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## How carbon affects hydrogen desorption in NaAlH<sub>4</sub> and Ti-doped NaAlH<sub>4</sub>

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### Abstract

The hydrogen storage properties of doped and undoped NaAlH<sub>4</sub> 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 NaAlH<sub>4</sub>. 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.

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### 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 LiN<sub>3</sub>) [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 NaAlH<sub>4</sub> 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 NaAlH<sub>4</sub>. 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 TiCl<sub>3</sub> or Ti(OBu<sup>n</sup>)<sub>4</sub> 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 NaAlH<sub>4</sub> is 5.6 and 5.1 wt.% hydrogen was desorbed from NaAlH<sub>4</sub> 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 NaAlH<sub>4</sub>. 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]

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44 modified  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$  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  $\text{NaAlH}_4$  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  $\text{NaAlH}_4$  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  $\pi$ -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  $\text{NaAlH}_4$  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  $\text{NaAlH}_4$  was also studied.

## 69 2. Experimental

70 Sodium aluminum hydride ( $\text{NaAlH}_4$ , 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  $120^\circ\text{C}$  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  $\text{NaAlH}_4$  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 temper-  
97 ature. 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](http://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-

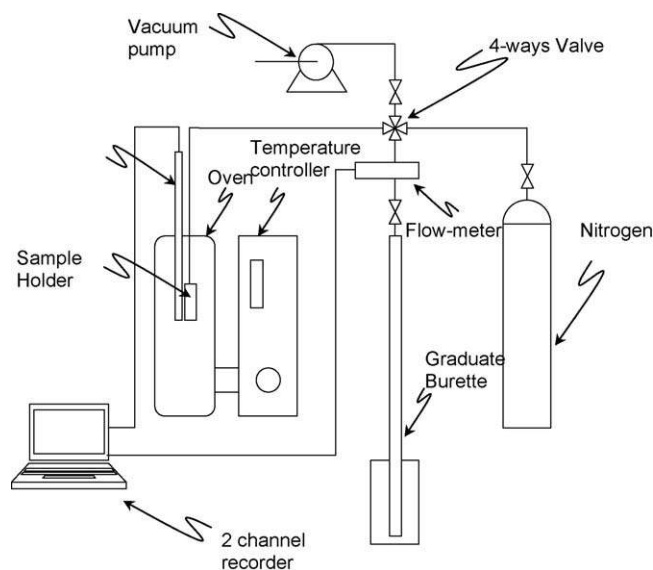


Fig. 1. Apparatus for desorption rate measurements.

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  $\text{NaAlH}_4$  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  $\text{NaAlH}_4$ -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  $\text{NaAlH}_4$  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

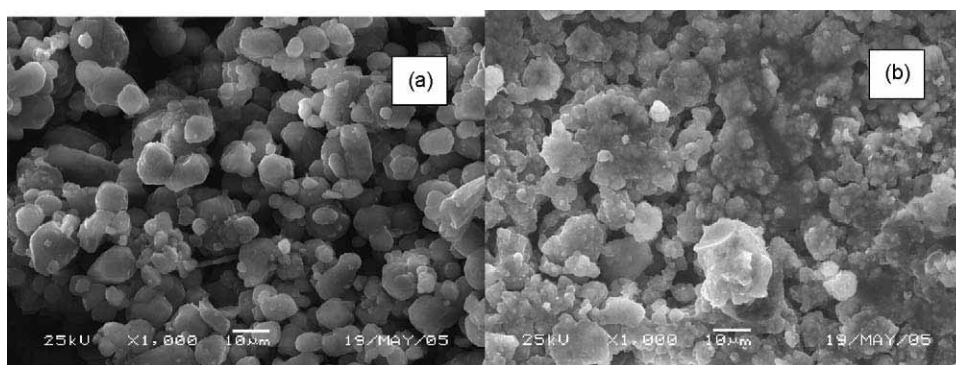


Fig. 2. SEM images of Ti-doped samples (a) before and (b) after de-hydrogenation.

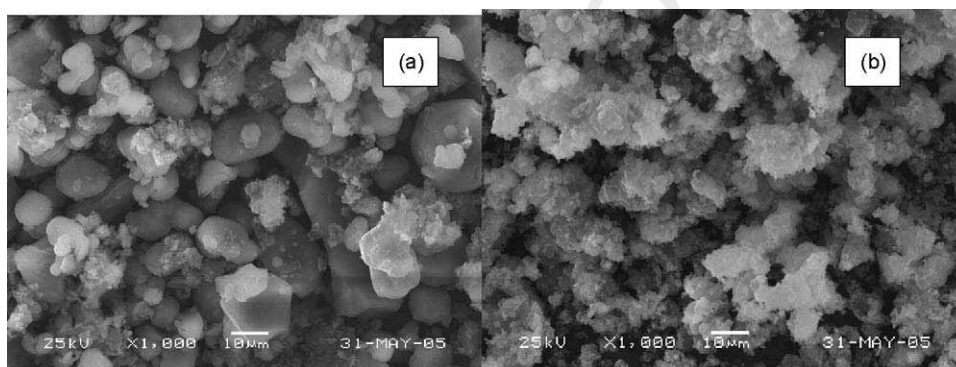


Fig. 3. SEM images of 10% C added samples (a) before and (b) after de-hydrogenation.

139 NaAlH<sub>4</sub> 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

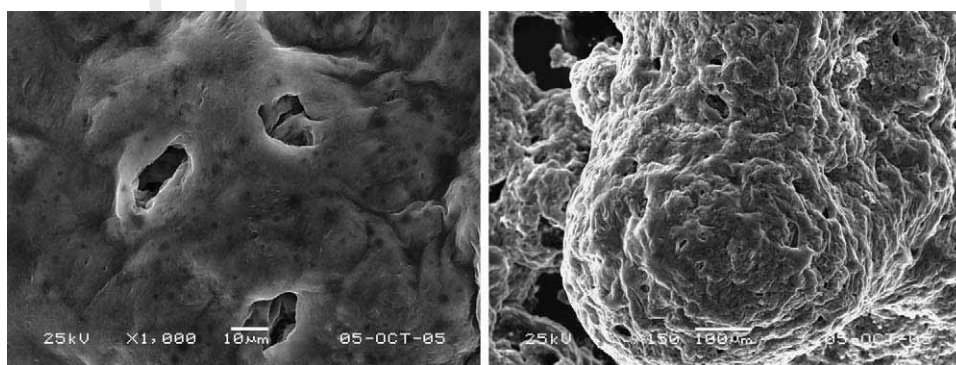


Fig. 4. SEM images of 10% C added ball-milled samples before de-hydrogenation at two magnifications.

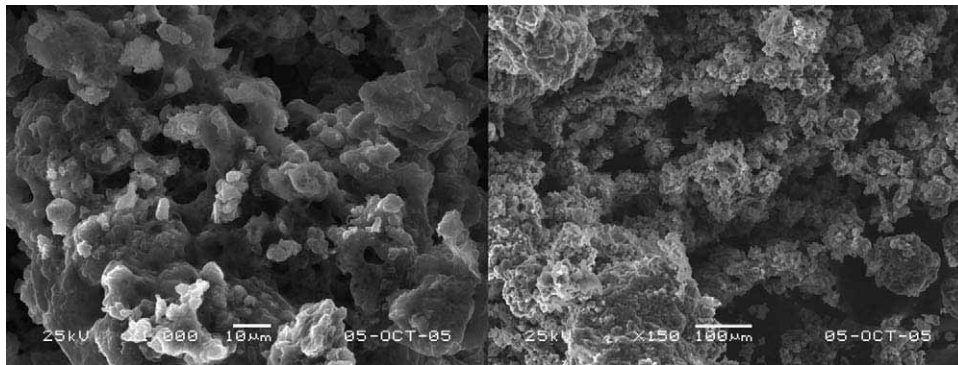


Fig. 5. SEM images of 10% C added ball-milled samples and after de-hydrogenation at two different magnification.

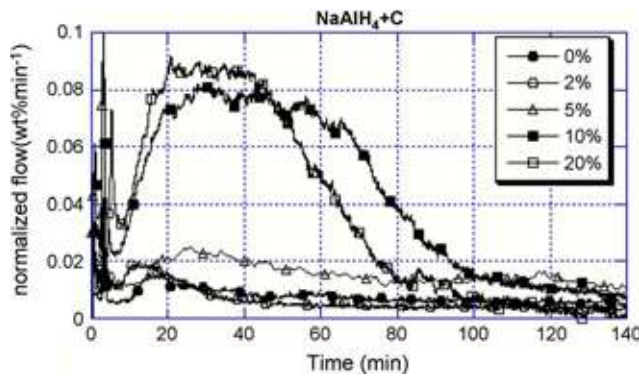


Fig. 6. Desorbed hydrogen flow of different C content NaAlH<sub>4</sub> samples at 220 °C; the flow is normalized to the alanate weight.

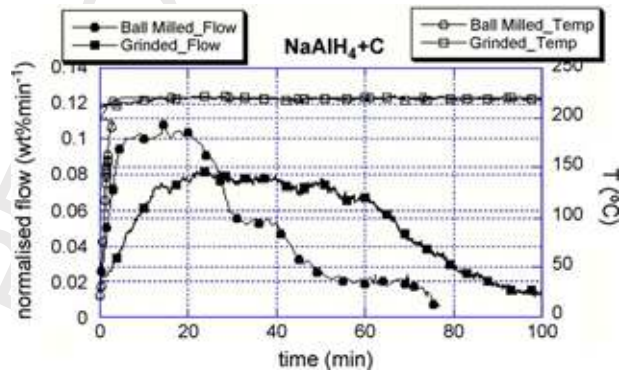


Fig. 8. Comparison between hydrogen flow released from a ball milled and a just grinded 10% C added samples.

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-

quently to increase the kinetics of the reaction, with respect to the undoped NaAlH<sub>4</sub> [5].

It is well known that the decomposition of NaAlH<sub>4</sub> is a two-step reaction described by the following formula:

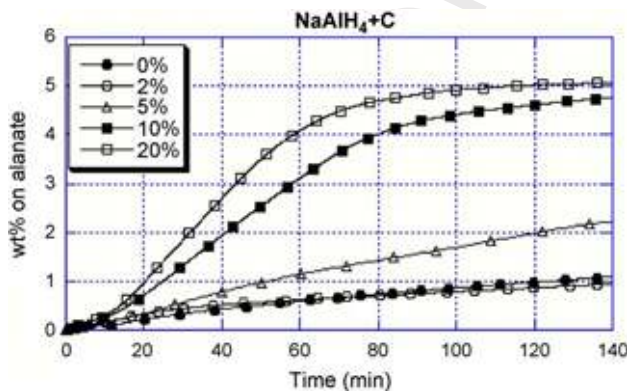
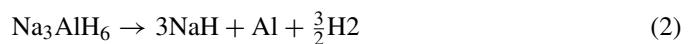


Fig. 7. Desorbed hydrogen of various C content NaAlH<sub>4</sub> samples at 220 °C; the hydrogen weight percentage is referred to the alanate weight.

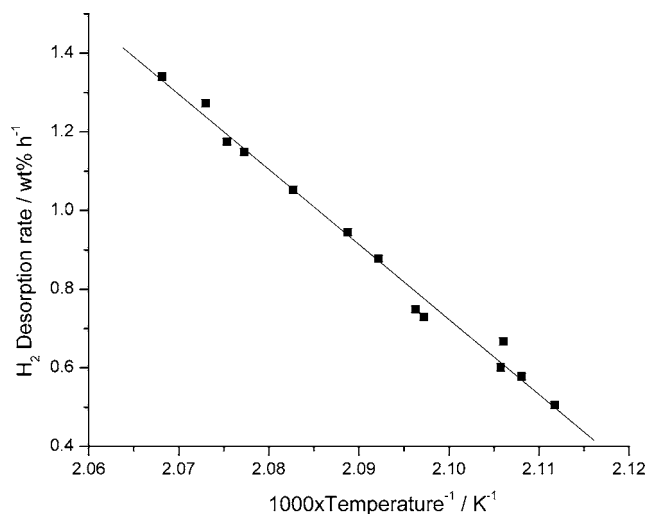


Fig. 9. Arrhenius plot of an undoped 20% C added sample.

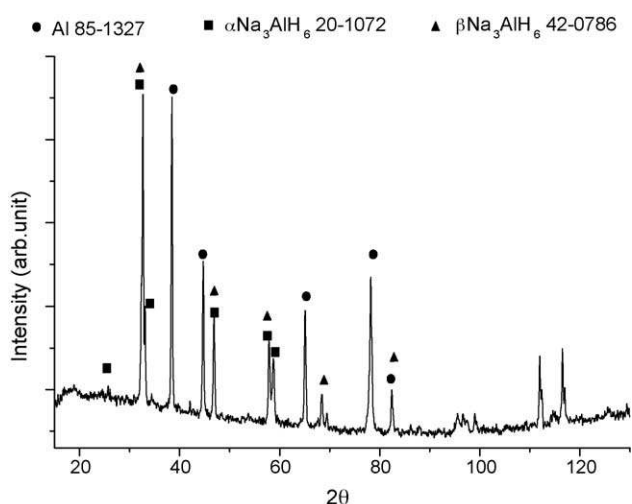


Fig. 10. XRD spectrum of a 10% C added sample after decomposition at 195 °C.

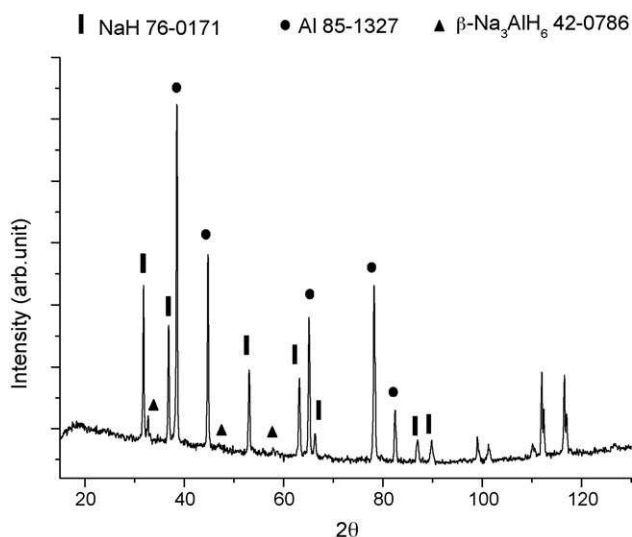


Fig. 11. XRD spectrum of a 10% C added sample after decomposition at 220 °C.

183 To detect only the first decomposition step of  $\text{NaAlH}_4$  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

188 The progressive turning from  $\text{NaAlH}_4$  into two different  
189  $\text{Na}_3\text{AlH}_6$  phases, the  $\alpha\text{-Na}_3\text{AlH}_6$  and  $\beta\text{-Na}_3\text{AlH}_6$ , 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 the  
192 10% carbon ball-milled sample after decomposition, respective-  
193 ly, at 195 and 220 °C are shown. In the low-temperature  
194 reaction (Fig. 10) the  $\text{NaAlH}_4$  completely decomposed into Al  
195 and  $\text{Na}_3\text{AlH}_6$  ( $\alpha$  and  $\beta$  phases) following Eq. (1); after a further  
196 increase in temperature (Fig. 11), together with a small amount  
197 of  $\text{Na}_3\text{AlH}_6$ , 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  $\text{NaAlH}_4$  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 X-ray diffraction spectra for a mixture of  $\text{NaAlH}_4$  containing  
207 5 wt.% carbon and doped with 0.5 mol% Ti shows exclusively  
208 crystalline  $\text{NaAlH}_4$ . The absence of any peak related to titanium  
209 metal does not allow to recognize whether Ti is in its metallic  
210 state or not. The absence of peaks attributed to carbon is not  
211 surprising since the carbon we used is amorphous.  
212

### 3.5. Hydrogen desorption in Ti-doped carbon added samples

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

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 decomposi-  
225 tion

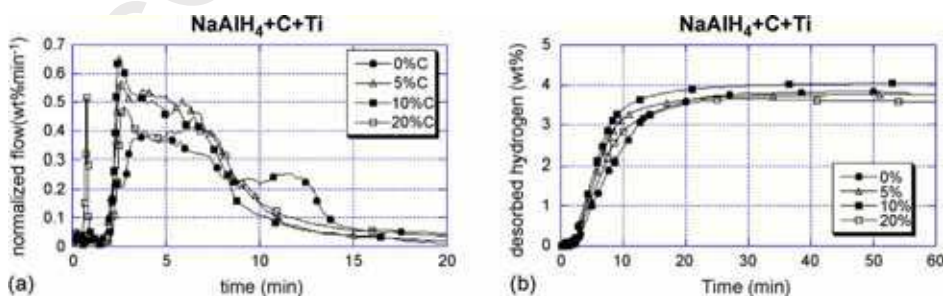


Fig. 12. Ti-doped, C added  $\text{NaAlH}_4$  samples in: (a) the desorbed hydrogen flow is shown for different C percentages; (b) the corresponding hydrogen content is plotted. Temperature of measurement: 200 °C.

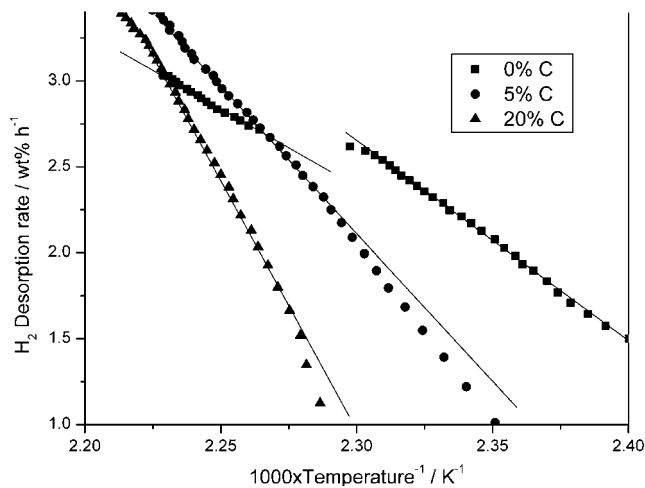


Fig. 13. Arrhenius plot of 0.5 mol% Ti-doped samples for different C added percentages; the 0% carbon curve shows the typical behavior with two different activation energies corresponding to the two decomposition steps.

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

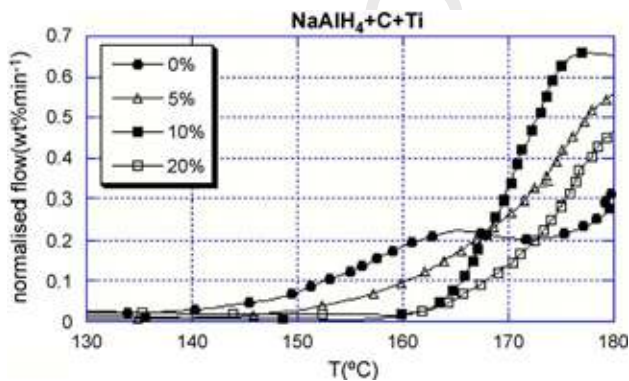
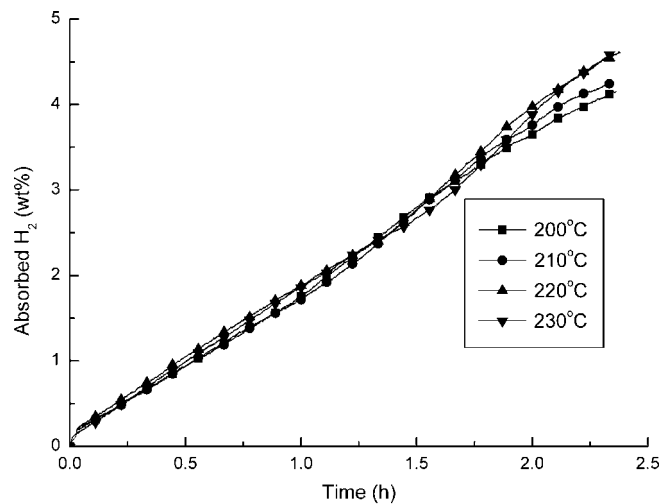


Fig. 14. Desorption temperatures for doped C added NaAlH<sub>4</sub>.

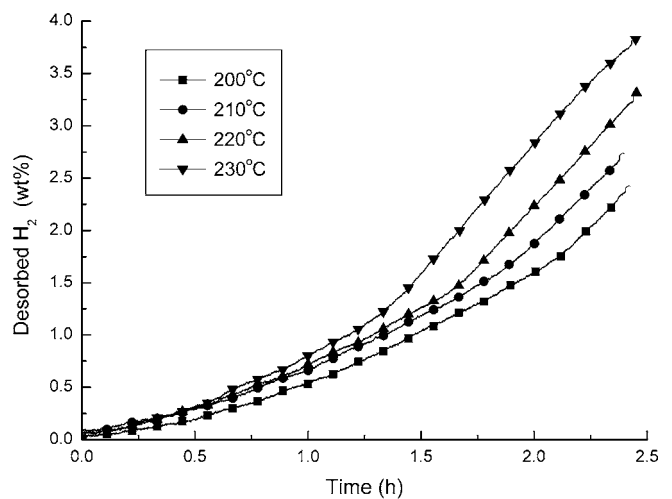


NaAlH<sub>4</sub> + 10wt% Carbon:  
 $P_{max}=80$ bar, Flow=40nccm/min,  $P_{gas\ in}=81$ bar

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 H<sub>2</sub> 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-



NaAlH<sub>4</sub> + 10wt% Carbon:  
 $P_{max}=80$ bar, Flow=40nccm/min,  $P_{gas\ in}=81$ bar

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 NaAlH<sub>4</sub> 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 NaAlH<sub>4</sub>.

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 NaAlH<sub>4</sub>  
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 NaAlH<sub>4</sub>, 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.

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