sample with 5 mol%.

The reversibility was confirmed by XRD analysis (cf. Fig. 2). In the representative XRD pattern of codoped NaAlH₄ prior to dehydrogenation and after three cycles of dehydrogenation and rehydrogenation Ti could not be detected directly, probably due to an overlap with the Al peaks of the finely dispersed catalyst. However, NaCl was found which is formed during the reduction of TiCl₄. As expected from Fig. 1, Na₃AlH₆ has not been detected, thus, indicating a low concentration. The XRD patterns of the other samples we investigated provide similar results and are therefore not presented.

SEM measurements prior to and after cyclization (cf. Fig. 3) of the codoped sample show the particle fragmentation that can explain the increasing activity after the first cycle, which we observed for all samples. This effect is consistent to the observations in Ref. [9].

Since for many fuel cell applications a hydrogen pressure of 4 bar is needed during desorption [17], the material systems investigated here were tested under such realistic operation conditions. Fig. 4 exhibits the dehydrogenation kinetics of the NaAlH₄ samples at 4 bar hydrogen pressure with three different catalytic additives and desorption of the codoped system at 1 bar for comparison. The

can be observed during both absorption and desorption (Scheme 1). At a constant temperature of $125\,^\circ C$ rehydrogenation of Na_3AlH_6

$$3 \operatorname{NaAlH_4} \longrightarrow \operatorname{Na_3AlH_6} + 2 \operatorname{Al} + 3 \operatorname{H_2} \quad (1)$$

$$Na_{3}AIH_{6} \longrightarrow 3 NaH + AI + 3/2 H_{2}$$
(2)

Scheme 1. Decomposition reactions of NaAlH₄ to NaH.

hydrogen desorption at 4 bar starts at higher temperature than in the case of 1 bar hydrogen pressure and proceeds slower. There is a characteristic step in the desorption curves of the systems with TiCl₄ and the Zr–TiCl₄ mixture at 4 bar and temperatures below 150 °C, indicating a temperature range where the desorption reaction nearly stops at the stage of Na₃AlH₆. The codoped system is superior to the other catalysts over the whole temperature range. About 4 wt% hydrogen were desorbed within 5 h.

4. Conclusions

Codoping NaAlH₄ with Zr and TiCl₄ considerably improves the kinetics for hydrogen desorption and reabsorption, compared to sole doping with Zr or TiCl₄. Reversible hydrogen storage of 4 wt% via pressure variation between 1 and 100 bar at a constant temperature of 125 °C with reasonable kinetics was demonstrated. It was shown for the first time that about 4 wt% of hydrogen could be released during dehydrogenation of NaAlH₄ against a hydrogen pressure of 4 bar, which will be needed for PEM fuel cells in automotive applications.

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Fig. 3. SEM micrographs (BSE mode) of NaAlH_4 + 2.5 mol% Zr + 2.5 mol% TiCl_4 prior to (a) and after (b) cyclization.



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Catalytic Effects of Nanometric Ni (n-Ni) on the Dehydrogenation of Ball Milled Sodium Alanate (NaAlH₄)

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Mixtures of sodium alanate (NaAlH₄) with the nanometric Ni (n-Ni) additive were processed by controlled ball milling for 15 min in a magneto-mill and subsequently investigated by Differential Scanning Calorimetry (DSC), X-ray diffraction (XRD) and volumetric hydrogen desorption in a Sieverts-type apparatus. The apparent activation energy of the decomposition of Na₃AlH₆, which is the decomposition product in the first dehydrogenation step of NaAlH₄, is equal to \sim 140 kJ/mol and ~101 kJ/mol for ball milled NaAlHa and NaAlHa H/5 wt% n-Ni, respectively, as determined by the Kissinger method in DSC tests. The apparent activation energy for the decomposition of NaH, which is the decomposition product in the second dehydrogenation step of Na₃AlH₆, is estimated as equal to \sim 143 kJ/mol and \sim 226 kJ/mol for ball milled NaAlH₄ and NaAlH₄ + 5 wt% n-Ni, respectively. It seems that the n-Ni additive accelerates the decomposition of Na₃AlH₆ but decelerates the decomposition of NaH. Volumetric desorption tests indicate a substantial enhancement of the rate of hydrogen desorption at 170 °C for the ball milled NaAlH₄ + 5 wt% n-Ni nanocomposite as a result of the catalytic action of n-Ni. No reaction of n-Ni with the NaAlH₄ matrix is observed during dehydrogenation at 170-280 °C. The n-Ni catalyst used in the present work compares very favorably with other catalytic additives reported in the literature (e.g., metal chlorides) which were used for the enhancement of dehydrogenation of NaAlH₄.

Keywords: Solid State Hydrogen Storage, Hydrogen Storage Materials, Desorption Temperature and Kinetics, Sodium Alanate (NaAlH₄), Nanometric Nickel, Ball Milling, X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Gravimetric and Volumetric Hydrogen Capacity.

SCIENTIFIC

1. INTRODUCTION

Hydrogen gas is the cleanest energy carrier. Its usage either in fuel cells or in combustion engines produces a by-product which is only water vapor. The advancement of the future Hydrogen Economy requires that three major obstacles must be overcome: (i) improvement of fuel cells which produce electrical current and water vapor when fuelled by hydrogen, (ii) inexpensive and carbonfree hydrogen production and (iii) hydrogen storage.¹ The latter obstacle is most likely the most important one, particularly for automotive applications. Since gaseous and liquid hydrogen storage techniques are quite cumbersome to commercialize1 a general consensus emerged that the final remaining option is solid state hydrogen storage in hydrides.

One of the attractive hydrides for solid state hydrogen storage is sodium alanate (NaAlH₄). Bogdanović and Schwickardi² were the first researchers to report that the addition of Ti alkoxide/halide catalytic precursors (e.g., TiCl₃) reduced the dehydrogenation temperature of NaAlH₄ and rendered it reversible under relatively mild conditions of temperature and hydrogen pressure. Their findings were followed by a large number of research papers which have been reviewed until the end of 2008 in our recent book.¹ At present, the general consensus has emerged that during decomposition (dehydriding) of pristine NaAlH₄ as well as the one containing a catalyst or catalytic precursor the following reactions may take place:1,3-5

> NaAlH₄ (s) \leftrightarrow NaAlH₄ (l) ($\Delta H = 23 \text{ kJ/mol}$) (1a)

NaAlH₄ (I) $\rightarrow 1/3\alpha$ -Na₃AlH₆ (s) + 2/3Al (s) + H₂ (g)

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 $(\Delta H = 9 \text{ kJ/mol})$ (1'b)

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 $\operatorname{NaAlH}_4(s) \leftrightarrow 1/3\alpha - \operatorname{Na}_3\operatorname{AlH}_6(s) + 2/3\operatorname{Al}(s) + \operatorname{H}_2(g)$

$$(\Delta H = 37 \text{ kJ/molH}_2)$$
 (1"b)

 α -Na₃AlH₆ (s) $\leftrightarrow \beta$ -Na₃AlH₆ (s)

$$(\Delta H = 3.6 \text{ kJ/molH}_2) \quad (1c)$$

$$1/3\beta$$
-Na₃AlH₆ (s) \leftrightarrow NaH (s) $+ 1/3$ Al (s) $+ 0.5$ H₂ (g)

 $(\Delta H = 47 \text{ kJ/molH}_2)$ (1d)

NaH (s)
$$\rightarrow$$
 Na (l) + 0.5H₂ ($\Delta H = 57 \text{ kJ/molH}_2$) (1e)

where ΔH is the enthalpy change of the reaction, and (s), (l) and (g) refers to "solid," "liquid" and "gas," respectively. Reactions (1'b or 1"b), (1d) and (1e) proceed with a maximum theoretical hydrogen release of 3.7, 1.9 and 1.8 wt% (and obviously with slightly lower purity-corrected capacities), at the approximate temperature ranges of 180, 270-300 and above 300 °C, respectively Hence, hydrogen is desorbed in three major steps although reaction (1e) is not accessible for practical storage purposes due to its high temperature (>300 °C) so the hydrogen capacity which can be theoretically obtained from two reactions (1'b or 1"b) and (1d) is around 5.6 wt%. If dehydriding occurs below melting point of NaAlH₄ (~180 °C)^{1,3,4} (reaction (1a)) then the first dehydriding reaction is (1"b) which occurs in solid state without NaAlH₄ going through liquid state. In addition, Claudy et al.^{1,3} reported a phase transition of pseudocubic α -Na₃AlH₆ into face-centered cubic β -Na₃AlH₆ at about 252 °C (reaction (1c)).

From the experimental Van't Hoff plot¹ it has been established⁴ that the dehydrogenation of Ti-doped NaAlH₄ according to reaction (1"b) and that of Ti-doped Na₃AlH₆ according to reaction (1d) reaches ~30 °C and ~100 °C, respectively, at the pressure of 1 bar H_2 (atmospheric). Unfortunately, due to very sluggish kinetics the Ti-NaAlH₄ hydride system can only operate with a reasonable hydrogen desorption rate at temperatures >100 °C4. These are the temperature/pressure limits for any practical application of Ti-doped NaAlH₄. They have some valid experimental support since it was reported in⁶ that NaAlH₄ doped with 2 mol% TiCl₃ decomposed to NaCl, Al and Na_3AlH_6 to a considerable degree at the only moderately elevated temperatures created during ball milling. This indicates that TiCl₃ adds, most likely, nanometric Ti component which acts as a potent catalyst in the desorption of NaAlH₄. The recent findings indicate that the role of TiCl₃ is to form Ti which alloys with Al to form an intermetallic compound whose local structure resembles Al₃Ti.⁵ This intermetallic compound is supposed to be formed during the following reaction:5

$$3NaAlH_4 + TiCl_3 \leftrightarrow 3NaCl + Al_3Ti + 6H_2$$
 (2)

It was also reported that the plateau pressures of the $TiCl_3$ -doped $NaAlH_4$ system, especially for the first dehydrogenation step (1"b) are markedly affected by the Ti

content.⁵ It has also been found that ScCl₃ and CeCl₃ are even better catalytic precursors than TiCl₃⁷ in particular for rehydrogenation. For example, NaAlH₄ doped with 4 mol% ScCl3 was rehydrogenated at 90 °C in the 9th cycle under about 50 bar H₂ pressure within 70 min to achieve $\sim 3.4 \text{ wt}\% \text{H}_2$.⁷ Furthermore, Wang et al.⁸ has reported that there is a synergistic effect of co-doping with TiCl₃ ZrCl₄ and FeCl₃ from which the combination of 3 mol% TiCl₃-1 mol% FeCl₃ exhibited the best synergistic performance. The studies on the synergistic effects of dopants were extended to pure elemental metals such as Ti (particle size 54–70 μ m) and Zr (particle size 50 μ m)⁹ and a combination of metallic Zr (particle size 2–3 μ m) and a TiCl₃ precursor.¹⁰ Xueping et al.¹¹ investigated the catalyzing effect of pure metallic elements such as Ti, Co, Ni of unspecified particle size together with LaCl₃ on hydrogen release of NaAlH₄. Bogdanović et al.¹² added colloidal titanium (Ti) nanoparticles (particle size unspecified) and the nanoparticles of titanium nitride (TiN) (size unspecified). Fan et al.¹³ used titanium carbide (TiC; particle size $\neq 4(\mu m)$ to catalyze the rate of desorption/absorption of NaAlH₄. A non-metallic catalyst such as carbon of unspecified particle size was used as a catalytic additive by Zaluska et al.14

However, catalytic precursors such as metal chlorides exhibit some disadvantage since they locally react (reaction (2)) with NaAlH₄ forming metal salts and free elemental metals and/or intermetallic compounds of nanometric size which most likely act as effective catalysts as discussed above. A by-product of a metal salt constitutes unnecessary "dead-weight" (ballast) for the microstructure and, in effect, reduces the total available hydrogen capacity. Therefore, it is imperative to search for some effective nanometric metallic catalytic additives which directly influence the desorption/absorption properties of alanates and other complex hydrides without exhibiting any unwanted reaction with the hydride matrix.

In the present work we report the results of the studies on the catalytic effect of nanometric nickel (n-Ni) produced by Vale Ltd. (Ontario, Canada) on the desorption behavior of the ball milled NaAlH₄. In our recent publications we have shown that after ball milling this particular n-Ni exerts a very strong catalytic effect on simple metal hydride MgH₂^{1,15} and complex metal hydride LiAlH₄.^{16,17} The latter has a very similar chemical make up and storage behavior as a complex metal hydride NaAlH₄. It is therefore very interesting if similar catalytic effects will be observed for NaAlH₄.

The nanocomposites of NaAlH₄ doped with n-Ni were processed by controlled ball milling in a magneto-mill and subsequently investigated by Differential Scanning Calorimetry (DSC), X-ray diffraction (XRD) and volumetric hydrogen desorption in a Sieverts-type apparatus. The results obtained in the present work are compared to the results reported in the literature for catalyzed NaAlH₄. The observed hydrogen storage behavior arising due to the catalytic action of n-Ni is discussed in view of the microstructural evolution as observed by XRD.

2. EXPERIMENTAL DETAILS

Technical grade purity (90%) NaAlH₄ (sodium aluminum hydride) was purchased from Sigma-Aldrich. It was used without any further purification since for any perceived commercial applications the additional purification would raise the cost. Specialty nanometric Ni (n-Ni) was produced by a proprietary carbonyl method by Vale Ltd., Mississauga, Ontario.¹⁸ The Specific Surface Area (SSA) of n-Ni is equal to 9.5 m²/g and was measured by the BET method in the Vale Ltd.'s laboratories. The chemical composition of n-Ni is as follows: 0.46% carbon, 0.11% oxygen and the rest Ni.^{16,17} Figure 1 shows the morphology of n-Ni which exhibits a very spherical shape with the average Equivalent Circle Diameter (ECD) = $[76 \pm 32 \text{ mby}]$ which was measured as described in Refs. [16, 17]. Guest

The mixture NaAlH₄ + 5 wt% n-Ni was processed $9\sqrt{236}$. Controlled Mechanical Milling (CMM) for 15 min (in) high purity hydrogen gas atmosphere (purity 99.999%: $O_2 <$ 2 ppm; $H_2O < 3$ ppm; $CO_2 < 1$ ppm; $N_2 < 6$ ppm; $CO \le 1$ 1 ppm; THC < 1 ppm) under ~ 600 kPa pressure in the magneto-mill Uni-Ball-Mill 5 manufactured by A.O.C. Scientific Engineering Pty Ltd, Australia.1, 16, 17, 19-21 The milling mode was a high energy impact (IMP68) with 2 magnets and 4 hard steel balls in the vial (for details see Refs. [16, 17]). The ball-to-powder weight ratio (R) used in this work was 132 (R132) and the rotational speed of milling vial was ~200 rpm. After loading with powder, an air-tight milling vial with an O-ring, equipped with a pressure valve mounted in the lid, was always evacuated and purged several times with high purity argon (Ar) gas (99.999% purity) before final pressurization with H₂ All the powder handlings before and after milling were



Fig. 1. Scanning electron micrograph of Vale Ltd. nanometric Ni (n-Ni) with $SSA = 9.5 \text{ m}^2/\text{g}$ used in this work. Secondary electrons (SE) contrast.

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performed in a purged glove box under overpressure of high purity Ar gas.

The crystalline structure of powders was characterized by X-ray diffraction (XRD) with Bruker D8 diffractometer using a monochromated CuK α_1 radiation ($\lambda =$ 0.15406 nm) produced at an accelerating voltage of 40 kV and a current of 30 mA. The scan range was from $2\theta = 10$ to 90° and the scan rate was 3° min⁻¹. Powder was loaded in a glove box filled with Ar into a home-made environmental brass holder with a Cu plate for powder support. Upper and lower part of the environmental holder is sealed through a soft-rubber O-ring and tightened using threaded steel bolts with nuts. The upper part of the holder contains a Kapton window transmittable to X-rays.

The hydrogen desorption at 170, 220 °C and 280 °C was evaluated using a second generation volumetric Sievertstype apparatus custom-built by A.O.C. Scientific Engineering Pty Ltd., Australia. This apparatus built entirely of [3][6L] austenitic stainless steel allows loading of a powder sample in a glove box under argon and its subseguent transfer to the main unit in a sealed 316L austenitic 20stainless steel sample reactor without any exposure to the environment. The weight of the powder sample in the desorption experiments was in the range of 20-30 mg. The calibrated accuracy of desorbed hydrogen capacity is about ± 0.1 wt% H₂ and that of temperature reading ± 0.1 °C. Before starting the desorption test, the inner tubing of the apparatus and reactor were evacuated and purged 4 times with high purity argon and then two times with hydrogen. The furnace of the apparatus was heated separately to the desired test temperature and subsequently inserted onto a tightly sealed powder sample reactor inside which an atmospheric pressure of 0.1 MPa H₂ was kept. Hence, the beginning of the desorption test was in reality pseudo-isothermal before the powder sample temperature reached the desired value. However, the calibrated time interval within which the powder sample in the reactor reaches the furnace temperature is on the order of \sim 400–600 s in the 100–350 °C range, which is negligible compared to the desorption completion time especially at temperatures below 200 °C. Therefore, one can consider the test as being "isothermal" for any practical purposes at this range of temperatures. Hydrogen desorption curves were corrected for the hydrogen gas expansion due to the increase in temperature. The amount of desorbed hydrogen in wt% was calculated from the ideal gas law as described in detail in Ref. [1] and is expressed with respect to the total weight of powder sample including 5 wt% of n-Ni.

The thermal behavior of powders was studied by Differential Scanning Calorimetry (DSC) (Netzsch 404) of ~6 mg powder sample with heating rate of 5, 10 and 15 °C/min and high purity argon flow rate of 100 ml/min. The powder was transported to a DSC instrument in a glass vial filled with Ar and then quickly loaded into an Al₂O₃ crucible with a lid. This operation took about 2–3 min and

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