



ELSEVIER

Journal of Alloys and Compounds xxx (2006) xxx-xxx

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

How carbon affects hydrogen desorption in NaAlH₄ and Ti-doped NaAlH₄

C. Cento, P. Gislou^{*}, M. Bilgili, A. Masci,
Z. Quiang, P.P. Prossini

ENEA CR Casaccia, Via Anguillarese 301, 00060 S. Maria di Galeria, Rome, Italy

Received 17 May 2006; received in revised form 25 August 2006; accepted 1 September 2006

Abstract

The hydrogen storage properties of doped and undoped NaAlH₄ samples are studied after mixing them with different percentages of high surface carbon. Manually mixed samples are compared with ball milled ones; it was found that manual mixing was a simple and effective way to dope NaAlH₄. A morphological and micro-structural analysis has been carried out in order to understand the effect of carbon. Carbon added samples show a marked enhancement of hydrogen desorption rate. The desorption temperature and the total hydrogen content remain almost unchanged for undoped sample. The desorption temperatures of Ti-doped samples increase with carbon content.

© 2006 Published by Elsevier B.V.

Keywords: Metal hydrides; Hydrogen storage materials

1. Introduction

Hydrogen storage for vehicle application is still an open challenge. Different routes have been followed but a satisfying solution has not achieved yet. Liquid hydrogen shows good volumetric and gravimetric density but its production cost is relatively high. Compressed hydrogen suffers for low volumetric hydrogen density whilst the use of traditional metal hydride is detrimental in terms of gravimetric hydrogen density. High amount of hydrogen (about 7 wt.%) can be absorbed at very high temperatures (350–450 °C) in light weight metals or metal nitrides (i.e. Mg or LiN₃) [1,2]. The desorption enthalpy (about 80 kcal/mol) can be supplied burning part of the stored hydrogen. In such a way the available hydrogen content is reduced to about 5wt.%.

Complex metal hydrides represent a good compromise between hydrogen content, desorption temperature and reaction enthalpy. Ti-doped NaAlH₄ is emerging as one of the most interesting candidate to efficiently store hydrogen since the discovery of its reversibility in hydrogen desorption.

Different techniques and precursors have been used to prepare Ti-doped NaAlH₄. A solution chemistry was followed by Bogdanovic and Schwickardi [3] and by Jensen and co-workers [4] to prepare the Ti-doped material. A solution of TiCl₃ or Ti(OBuⁿ)₄ in THF was added to a solution or a suspension of the hydride in the same solvent. The doped material was obtained by removing the solvent under vacuum.

The theoretical hydrogen content of NaAlH₄ is 5.6 and 5.1 wt.% hydrogen was desorbed from NaAlH₄ at 225 °C [5]. Material modifications induced by ball milling strongly decrease the desorption temperature. The rate of decomposition of 2 h milled sample was so fast to release about 3.0 wt.% hydrogen in 2 h at 160 °C [6]. Impressive results were obtained with Ti-doped NaAlH₄. Three weight percent hydrogen was desorbed in 4 h from 0.9 mol% doped sample at temperature as low as 125 °C and still faster desorption rate have been observed increasing the doping level [5]. Since part of the hydride reacts irreversibly with the dopant, high dopant levels are detrimental from gravimetric point of view. Thus, the very positive kinetics benefits of Ti-catalyst are seriously offset by losses in reversible H-capacity [5,7]. It has been shown that many types of dopant precursors including non-titanium based compounds result in enhancing sorption kinetics. Among them carbon and graphite was found effective to increase the desorption kinetics. Zaluska et al. [6]

^{*} Corresponding author. Tel.: +39 06 30483797; fax: +39 06 30486357.
E-mail address: paola.gislou@casaccia.enea.it (P. Gislou).

44 modified NaAlH_4 and Na_3AlH_6 by mechanical grinding with
45 or without carbon. Milled materials showed enhanced desorp-
46 tion kinetics, and the addition of carbon in the milling process
47 remarkably improved their performance. The amount of added
48 carbon was varied from 7 to 18 wt.%. It was found that in the
49 case of activated carbon or powdered graphite the results did not
50 significantly depend on the initial form of carbon, whilst carbon
51 nanotubes (CNT) admixed NaAlH_4 shows higher performances
52 [8]. In a recent study, the positive synergistic effect of 10 wt.%
53 graphite powder as co-dopant of 2 mol% Ti-doped NaAlH_4 was
54 demonstrated [9].

55 The observed phenomena were interpreted in mechanical
56 and electronic terms. Graphite can serve as lubricant or micro-
57 grinding agent through the formation of titanium carbide. The
58 electronic interaction of graphite π -electrons with Ti could
59 also facilitate Ti-hydrogen bond formation and consequently
60 enhancing Al-hydrogen bond cleavage. In the same work it was
61 shown that graphite in absence of titanium is essentially inactive
62 as a catalyst [9].

63 In this work the effect of high surface carbon on de-
64 hydrogenation and re-hydrogenation of NaAlH_4 was investi-
65 gated. Hydrogen desorption properties of manually mixed and
66 high energy milled materials were compared. The effect of car-
67 bon as a co-dopant on the de-hydrogenation kinetics of Ti-doped
68 NaAlH_4 was also studied.

69 2. Experimental

70 Sodium aluminum hydride (NaAlH_4 , Aldrich, tech. 90%) and hydrogen
71 titanium ortobutylate ($\text{Ti}(\text{O}i\text{Bu})_4$, Aldrich, purity $\geq 97\%$) were used as received.
72 High surface area carbon (Carbon Ketjen Black, Akzo Nobel, specific surface
73 $1250\text{ m}^2/\text{g}$) was dried at 120°C for 12 h. The amount of added carbon var-
74 ied from 2 to 20 wt.%. Carbon was added following two methods, namely
75 ball milling or manual mixing. In a typical ball-milled sample NaAlH_4 and
76 carbon were weighed to form 0.5g-batches which were loaded in a stainless
77 steel vial together with two stainless steel balls. The vial was evacuated and
78 filled with hydrogen. It was mounted in a shaker mill (SPEX 8000, CertPrep,
79 Metuchen, NJ) and milled for 30 min. Manually mixed samples were prepared
80 by grinding the powders in a mortar for 5 min. Doped samples were obtained
81 by gently mixing the mixture with titanium ortobutylate in its liquid form
82 for additional 5 min. The amount of added titanium was varied from 0.5 to 4
83 mol%.

84 The materials were characterized by X-ray diffractometry (XRD) analysis
85 (Miniflex Rigaku diffractometer) using $\text{Cu K}\alpha$ radiation.

86 Powders morphology was studied by scanning electron microscopy (SEM,
87 JEOL JSM-5510LV). Energy dispersive X-ray (EDS) analysis was performed
88 with an IXRF EDS-2000 System. The conditions were: accelerating voltage
89 25 kV, spot size 21 and working distance 21 mm.

90 Thermal decomposition was monitored by the home-made apparatus illus-
91 trated in Fig. 1. The sample (about 200 mg-batches) was introduced in a
92 cylindrical glass holder. Before each measure the sample holder was evacuated
93 and filled with nitrogen for three times and finally connected to the measure
94 apparatus. This latter consists in a BronkHorst F-100 flow-meter, 30 nl/h range.
95 The volume of desorbed hydrogen was calculated by numerical integration. A
96 thermocouple positioned on the sample holder was used to record the tempera-
97 ture. When the set temperature was reached, the sample was introduced into
98 the oven, a B-585 Buchi Glass Oven. Both the signals from thermocouple and
99 flow-meter were digitally recorded.

100 Hydrogenation/de-hydrogenation cycles at various temperatures were car-
101 ried on in a specifically designed pressure composition isotherm apparatus (PCI
102 from DeltaE, University of Calabria, Italy (www.deltae.it)). About 1.0 g of sam-
103 ple was loaded in a cylindrical SS reactor (1.0 cm inner diameter). In order to
104 achieve identical starting condition, the reactor was heated at the operative tem-

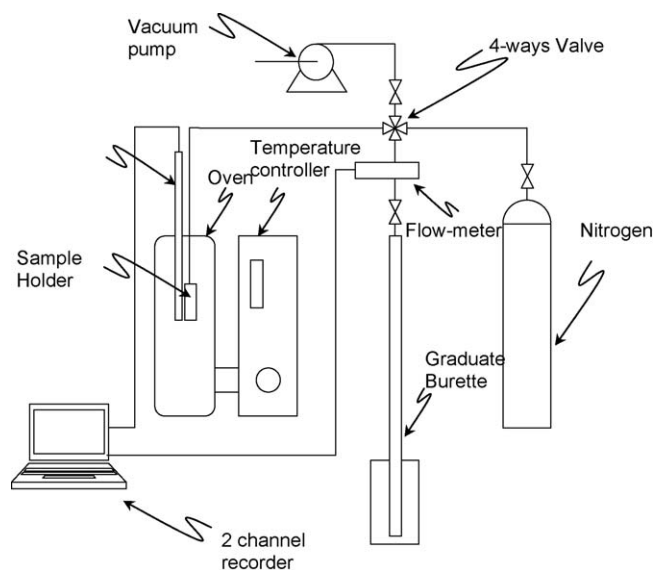


Fig. 1. Apparatus for desorption rate measurements.

105 perature and evacuated at low pressure (300 Pa) using a turbomolecular pump
106 before each hydrogenation process.

107 The reactor was heated by an external oven. To monitor the temperature a
108 thermocouple was connected to the reactor. After thermal equilibration hydrogen
109 was injected into the sample holder at constant flow and pressure changes quan-
110 tified by a calibrate 8 MPa range pressure transducer. An additional 0.08 MPa
111 pressure transducer was used for a good resolution at low pressure fields. The
112 flow was accurately monitored by a flow controller. The signal from the flow-
113 meter was recorded via computer and the volume of flowed hydrogen obtained
114 by numerical integration.

115 3. Results

116 Ball-milled Ti-doped samples showed a very high reactivity
117 with air: the powder burned immediately after the evacuated vial
118 was opened, even if this operation was carried out in a glove
119 box. The reactivity of ball-milled samples induced us to find
120 an alternative method to prepare Ti-doped alanate. It was found
121 that manually grinding the NaAlH_4 powder together with the
122 Ti precursor was an effective method to prepare air-stable Ti-
123 doped alanate. There are several practical merits related to the
124 dry approach since it is very easy to produce large amounts of
125 doped material and it avoids the handling of solvents.

126 3.1. SEM analysis results

127 A morphological investigation has been carried out to detect
128 modifications in the alanate structure due to addition of carbon
129 or to ball milling, before and after de-hydrogenation. In Fig. 2a,
130 SEM image of the NaAlH_4 -0.5mol% Ti sample is shown, before
131 (Fig. 2a) and after (Fig. 2b) de-hydrogenation. The very small
132 amount of Ti has not been revealed by micro-analysis.

133 In Fig. 3a and b, the mortar grinded 10% carbon sample is
134 shown, before and after de-hydrogenation, respectively. The car-
135 bon clusters are easily recognized in Fig. 3a since their grain size
136 is smaller, as compared to the smoother NaAlH_4 grains.

137 The sample with the same C content as Fig. 3 but prepared
138 by ball milling is shown in Fig. 4a. The structures of both the

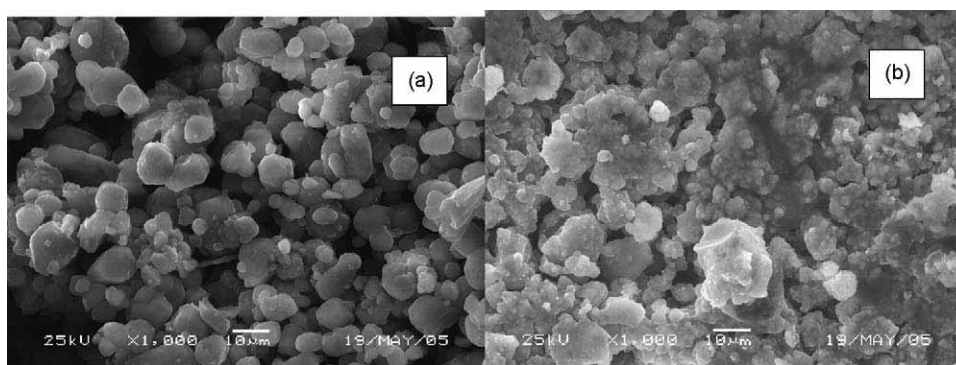


Fig. 2. SEM images of Ti-doped samples (a) before and (b) after de-hydrogenation.

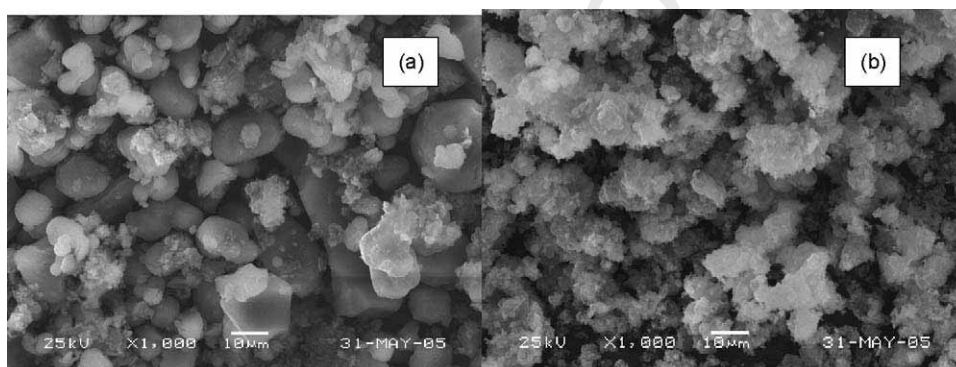


Fig. 3. SEM images of 10% C added samples (a) before and (b) after de-hydrogenation.

139 NaAlH₄ and C grains are no more distinguishable, the ball
140 milling had the effect of “flattening” the hydride; in reality, as
141 the XRD analysis showed (Section 3.3), the macroscopic loss
142 of granularity corresponds to a loss of microscopic crystallinity.
143 The same picture at a larger view shows a columnar stratification
144 of planes, Fig. 4b.

145 The “flat aspect” disappears after the first de-hydrogenation,
146 and the de-hydrogenated product appears similar to the non-ball
147 milled one (Fig. 5a and b).

148 3.2. Hydrogen desorption in carbon added samples

149 A plot of the hydrogen flow, normalized to the sample weight,
150 versus time, released by non-doped, carbon added samples with

151 different carbon percentage, is shown in Fig. 6. The temperature
152 was kept constant at 220 °C for several hours. The effect of the
153 carbon content on desorption kinetic is evident: passing from
154 2 to 20% carbon, the hydrogen flow increases by a factor of
155 4.

156 In Fig. 7, the plot of the hydrogen yield versus time at 220 °C
157 for various carbon content samples is shown. Again it is evident
158 that increasing carbon content has the effect of speeding up the
159 hydrogen dissociation: after 150 min the 20% carbon samples
160 attained the maximum hydrogen yield, 5.1 wt.%, whilst lower
161 percentage carbon samples are still desorbing.

162 The weight percentage refers to the alanate weight only; if we
163 calculate the hydrogen yield with respect to the sample weight,
164 the 10% C sample shows better results in terms of gravimetric

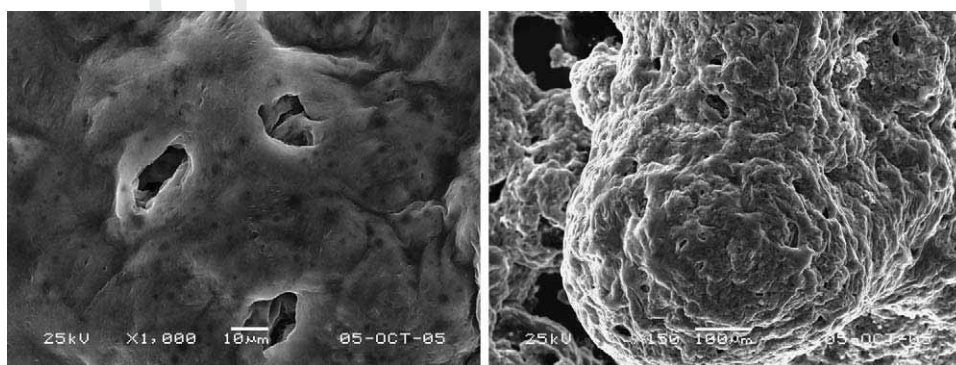


Fig. 4. SEM images of 10% C added ball-milled samples before de-hydrogenation at two magnifications.

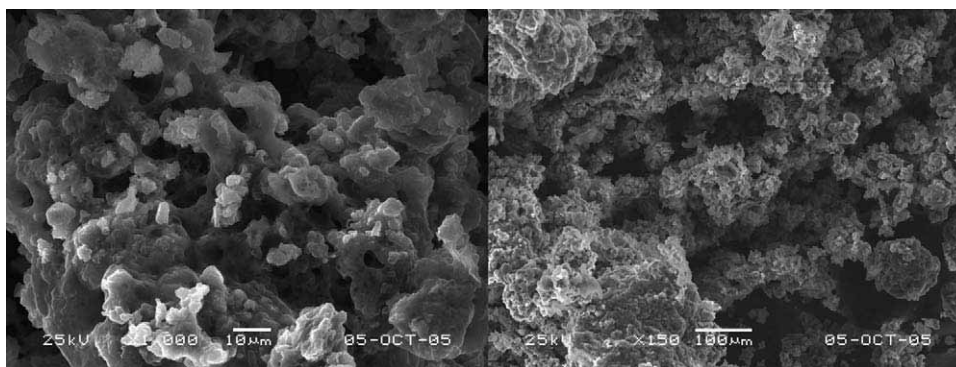


Fig. 5. SEM images of 10% C added ball-milled samples and after de-hydrogenation at two different magnification.

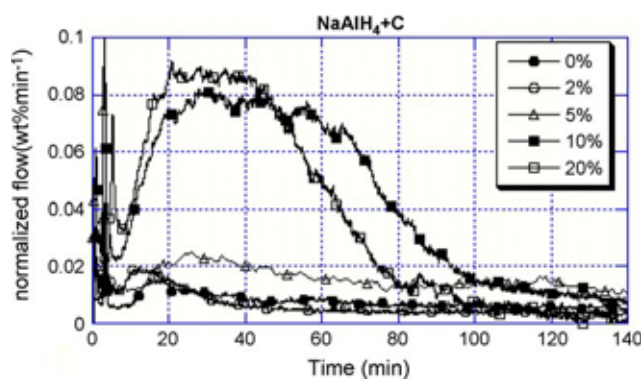


Fig. 6. Desorbed hydrogen flow of different C content NaAlH₄ samples at 220 °C; the flow is normalized to the alanate weight.

hydrogen density than the 20% C still at a reasonable desorption rate.

The behavior of the just grinded samples compared to the ball milled one with the same carbon content, is shown in Fig. 8. The hydrogen flow is reduced in the just grinded sample, although the hydrogen amount and the desorption temperature of the two samples are very similar.

The Arrhenius plot of the flow versus temperature for the non-doped 20% carbon added sample (Fig. 9) shows a single decomposition step characterized by an activation energy of 158 kJ/mol/K and a pre-exponential factor of 5.3E18. The effect of carbon is to increase the pre-exponential factor, and conse-

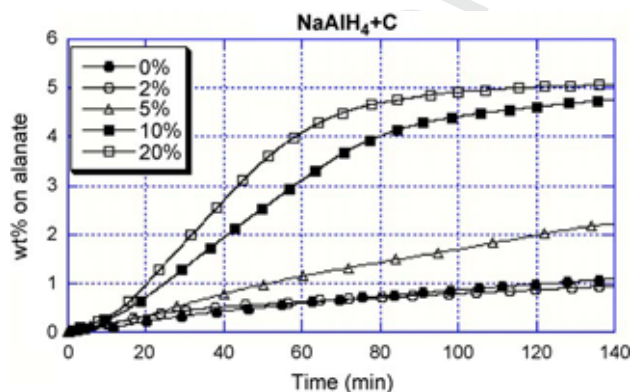


Fig. 7. Desorbed hydrogen of various C content NaAlH₄ samples at 220 °C; the hydrogen weight percentage is referred to the alanate weight.

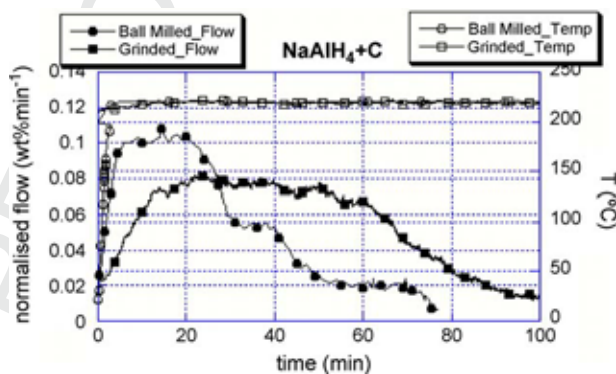


Fig. 8. Comparison between hydrogen flow released from a ball milled and a just grinded 10% C added samples.

quently to increase the kinetics of the reaction, with respect to the undoped NaAlH₄ [5].

It is well known that the decomposition of NaAlH₄ is a two-step reaction described by the following formula:

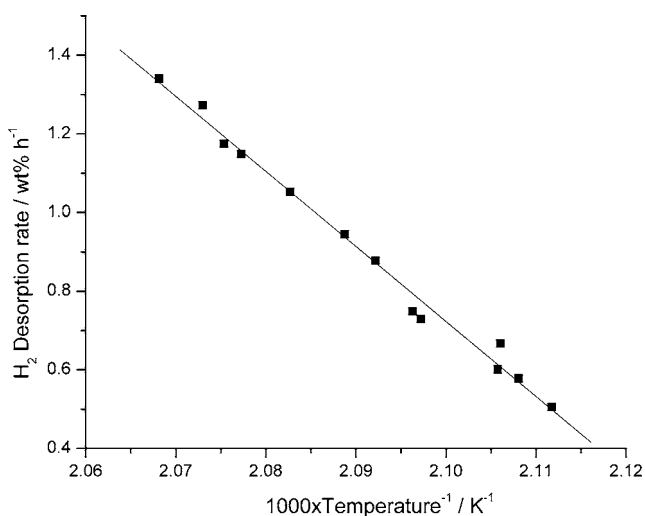
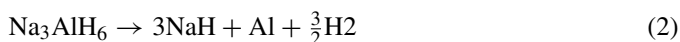
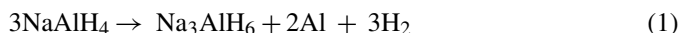


Fig. 9. Arrhenius plot of an undoped 20% C added sample.

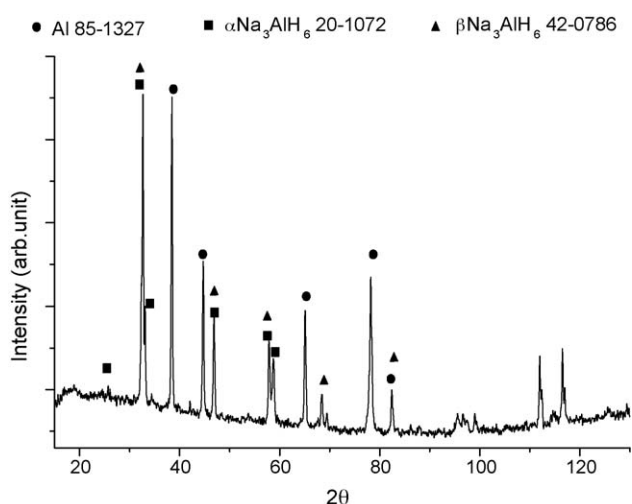


Fig. 10. XRD spectrum of a 10% C added sample after decomposition at 195 °C.

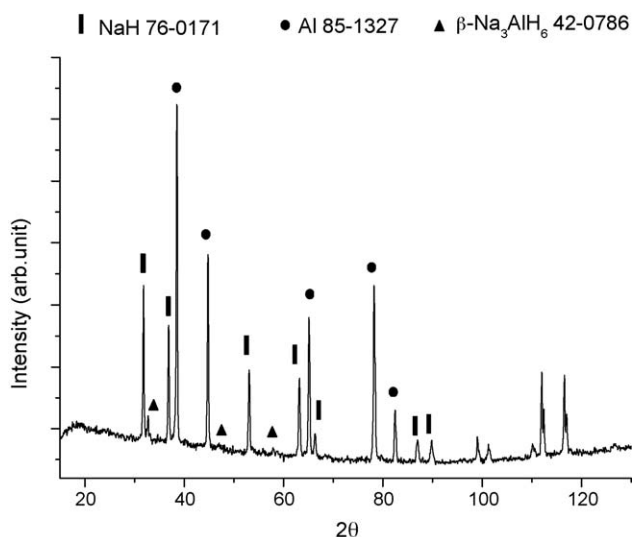


Fig. 11. XRD spectrum of a 10% C added sample after decomposition at 220 °C.

183 To detect only the first decomposition step of NaAlH₄ we set
184 the temperature at 195 °C and analyzed the decomposition the
185 reaction products by XRD. The hydrogen released by the first
186 step of reaction was 3.7 wt.%.

3.3. X-ray of carbon added samples

187
188 The progressive turning from NaAlH₄ into two different
189 Na₃AlH₆ phases, the α-Na₃AlH₆ and β-Na₃AlH₆, and succes-
190 sively into Al and NaH, was clearly detected by X-ray analysis.

191 In Figs. 10 and 11, the X-ray of the desorption products of
192 the 10% carbon ball-milled sample after decomposition, respec-
193 tively, at 195 and 220 °C are shown. In the low-temperature
194 reaction (Fig. 10) the NaAlH₄ completely decomposed into Al
195 and Na₃AlH₆ (α and β phases) following Eq. (1); after a further
196 increase in temperature (Fig. 11), together with a small amount
197 of Na₃AlH₆, the peaks of Al and NaH appear, as predicted by
198 Eq. (2).

199 The spectra for the ball-milled sample, before any de-
200 hydrogenation process, evidences that the macroscopic amor-
201 phous structure seen by SEM corresponds effectively to an
202 absence of microscopic structure: the peak intensity related to
203 NaAlH₄ was strongly decreased and Al was found in the spec-
204 trum. The presence of Al evidences that some decomposition
205 reaction occurred during the ball milling.

3.4. X-ray diffraction in carbon-added doped samples

206
207 X-ray diffraction spectra for a mixture of NaAlH₄ containing
208 5 wt.% carbon and doped with 0.5 mol% Ti shows exclusively
209 crystalline NaAlH₄. The absence of any peak related to titanium
210 metal does not allow to recognize whether Ti is in its metallic
211 state or not. The absence of peaks attributed to carbon is not
212 surprising since the carbon we used is amorphous.

3.5. Hydrogen desorption in Ti-doped carbon added samples

213
214 As stated by different authors [4,5], Ti doping is a very effec-
215 tive way to improve performance and de-hydrogenation kinetic.
216 We tested therefore if the beneficial effect found by adding car-
217 bon to the alanates is effective also for Ti-doped samples.

218 In Fig. 12a, the desorbing curves of four 0.5 mol% Ti samples
219 added, respectively, with 0, 5, 10 and 20% carbon are compared.
220 According to Sandrock et al. [5] the Ti-doped sample without
221 carbon shows two well defined decomposition step. The addition
222 of carbon results in an increasing of flow that again reaches its
223 maximum for the sample containing 10 wt.% carbon. At the
224 same time there is a disappearance of the second decomposition
225

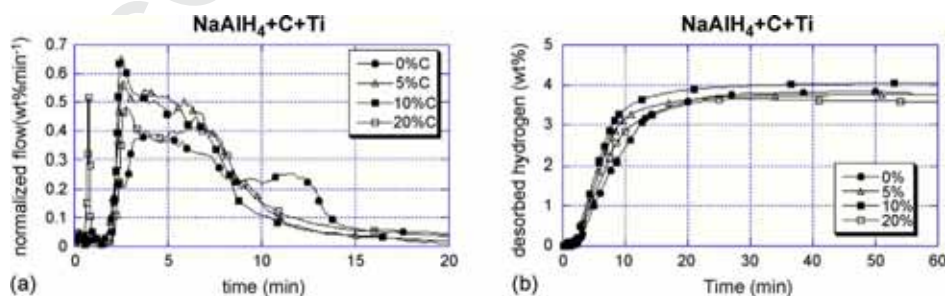


Fig. 12. Ti-doped, C added NaAlH₄ samples in: (a) the desorbed hydrogen flow is shown for different C percentages; (b) the corresponding hydrogen content is plotted. Temperature of measurement: 200 °C.

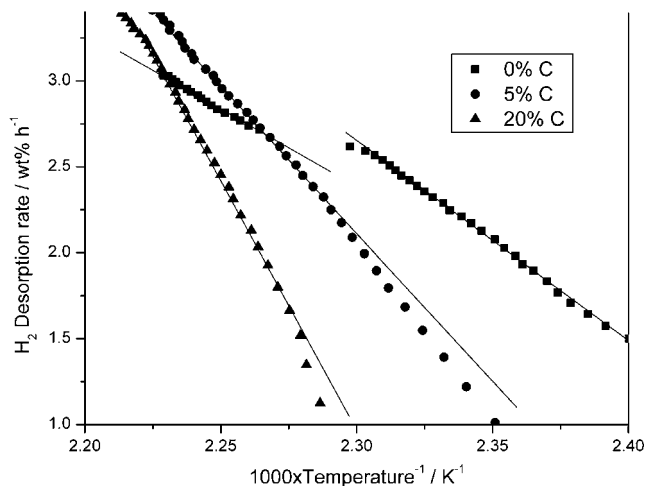


Fig. 13. Arrhenius plot of 0.5 mol% Ti-doped samples for different C added percentages; the 0% carbon curve shows the typical behavior with two different activation energies corresponding to the two decomposition steps.

step and it seem that the reaction follows a single decomposition pathway.

The total amount of hydrogen evolved is plotted in Fig. 12b versus time. The temperature was raised up to 200 °C, so only the first reaction step is likely to occur; the hydrogen yield is therefore only the 3.8%.

The Arrhenius plots for three 0.5 mol% Ti-doped samples at various carbon content, 0, 5 and 20%, are plotted in Fig. 13. By increasing the carbon content both the activation energy and pre-exponential factor are increased with respect to the no-carbon, Ti-doped samples.

Differently from the non-doped samples, the desorption temperatures are strongly affected by carbon content. The effect of the carbon content on the doped sample desorption temperature can be argued from Fig. 14, where the flow curves of Fig. 12a are plotted versus temperature: increasing the carbon percentage from 0 to 20% has the effect to move the desorption onset at higher temperatures, from 140 to 160 °C.

3.6. Hydrogenation and cyclability

The PCT apparatus has been used with $P=80$ bar maximum pressure, $F=40$ ncc/min hydrogen flow, temperatures in

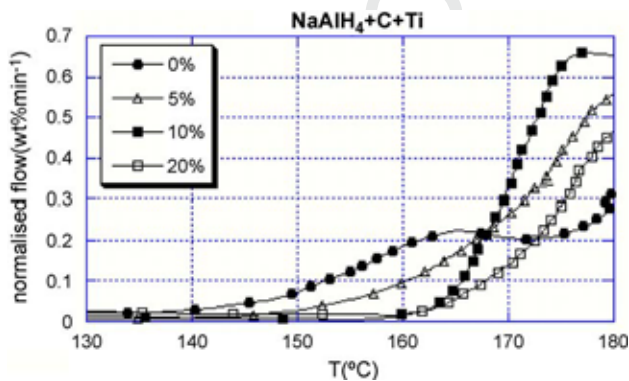


Fig. 14. Desorption temperatures for doped C added NaAlH₄.

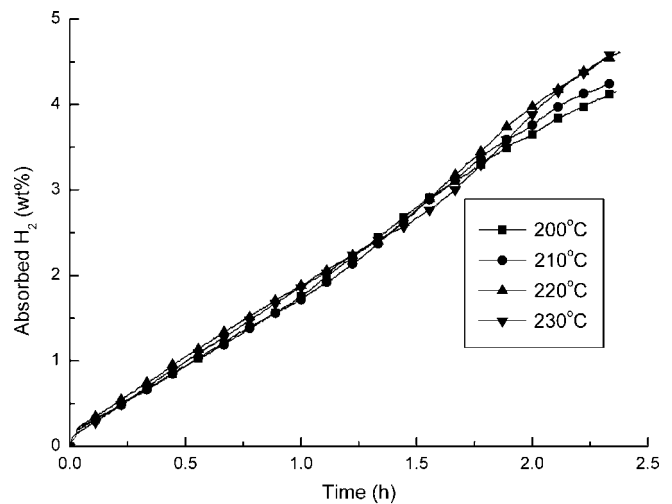


Fig. 15. Hydrogen absorbed by a 10% C sample during a PCT cycle, with a constant pressure ramp up to 80 bar at various temperatures.

the 200–230 °C range. Before any subsequent re-hydrogenation, the sample was completely de-hydrogenated by pumping it at 230 °C till a 0.1 mbar pressure was attained.

The absorption and desorption curves of the 10% C added sample are shown in Figs. 15 and 16, respectively, at various temperatures; the sample absorbed reversibly about 5 wt.% hydrogen. It is worth to note that the pure alanate do not exhibit any re-hydrogenation property at those conditions. For the 2.5 h charging time, the rate of hydrogenation as well as the total amount of H₂ absorbed does not seem to be affected by temperature. A little change in the absorption rate is observed at the end of process and it causes a little variation in the amount of absorbed hydrogen with temperature. The desorption curves show a more pronounced dependence on temperature: the des-

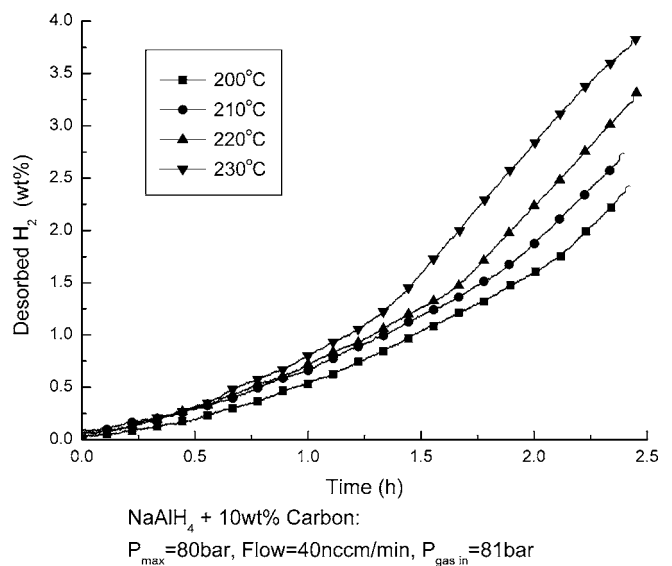


Fig. 16. Hydrogen desorbed by a 10% C sample during a PCT cycle, with a constant pressure ramp down from 80 bar at various temperatures.

261 orbbed hydrogen amount is larger at higher temperature, and
262 larger is also the desorption rate.

263 4. Discussion

264 Beneficial effects in both desorption hydrogen rate and des-
265 orption temperature due to carbon presence have been detected
266 by different authors [6,8]. How the carbon could enhance the
267 alanate performance is anyway still an open question. Mor-
268 phological analysis shows that the aggregate structure of the
269 de-hydrogenated samples has been modified by carbon. The
270 presence of carbon produces rough particles. By examining
271 every single particle it is possible to observe that it is an aggre-
272 gation of particles of smaller diameter (few micron); anyway
273 X-ray spectra after de-hydrogenation show that no modification
274 occurred in the crystalline structure of alanate. The role of car-
275 bon could be more “physical” than “chemical” in the sense that it
276 modifies the grain surface of the de-hydrogenated phases prob-
277 ably due to the inhibition of grain aggregation. The increase of
278 the surface/volume ratio upon the first de-hydrogenation could
279 enhance the second de-hydrogenation step. This is in accordance
280 with the obtained results, which show that only the desorption
281 rate is improved by carbon addition, being the desorption tem-
282 perature and the hydrogen yield only slightly affected.

283 The effect of carbon to increase the hydrogen desorption rate
284 is noticeable for carbon content as high as 10 wt.%. By dou-
285 bling this amount only a slight change in the hydrogen rate
286 was observed. The amounts of hydrogen desorbed from 10 to
287 20 wt.% carbon added samples was almost the same. It is easy
288 to recognize a “threshold” behavior appearing when the car-
289 bon content lies between 5 and 10%. By considering that large
290 amount of dopant is detrimental in term of gravimetric hydro-
291 gen density, the 10 wt.% sample can be considered the best
292 compromise between the de-hydrogenation rate and the hydro-
293 gen yield.

294 Also in Ti-doped materials the rate of the second de-
295 hydrogenation step is increased after carbon was added. As a
296 result the two desorption steps clearly visible in the Ti-doped
297 material, disappear in presence of carbon (Figs. 12 and 13)
298 and a single desorption process was observed in carbon added
299 titanium-doped NaAlH₄ samples. The temperature of the first
300 desorption step is slightly increased by increasing the amount
301 of carbon. This could be explained by considering that Ti-doped
302 samples are very sensitive to the amount of Ti used as cata-
lyst [5]. Carbon inhibits the effect of the titanium through an

303 increase of the activation energy of the process. It could be due
304 to some interaction of Ti with carbon that decreases the amount
305 of “active” titanium or reduces Ti mobility. As stated for non-
306 doped samples, the presence of carbon on doped samples inhibits
307 the grain aggregation of NaAlH₄.

308 With respect to what previously found [9] our results pointed
309 out that the effect of carbon, independently from its allotropic
310 state, has beneficial effect on both Ti-doped or undoped NaAlH₄
311 decomposition. The main differences between what has been
312 found by Wang et al. by adding graphite instead of high surface
313 carbon [9] and our results are in the lower decomposition tem-
314 perature; a very light effect on it should be ascribed to the ball
315 milling of the sample.

316 5. Conclusions

317 In this paper, it was showed the positive effect of carbon
318 on hydrogen absorption/desorption process. Carbon acts with
319 a threshold behavior and 10 wt.% carbon was found the best
320 carbon content. The 10% carbon sample, obtained by manual
321 mixing carbon and NaAlH₄, showed to reversibly desorbed up
322 to 4 wt.% hydrogen in the temperature range between 200 and
323 300 °C. The smaller grain size noted for carbon-doped materi-
324 als could enhance the rate of the second de-hydrogenation and
325 the following hydrogenation/de-hydrogenation steps. Syner-
326 gism was found between carbon and Ti in double-doped samples.
327 It follows that the two dopants act with different mechanisms.
328 The higher desorption temperature showed from Ti-doped sam-
329 ples mixed with carbon was related to a decrease of the amount
330 of available titanium.

331 References

- 332 [1] H. Imamura, K. Masanari, M. Kusuhara, H. Katsumoto, T. Sumi, Y. Sakata,
333 J. Alloys Compd. 386 (2005) 211–216.
334 [2] P. Chen, Z. Xiong, J. Luo, J.L. Lin, K.L. Tan, Nature 420, 302–304.
335 [3] B. Bogdanovic, M. Schwickardi, J. Alloys Compd. 253–254 (1997) 1.
336 [4] S.S. Srinivasan, H.W. Brinks, B.C. Hauback, D. Sun, C.M. Jensen, J. Alloys
337 Compd. 377 (2004) 283–289.
338 [5] G. Sandrock, K. Gross, G. Thomas, J. Alloys Compd. 339 (2002) 299–308.
339 [6] A. Zaluska, L. Zaluski, J.O. Strom-Olsen, J. Alloys Compd. 298 (2000)
340 125–134.
341 [7] J.M. Bellosta von Colbe, B. Bogdanovic, M. Felderhoff, A. Pommerin, F.
342 Schuth, J. Alloys Compd. 370 (2004) 104–109.
343 [8] D. Pukazhelvan, J. Alloys Compd. 403 (2005) 312–317.
344 [9] J. Wang, A.D. Ebner, T. Prozorov, R. Zidan, J.A. Ritter, J. Alloys Compd.
345 395 (2005) 252–262.