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# Synthesis of Sr<sub>2</sub>AlH<sub>7</sub> by ball milling followed by hydrogenation

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#### Abstract

The hydride  $Sr_2AlH_7$  was synthesized by ball milling of the alloy consisting of Sr and Al (2:1) under hydrogen at 150 rpm for 10 h followed by hydrogenation or sintering at 533 K for 2 days. The yield of  $Sr_2AlH_7$  in the hydrogenated product was 66 wt.%, which is larger than that in the sintered product. However, the mass fraction of Al in the milled samples decreased largely when the  $Sr_2Al$  alloy was milled at 300 rpm for 50 h or longer. In such a case, the  $Sr_2AlH_7$  hydride cannot be obtained during the subsequent hydrogenation. © 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrogen absorbing materials; Ball milling; Crystal structure; Gas-solid reaction

# 1. Introduction

As reported previously [1-3], SrAl<sub>2</sub> can be hydrogenated to SrAl<sub>2</sub>H<sub>2</sub> at about 463 K. Increasing the hydrogenation temperature to 513 K, SrAl<sub>2</sub>H<sub>2</sub> further absorbs hydrogen to form Sr<sub>2</sub>AlH<sub>7</sub> and Al. These reactions are shown below.

$$SrAl_2 + H_2 \rightarrow SrAl_2H_2$$
 (1)

$$4SrAl_2H_2 + 3H_2 \rightarrow 2Sr_2AlH_7 + 6Al \tag{2}$$

The hydride  $Sr_2AlH_7$  decomposes to  $SrH_2$ , Al and  $H_2$  when the temperature is raised to about 563 K.  $Sr_2AlH_7$  has a large H/M (where H and M indicate hydrogen and metals, respectively) ratio. Thus, it can be considered as a possible candidate for hydrogen storage application.

In the binary Sr–Al system, several intermetallic compounds like SrAl<sub>4</sub>, SrAl<sub>2</sub>, Sr<sub>5</sub>Al<sub>9</sub> and Sr<sub>8</sub>Al<sub>7</sub> were reported, but Sr<sub>2</sub>Al does not exist [4–8]. Therefore, SrAl<sub>2</sub> has been used as the starting material to synthesize Sr<sub>2</sub>AlH<sub>7</sub> [2]. However, the hydrogenation reaction rate is very slow because longrange diffusion of Al is necessary during the formation of Sr<sub>2</sub>AlH<sub>7</sub>. Moreover, the Sr<sub>2</sub>AlH<sub>7</sub> hydride is always accompanied by Al in the product as shown in Eq. (2), which limits the yield of  $Sr_2AlH_7$ .

Ball milling has been proved to be a powerful technique to synthesize hydrides, such as  $Mg_2FeH_6$  and  $Mg_2CoH_5$ , which are hard to be obtained by conventional methods [9,10]. We have used the ball milling technique to synthesize  $Sr_2AlH_7$ from the alloy of Sr and Al in a ratio of 2:1. Generally speaking, two methods of ball milling were used for the direct synthesis of the hydrides [11]. One is reactive milling, in which ball milling is carried out under a hydrogen atmosphere. The other method is milling of elemental hydrides to produce complex hydrides. In this work, we synthesized the  $Sr_2AlH_7$ hydride by ball milling of a  $Sr_2Al$  alloy under hydrogen but it was followed by further hydrogenation of different types of samples.

## 2. Experimental details

The Sr<sub>2</sub>Al alloy was prepared by induction melting of Sr and Al metals. On the basis of the stoichiometric amounts of the starting materials, an extra 3 wt.% of Sr was added to compensate the loss of Sr during induction melting. The alloy prepared was used without further treatment. In order to prevent exposure to air, the subsequent procedures were carried out in a glove box under a dry argon atmosphere. The alloy

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ingot was ground to powders with particle size smaller than  $300 \,\mu\text{m}$  for subsequent ball milling. The milling was made using a Fritsch Pulverisette 5 planetary mill under hydrogen (0.6 MPa). Stainless steel bowls and balls (the diameter was 10 mm) were used. The weight of the powder was 2 g and the ball to powder weight ratio was 20:1.

Q.A. Zhang, E. Akiba / Journal of Alloys and Compounds 394 (2005) 308-311

After ball milling, the milled samples were loaded into stainless steel containers and placed in stainless steel autoclaves. Hydrogenation reactions were carried out under a hydrogen pressure of 7 MPa at 533 K for 2 days. A part of the milled samples was pressed under 20 MPa into a pellet of 5 mm radius. The pellet was sintered under hydrogen (7 MPa) at 533 K for 2 days. To evaluate the phase structures of the samples, XRD measurements were performed using a Rigaku RINT2500V diffractometer with Cu K $\alpha$  radiation at 50 kV and 200 mA. The XRD profiles were analyzed with the Rietveld refinement program RIETAN-2000 [12].

### 3. Results and discussion

12000 10000

4000

20

30

Fig. 1 shows the result of the Rietveld analysis for the  $Sr_2Al$  alloy. Three phases  $Sr_8Al_7$ , hexagonal Sr and fcc Sr were found in the alloy. For the Rietveld refinement, the structure models for the phases were taken from the reported structures [8,13,14]. As shown in the figure, the diffraction pattern calculated from the structure model is in good agreement with that measured. The amounts of the  $Sr_8Al_7$ , hexagonal Sr and fcc Sr phases were calculated to be 65, 31 and 4 wt.%, respectively. In fact, the  $Sr_2Al$  alloy should consist of  $Sr_8Al_7$  and fcc Sr under the equilibrium condition according to the phase diagram [4]. However, the hexagonal Sr was also found in this case.

Fig. 2 shows the XRD patterns for the samples milled under hydrogen at a rotation speed of 300 rpm for 50, 100 and 150 h, respectively. It can be seen that the samples consist of  $SrH_2$  and Al with a small amount of impurity Fe. This means that the Sr absorbed hydrogen to form  $SrH_2$ ; while the  $Sr_8Al_7$  phase reacted with hydrogen to form  $SrH_2$  and Al

Fig. 1. Rietveld refinement of the observed XRD pattern for  $Sr_2Al$  alloy. Reflection markers are for  $Sr_8Al_7$ , hexagonal Sr and fcc Sr phases (from above), respectively.

50

 $2\theta/3$ 

60

70

80

40

Fig. 3. XRD patterns for the hydrogenated samples with a prior ball milling under hydrogen at 300 rpm for (a) 50 h; (b) 100 h; (c) 150 h.





Fig. 2. XRD patterns for the samples milled under hydrogen at a rotation speed of 300 rpm for (a) 50 h; (b) 100 h; (c) 150 h.

during the milling. However, Sr<sub>2</sub>AlH<sub>7</sub> cannot be synthesized

by prolonging the milling time. Even though the milled prod-

ucts were further hydrogenated, there was no evidence of the

form in the above experimental conditions, the XRD pat-

terns of the samples milled at 300 rpm for 50, 100 and 150 h

were refined by the Rietveld method. The phase abundance

calculated is listed in Table 1. The amount of Al decreased

with prolonged milling time. The original mass fraction of

Al in the as-cast alloy was 13 wt.%. However, the mass frac-

tion of Al decreased to 6 wt.% after ball milling for 50 h.

A similar phenomenon was also reported by Huot et al. [9].

They found that the mass fraction of Co in the milled mixture

In order to understand the reason why Sr<sub>2</sub>AlH<sub>7</sub> did not

formation of  $Sr_2AlH_7$  (as shown in Fig. 3).

Table 1 Phase abundance (wt.%) of the products milled under hydrogen at a rotation speed of 300 rpm for 50, 100 and 150 h

Phase	50 h	100 h	150 h
Al	6	5	2
SrH <sub>2</sub>	93	94	96
Fe	1	1	2



Fig. 4. Calculated and observed X-ray diffraction patterns for the sample milled under hydrogen at a rotation speed of 150 rpm for 10 h. Reflection markers are for Al,  $SrH_2$  and Fe (from above), respectively.

of 2Mg + Co was 15-20 wt.% but it was originally 55 wt.%. However, they also found that the mass fraction of Fe in the milled mixture of 2Mg + Fe was close to the starting ratio. Moreover, we found that the lattice parameter of the impurity Fe in the milled products was 3.717(2) Å, which is larger than the reported value 3.6599 Å [15]. This indicates that the impurity Fe is probably a (Fe, Al) solid solution. We noted that the mass fraction of Al in the Sr<sub>2</sub>AlH<sub>7</sub> hydride is around 13 wt.%. Thus the low mass fraction of Al in the above milled products might be the reason for the absence of Sr<sub>2</sub>AlH<sub>7</sub>.

In order to decrease the loss of Al during ball milling, the  $Sr_2Al$  alloy was milled under hydrogen at a rotation speed of 150 rpm for 10 h. Fig. 4 shows the calculated and observed XRD patterns for the milled sample. The sample consisted of  $SrH_2$  and Al with a small amount of impurity Fe (1 wt.%). The mass fraction of Al was calculated to be 11 wt.%, as shown in Table 2. Thus, the mixture of  $SrH_2$  and Al with a small loss of Al can be easily produced by milling of the alloy under hydrogen at 150 rpm for 10 h.

The milled product was further hydrogenated at 533 K for 2 days. The calculated and observed XRD patterns of the hydrogenated sample are shown in Fig. 5. The  $Sr_2AlH_7$  hy-

Table 2 Phase abundance (wt.%) of the products milled under hydrogen at 150 rpm for 10 h followed by hydrogenation or sintering

Phase	Milling	Hydrogenation	Sintering
Sr <sub>2</sub> AlH <sub>7</sub>	_	66	54
Al	11	1	2
SrH <sub>2</sub>	88	31	42
Fe	1	1	1
SrO	_	1	1



Fig. 5. Calculated and observed XRD patterns for the sample milled under hydrogen at a rotation speed of 150 rpm for 10 h followed by hydrogenation at 533 K for 2 days. Reflection markers are for Sr<sub>2</sub>AlH<sub>7</sub>, Al, SrH<sub>2</sub>, SrO and Fe (from above), respectively.

dride is obviously present. This means that the milled product consisting of SrH<sub>2</sub> and Al reacted with hydrogen to form Sr<sub>2</sub>AlH<sub>7</sub>, which can be expressed as

$$4SrH_2 + 2Al + 3H_2 \rightarrow 2Sr_2AlH_7 \tag{3}$$

Table 2 compares the phase abundance of the products before and after hydrogenation. The hydrogenated sample contains 66 wt.% of Sr<sub>2</sub>AlH<sub>7</sub>, 31 wt.% of Sr<sub>2</sub>H, 1 wt.% of Al, SrO and Fe. The remained SrH<sub>2</sub> was caused by the loss of Al during ball milling, which has a great effect on the yield of Sr<sub>2</sub>AlH<sub>7</sub>.

The milled sample was also sintered in hydrogen at 533 K for 2 days. Fig. 6 shows the Rietveld refinement of the XRD pattern of the sintered sample. We found that the result in the sintered sample is similar to that in the hydrogenated sample. However, the yield of  $Sr_2AlH_7$  is 54 wt.%, which is lower than that in the hydrogenated sample as shown in Table 2. Actually, the difference between the two treatment methods is only the distinct shapes of the samples. The hydrogenated sample was treated in a powder form but the sintered one was in a pellet form. The lower yield of  $Sr_2AlH_7$  in the sintered sample might be caused by the lower surface area for reaction.



Fig. 6. Calculated and observed XRD patterns for the sample milled under hydrogen at a rotation speed of 150 rpm for 10 h followed by sintering at 533 K for 2 days. Reflection markers are for Sr<sub>2</sub>AlH<sub>7</sub>, Al, SrH<sub>2</sub>, SrO and Fe (from above), respectively.

Zhu and Akiba reported that  $Sr_2AlH_7$  which was prepared by hydrogenation of  $SrAl_2$  reversibly dehydrogenated and hydrogenated in a commercially available pct apparatus without a catalyst at 543 K [16]. This reaction is expressed by Eq. (4) being the same as Eq. (3) obtained in the present work.

$$2Sr_2AlH_7 \leftrightarrow 4SrH_2 + 2Al + 3H_2 \tag{4}$$

It was confirmed that Eqs. (3) and (4) are reversible at 543 K without catalyst.

#### 4. Conclusions

The hydride  $Sr_2AlH_7$  was successfully synthesized by ball milling of  $Sr_2Al$  alloy under hydrogen at 150 rpm for 10 h followed by hydrogenation or sintering at 533 K for 2 days. The hydrogenated product had a higher yield of  $Sr_2AlH_7$  than the sintered product. During ball milling, the mass fraction of Al decreased, leading to the formation of some  $SrH_2$ . However, if the  $Sr_2Al$  alloy is milled at 300 rpm for 50 h or longer, the mass fraction of Al decreases strongly. As a result, the  $Sr_2AlH_7$  hydride cannot be obtained during a subsequent hydrogenation.

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