

## The Effect of CNT Doping on the Hydrogenation Behavior of $Y_5Si_3$ Phases

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### Abstract

The reactivity of the CNT-doped  $Y_5Si_3$  compared to  $Y_5Si_3$  phase system has been investigated. Both alloys have been prepared by arc melting and their reactivity with hydrogen has been studied. Single-phase CNT-doped  $Y_5Si_3$  can only be made by melting preformed  $Y_5Si_3$  with the CNT. An activation process has been developed to induce reaction of the doped alloy with hydrogen. It involves cycling in  $H_2$  gas pressures above 1.2 atm at temperature higher than  $435^\circ C$  depending on the CNT content. Conditioned samples, will repeatedly (above 50 cycles) cycles  $2.5 H (fu)^{-1}$  between room temperature and  $500^\circ C$  with 0.9 and  $1.2 H (fu)^{-1}$  being desorbed and absorbed with fast kinetic within a very small temperature range. This behavior is believed to arise from the polymorphic change between an  $\alpha$ -form of the  $D8_8$  structure and a supercell  $\beta$ -form. An attempt to quantify the enhanced stability, compared to  $Y_5Si_3$ , is made by measuring reaction enthalpies using Van't Hoff isopleths.

**Keywords:** carbon nanotube CNT,  $D8_8$ -phases, Hydrogen Storage materials SEM, Hydrogen Sorption, Polymorphic Change, X-ray diffraction XRD,.

3Si5Y

3Si5Y

CNT

Si5Y3

CNT

CNT

Si5Y3

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## Introduction

Hydrogen energy content on a mass for mass basis is better than petrol, yet it has difficulties compared with conventional fuel because it is highly flammable gas. Storing hydrogen is expensive, bulky and safety compromised. Because of its small atomic size hydrogen can insert itself in the interstitial sites between atoms of larger size leading to a high capacity of hydrogen per formula unit. For example, the number of H atoms per  $\text{cm}^3 \times 10^{-22}$  for liquid hydrogen at 20K is 4.2, for solid hydrogen at 4.2K is 5.3, however for  $\text{UH}_3$  it is 8.2.

For a system to be used for hydrogen storage, a reversibility at lower temperature is an essential requirement and not all alloys which take up hydrogen can reverse it easily. Palladium was the first Hydrogen storage materials HSM system followed by the major discovery of other HSM systems such as FeTi and LaNi5 and their derivatives<sup>[1-4]</sup>

The  $\text{D8}_8$  structure, first reported for  $\text{Mn}_5\text{Si}_3$ , applies to an atomic arrangement with hexagonal unit cell (space group  $\text{P6}_3/\text{mcm}$ , axial ratio about

0.7) with atomic sites as refined by Aronson<sup>[5]</sup> are; M in 4d, and 6X in 6g(II) with  $X(\text{II}) = 0.5992 \pm 0.0015$ , where

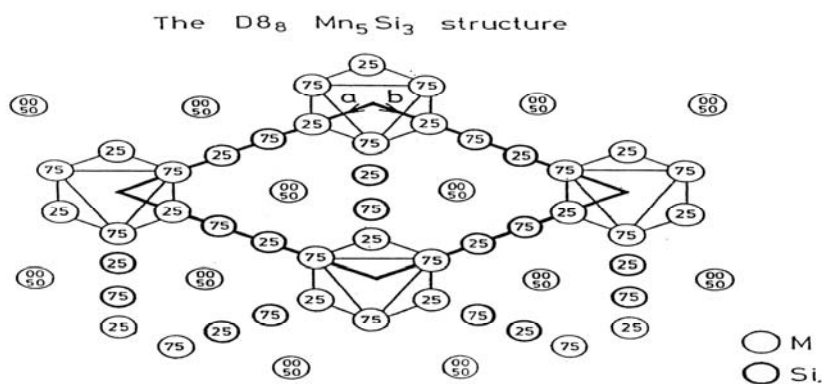
M is metal and X is Si or Ge. The  $\text{D8}_8$  Y-Si phases, specifically  $\text{Y}_5\text{Si}_3$  phase, have atomic positions as:

$4\text{Y}_I$  in 4d:  $1/3, 2/3, 0 : 2/3, 1/3, 0 : 1/3, 2/3, 1/2 : 2/3, 1/3, 1/2 :$

$6\text{Y}_{II}$  in 6g with  $x = 0.25$ :  $x, 0, 1/4 : 0, x, 1/4 : x^-, x^-, 1/4 : x^-, 0, 3/4 : 0, x^-, 3/4 : x, x, 3/4$

$6\text{Si}$  in 6g: as above with  $x = 0.61$ .

The  $\text{D8}_8$  structure can be visualized as two linked structural features. There are columns of face sharing metal octahedral set in metal-silicon matrix (which is formed from groups of 6 metal atoms in the main layers). The columns are aligned parallel to the c axis of the hexagonal unit cell. There are no readily identified tetrahedral sites formed from 4 metals<sup>[6]</sup>, however, silicon atoms from the M-Si matrix form a network around the metal octahedral and give rise to tetrahedral site formed by three metal atoms from the octahedral unit plus one silicon atom. Fig. 1 shows a projection of the  $\text{D8}_8$  structure.



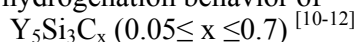
**Fig. 1. Projection of the  $\text{D8}_8$  structure**

An important characteristic of the  $D8_8$  silicides is that small atoms such as C, B, O, N and H can be inserted into it without any apparent major structural effect. A study on the  $MoSi_3$  has shown [7] a possible stabilizing effect on the hexagonal structure of stabilizing amount of C, B and N. The non-metal mainly occupies the octahedral sites formed by six metal atoms in the hexagonal structure.

Of all these non-metals, carbon seems to have attracted more attention due to the certainty about carbon content and phase purity [8-13]

C doping had no major effect on the unit cell volume up to C content  $x = 0.3$  in  $Y_5Si_3C_x$ . At  $x = 0.3-0.5$ , a-axis increased by a factor of square root of 3 and unchanged c-axis. This was called type one superstructure. At  $x = 0.65-0.9$ , lack of order in the planar stacking in the c-axis producing amorphous appearance on x-ray. At  $x = 0.9-1.0$ , new superstructure called type 2 occurred where:  $a_{ss} = \text{square root of } 3 \text{ of } a$  and  $c_{ss} = 3c$ . Some evidence for yttrium carbide,  $Y_{15}C_{19}$ , precipitating in a way ordered by the structure, was also present. At  $x = 1.8$ , a completely new structure appeared which was orthorhombic, and at  $x = 2.0$ , the structure changed to a so far unresolved variant [10, 11].

The resemblance between the carbides and the hydrides phases of these alloys has prompted an earlier study of the hydrogenation behavior of



The main features of hydrogen absorption by  $Y_5Si_3C_x$  are as follow:

- (i) rapid absorption during the  $\alpha$ -phase,
- (ii) slow drift during the  $\beta$ -phase,
- (iii) fast transfer between  $\beta$  to  $\beta'$ -phase,
- (iv) slow drift during the  $\gamma$ -phase.

However, the hydride as  $\beta'$ -phase or  $\beta$ -phase suffer a rapid reversal to  $\beta$ -phase or  $\alpha$ -phase and from  $\beta$  back to  $\beta'$ -phase or  $\alpha$  back to  $\beta$ -phase by changes in temperature and pressure. Such a process occurs at relatively high temperatures of  $438^\circ\text{C}$  for  $\alpha$ - $\beta$ - $\alpha$  and  $446^\circ\text{C}$  for  $\beta$ - $\beta'$ - $\beta$

polymorphic phase transformation. A total of 2.5 H/fu was able to be reversed of which 0.9-1.2 H/fu had a fast kinetics [12].

Carbon nano-tube CNT has recently gained a ground as hydrogen storage materials HSM [14, 15], in a process where hydrogen can be encapsulated inside these tubes and be reversed at relatively low temperature. The arc melting process of making the carbide alloy has a striking similarity to the way the CNT can be made by arc melting [16]. It was felt that earlier work may have well prepared CNT-doped unknowingly while attempting to make the carbide alloy, hence the improved hydrogenation behavior. This work is an attempt to verify this hypothesis by making doped  $Y_5Si_3$  with CNT in order to see its effect on the H-reactivity while establishing this effect thermodynamically.

### Experimental details

The  $Y_5Si_3$  were made by arc melting small pieces of yttrium (supplied by Rare Earth Product Ltd in 99.99% in sublimed ingot form) with silicon (supplied by Koch-light Ltd in 99.99% purity) under argon stream a small home-made arc melting furnace the detail of which are shown in Fig. 2. If the weight loss after melting was more than 0.5% then the sample was not used. Two methods were used for the preparation of the CNT doped alloy:

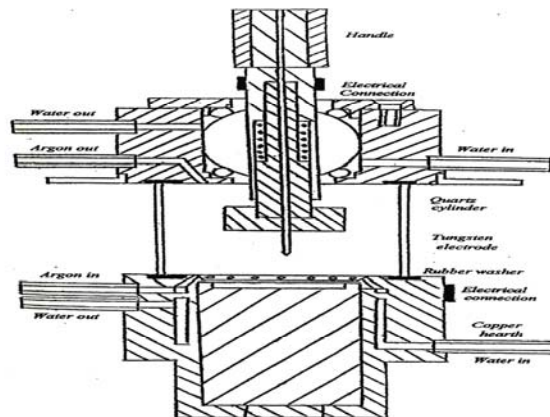
1. From elemental constituents (yttrium + silicon) with CNT (single-walled carbon nanotube SWCNT was used as received from Sigma Aldrich, Raman Spectroscopy confirmed a high percentage of SWCNT).

2. Preformed  $Y_5Si_3$  with CNT.

Powder was avoided in all preparations in order to restrict possible oxidation. The homogeneity and the stoichiometry of the alloys were measured by using metallographic (scanning electron microscopy SEM, energy dispersive X-ray EDX) and X-ray diffraction XRD analysis. Silicon with lattice parameter  $a = 0.543088 \text{ nm}$  was used for calibration to measure the alloys' lattice parameters.

Hydrogenation was monitored thermogravimetrically using two systems based on Sartorius Model 4406 microbalance <sup>[17]</sup>. Hydrogen used was

further purified using an oxygen column in the hydrogen entry train.



**Fig. 2. Homemade arc-melting Furnac**

## Results and Discussion

### Sample preparation

Past experience <sup>[12]</sup> have shown that samples made from elemental constituent have given a multiphase samples while sample made by arc melting  $Y_5Si_3$  with the dopant (in this case the SWCNT) gave a single phase as an outcome. This was tested in this work and found to be no exception. Table 1 shows samples made from the elemental constituents while Table 2 shows samples made from arc melting  $Y_5Si_3$  with the SWCNT.

Table 1 showed that  $Y_5Si_4$  phase exist in all preparations that are made from the elemental constituents. This has always been the case in all previous work <sup>[17]</sup>, it was attributed to the stabilizing effect other phases have on the  $Y_5Si_4$  phase. In some cases this was an advantageous as it creates a structural disorder in the crystal structure leading to unstable hydride that can easily desorb hydrogen, thus creating the required reversibility. This was particularly seen with nitrogen doping as nitrogen seem to have such effect on nearly all Y-Si phases along with the formation of yttrium nitride that was disintegrating during hydrogenation giving out ammonia odor.

Fig. 3 shows an example of the multi-phases system.

Table 2 shows a single phase alloy formed in all preparation. Fig. 4 shows such phase, where the plate-like crystal structure are reminiscent of those produce in earlier publications <sup>[13]</sup>.

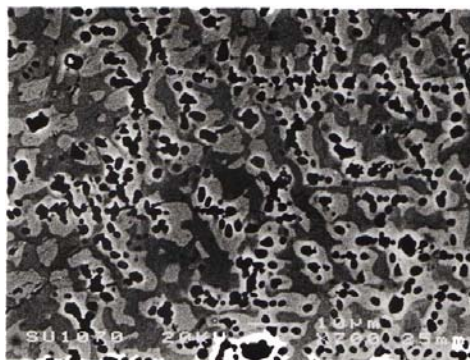
In both preparations, no major structural effect has been seen up to carbon content 0.3, where evidence of supercell type one started to appear. The preparation did not exceed carbon content 0.7, the reason was to avoid any complications that may arise from the lack of order that usually associated with higher amount of dopent. The appearance of the carbide phases is an indication of the disintegration of some of the CNT into carbon atoms giving rise to the formation of carbide phases, and this may be the reason for the improved reversibility of the alloys as the carbon nano-tubes were breaking as the result of arc melting giving way to the absorption desorption process .

The carbon doping of these alloys showed similar properties with regards to the unit-cell variations and phase purity in both methods of preparations as the elemental constituents did not give single phase. The unit-cell size and type also showed similar

trends indicating that our last attempt for preparing carbide phases of D8<sub>8</sub> alloys had unintentionally produced CNT doping [15].

**Table 1. Samples made from the elemental constituents (Y+Si+CNT)**

<b>X in Y<sub>5</sub>Si<sub>3</sub>CNT<sub>x</sub></b>	<b>a (nm)</b>	<b>c (nm)</b>	<b>Other phases</b>
<b>0.1</b>	0.8440	0.6361	Y <sub>5</sub> Si <sub>4</sub> , unknown phase (possibly Y <sub>3</sub> Si <sub>2</sub> )
<b>0.3</b>	1.4561	0.6391	Y <sub>5</sub> Si <sub>4</sub> , unknown phase (possibly Y <sub>3</sub> Si <sub>2</sub> )
<b>0.7</b>	1.4611	0,6417	Y <sub>5</sub> Si <sub>4</sub> , Y <sub>15</sub> C <sub>19</sub> , Y <sub>3</sub> Si <sub>2</sub>



**Fig. 3. Multi-phase system for alloy made from the elemental constituent**

**Table 2. Samples made from preformed alloy + CNT**

x in Y <sub>5</sub> Si <sub>3</sub> CNT <sub>x</sub>	a (nm)	c (nm)
0.0	0.8417	0.6351
0.1	0.8472	0.6388
0.2	0.8477	0.6412
0.3	1.4591	0.6472
0.5	1.4632	0.6480
0.7	1.4583	0.6497



Fig. 4. Single phase alloy made from melting pre-form alloy with CNT

### ***Hydrogen reactivity***

The above observation regarding alloy preparation has given an incentive to explore the possibility of similarity between carbon and CNT doping with regards to the hydrogenation behavior. As was observed in all carbon doping, alloys made from preformed Y<sub>5</sub>Si<sub>3</sub> with CNT needed a conditioning process which involved heating the alloys to 600°C in 2 atm hydrogen pressure. Multiphase alloys made from the elemental constituents needed less harsh conditioning process and started absorption at lower temperature. Table 3 show data produced from both preparations.

Concentrating on data from preformed alloys; the starting temperature increased as CNT increased. Up to  $x=0.3$ , increased CNT caused decrease in H needed for the  $\alpha$  polymorphic transformation. At  $x=0.3$ , hydrogen is absorbed into the  $\beta$ -phase which was able to desorb 1.2H/fu. Such abs./desorption occurred over a small range of temperature (442-469 °C). The method of preparation seems to have had little effect on the sorption temperature but did have effect on the amount exchange; this would be expected as the amount of the main phase would be reduced due to the formation of other

phases if the alloy is made from the elemental constituents.

At CNT content up to 0.3, it appears that C-atoms from some degraded CNT seem to occupy the octahedral sites available for H leading to reduction in the amount of exchanged at the  $\alpha \rightleftharpoons \beta$  phases. At CNT 0.3 or above, the superstructure already occurred, hence the process is related to phase change between  $\beta \rightleftharpoons \beta'$  polymorphic transformation. The unusually high reversible hydrogen (1.2H/fu) is most likely related to the CNT. This behavior seems to mimic the hydrogenation behavior of the carbide phases of these alloys as C-doping had exactly the same behavior. This indeed confirms the early said hypothesis as the process of making the carbide had unintentionally made CNT-doped alloys. At the time the carbide phases was made, the hydrogenation behavior of the CNT was unheard of, thus this issue was not noticed.

To establish the effect of the CNT on the Y-Si phases thermodynamically, an isopleths were made from which the enthalpy of the reaction could be worked out for the alloy and its doped alloys. The results are shown in Table 4 and two of the isopleths are shown in Fig. 5.

From the results the following can be concluded; it's assume that the fast H-uptake is a function of:  $\alpha + H_2 \rightarrow \beta$  where  $\Delta H = -43.8$  kJ/mol  $H_2$  and  $\beta + H_2 \rightarrow \beta'$  where  $\Delta H = -50.8$  kJ/mol  $H_2$ .

The difference of -7kJ/mol $H_2$  represents the increased reactivity of  $\beta$ -polymorph towards hydrogen compared to  $\alpha$ -structure. Similarly,  $\beta'$ -polymorph is

11kJ/mol $H_2$  more reactive. The curvature appeared in most of the isopleths may be due to two parallel mechanisms working at the same time, one related to  $Y_5Si_3$  while the other is related to the CNT. Inclusion of CNT leads to significant structural disorders which might be the reason why, like the carbides, these doped alloys show resistance to hydrogen amorphatization.

### Conclusion

The following conclusion can be drawn:

1. Preparation of single phase  $Y_5Si_3CNT_x$  is dependent on the starting materials.
2. Reversible sorption process require conditioning.
3. 2.5 H/fu could be cycled between RT-500°C of which 0.9-1.2H/fu had fast kinetic.
4. The process involve  $\alpha \rightleftharpoons \beta \rightleftharpoons \alpha$  polymorphic change.
5. The enhanced stability of the doped alloys has been quantified using Van't Hoff isopleths.
6. Striking similarity to the carbides which may be due to degradation of the CNT and accidentally forming CNT while preparing the carbides.

**Table 3. Hydrogen reactivity of  $Y_5Si_3CNT_x$  alloys. Bold for samples made from elemental constituents, un-bold for samples made from preformed alloy & SWCNT**

x in	Reaction start temperature °C	H absorbed up to 500°C H/fu	H content at room temp. H/fu	Amount/T desorbed rapidly H(fu)-1/°C	Amount/T absorbed rapidly H(fu)-1/°C
$Y_5Si_3CNT_x$					

<b>0.0</b>	<b>381</b>	<b>1.41</b>	<b>2.43</b>	<b>0.91/469</b>	<b>0.91/467</b>
<b>0.1</b>	<b>489</b>	<b>0.71</b>	<b>1.39</b>	<b>0.55/450</b>	<b>0.54/449</b>
<b>0.3</b>	<b>458</b>	<b>0.79</b>	<b>1.59</b>	<b>0.47/442</b>	<b>0.47/323</b>
<b>0.5</b>	<b>540</b>	<b>0.40</b>	<b>0.41</b>	<b>N.O.a</b>	<b>N.O.a</b>
<b>0.1</b>	493	1.00	1.58	0.65/442	0.64/442
<b>0.3b</b>	505	1.31	2.84	1.20/446	1.10/446
<b>0.5c</b>	-	-	2.5	0.90/446	0.90/446

aN.O. not observe

bThis sample has a final H-content of 5.9 after more than 50 abs./des. cycles

cThis sample has a final H-content of 7.33 after more than 50 abs./des. cycles

**Table 4. Shape and values of enthalpy produced from Van't Hoff isopleth**

<b>x in Y<sub>5</sub>Si<sub>3</sub>CNT<sub>x</sub></b>	<b>Shape of Van't Hoff plot</b>	<b><math>\Delta H_{abs}</math> kJ/mol H<sub>2</sub></b>	<b><math>\Delta H_{des}</math> kJ/mol H<sub>2</sub></b>
<b>0.0</b>	Linear for both abs and des	-43.8	50.5
<b>0.1</b>	Curved, two lines intersecting (abs)	-15.3	27.0
<b>0.2</b>	Curved, two lines intersecting (des)	-11	33.5
<b>0.3</b>	Very Curved, two lines intersecting (abs)	-31.6	44.7
<b>0.5</b>	Linear for both abs and des	-50.8	39.5



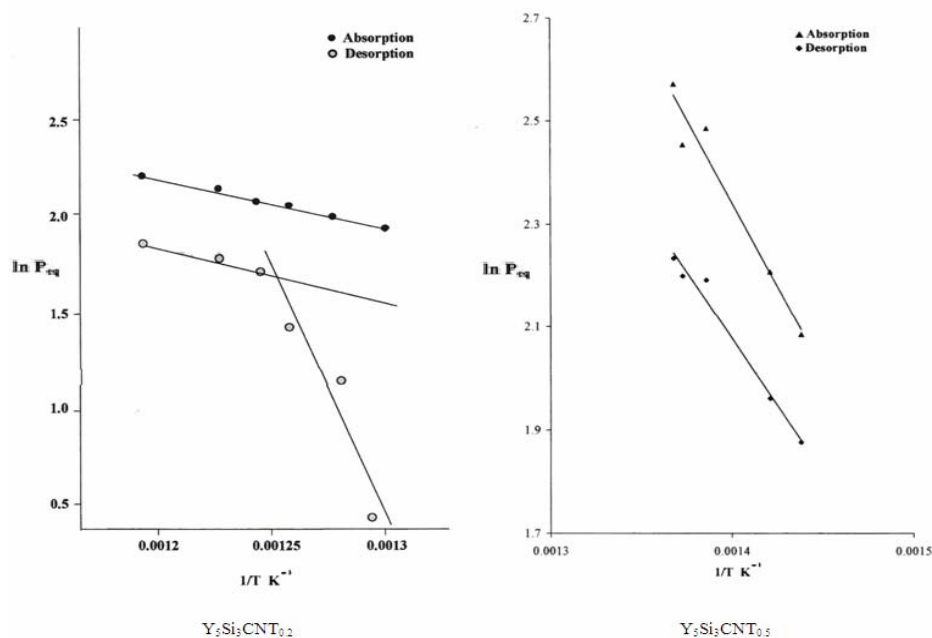


Fig. 5. Isoleths for the reaction of hydrogen with  $Y_5Si_3CNT_{0.2}$  and  $Y_5Si_3CNT_{0.5}$

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