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Journal of Alloys and Compounds 329 (2001) L5–L8

Journal of  
ALLOYS  
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Letter

## Preparation of alkali metal hydrides by mechanical alloying

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Received 6 April 2001; accepted 14 May 2001

### Abstract

Rubidium and cesium hydrides are not commercialized and we have set up, a few years ago, a method of synthesis at the laboratory scale. It is based on the reaction of alkali metal with hydrogen obtained by thermal decomposition of uranium hydride  $\text{UH}_3$  at a temperature of  $450^\circ\text{C}$ , which gives a pressure of hydrogen close to 3 bars. This synthesis leads to a very pure alkali metal hydride MH, but the rate of the reaction remains quite small: a few hundreds of milligrams in 24 h. A new method, based on mechanical alloying, consists in milling the alkali metal, at room temperature, under a pressure of hydrogen close to 5 bars. The reaction proceeds in 16 h and gives 3–15 g of very pure MH (from sodium to cesium, respectively) at once. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Gas–solid reactions; Mechanical alloying; X-ray diffraction

### 1. Introduction

The formation of the alkali metal hydrides is exothermic (between 50 and 180 kJ/mole) [1], however the direct synthesis by reaction of hydrogen on the molten metal is very slow due to the protection role played by the hydride layer, formed readily on the surface of the metal and which slows down the diffusion of the metal vapor as well as hydrogen. The rubidium and cesium hydrides are not commercially available and should be synthesized at the laboratory scale. There are two methods, based on the reaction of hydrogen on the molten metal in the presence of a temperature gradient: the metal is heated at around  $250^\circ\text{C}$ , temperature high enough to decompose partially the hydride formed on its surface. The metal vapor (pressure around 5 Torr), in equilibrium with hydrogen and the free metal distillates towards the cold part of the apparatus, whose temperature is  $150^\circ\text{C}$ . Close to the cold wall, it reacts with hydrogen and the formed hydride is deposited on that cold part. At that temperature, the decomposition pressure of the hydride is negligible: around  $10^{-2}$  Torr. The reaction rate is limited due to the low metal vapor pressure and the yield is about 400 mg per day for  $1\text{ cm}^2$  of surface of the molten metal. The hydrogen source

is either a flow of gas in an open circuit at atmospheric pressure, with the risk of explosion [2] or the gas coming from the thermal decomposition of uranium hydride heated at  $450^\circ\text{C}$ , which provides a pressure of 3 bars in a sealed tube, with the problems connected to the radioactivity and toxicity of uranium [3]. It is necessary to set up a new synthesis method for quantities larger than 1 g.

The industrial preparation of the alkali metal hydrides is based on the reaction of hydrogen on the molten metal dispersed in a mineral oil stirred, (with generally addition of dispersing agents, which leads to the presence of impurities [4–6]), in order to renew the surface of the metal. The mechanical alloying is precisely known to clean continuously the surface of the reactants [7] and, then, constitutes a chosen tool for such a synthesis. The mechanical alloying is also used for synthesis of several hydrides with, in particular Mg, Ti, Zr [8,9].

### 2. Experimental

The balls and alkali metal are introduced in the vial under the purified argon atmosphere of a glove box. The desired hydrogen pressure is adjusted, after removal of the argon, at a maximal value of 30 bars. Taking into account the volume of the vial and that of balls and alkali metal, the hydrogen volume is around 7 l (NTP). Practically, the initial amounts are generally as follows: 2 g of alkali

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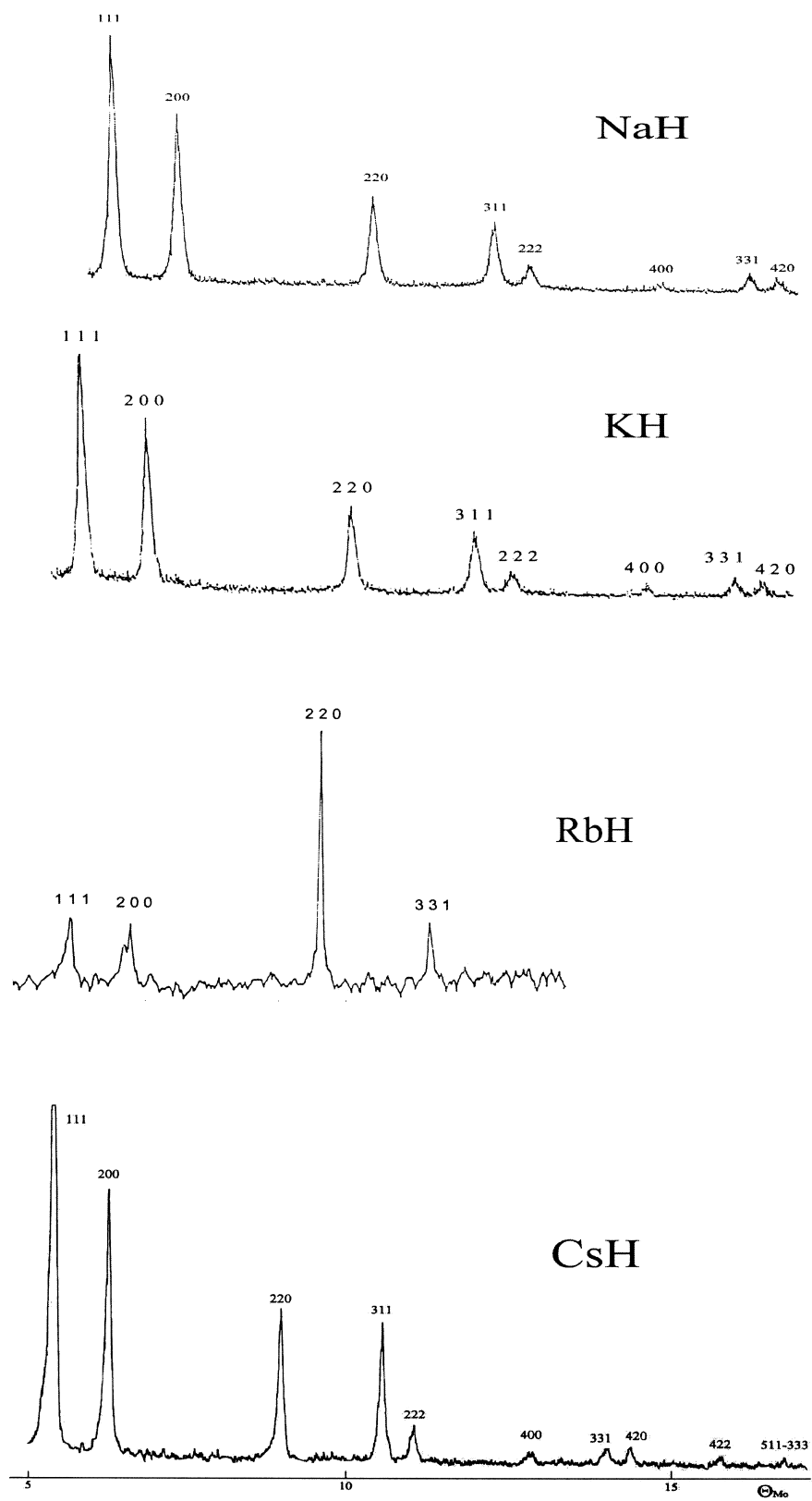


Fig. 1. XRD pattern of alkali metal hydride powders.

Table 1  
X-ray data on the alkali metal hydrides ( $\lambda$  MoK $\alpha$ =0.70926 Å)

<i>hkl</i>	NaH			KH			RbH			CsH		
	$d_{hkl}$ (Å)	$I_{hkl}/I_{111}$ exp.(%)	$I_{hkl}/I_{111}$ calc.(%)	$d_{hkl}$ (Å)	$I_{hkl}/I_{111}$ exp.(%)	$I_{hkl}/I_{111}$ calc.(%)	$d_{hkl}$ (Å)	$I_{hkl}/I_{111}$ exp.(%)	$I_{hkl}/I_{111}$ calc.(%)	$d_{hkl}$ (Å)	$I_{hkl}/I_{111}$ exp.(%)	$I_{hkl}/I_{111}$ calc.(%)
111	2.822	100.0	100.0	3.30	100.0	100.0	3.48	100.0	100.0	3.65	100.0	100.0
200	2.445	79.3	76.9	2.86	78.8	76.6	3.02	96.0	76.6	3.19	54.0	79.7
220	1.727	35.0	36.1	2.02	35.0	36.4	2.13	375.0	36.4	2.27	49.2	43.2
311	1.470	24.4	23.5	1.72	25.0	24.6	1.82	9.3	24.6	1.92	45.4	31.6
222	1.409	9.8	25.2	1.65	7.5	22.0				1.82	13.1	28.9
400	1.220	2.4	13.2	1.426	2.5	15.0				1.59	62.0	21.4
331	1.117	7.3	9.8	1.31	7.5	12.0				1.46	18.5	17.7
420	1.089	3.7	8.9	1.276	5.0	8.7				1.42	15.4	13.6
422	0.994	<1	5.1							1.30	9.2	11.9
511–333	0.938	<1	5.1							1.23	1	11.9
440										1.13	<1	9.7
531										1.08	<1	8.7
$\bar{a}$	4.88±0.01 Å			5.71±0.01 Å			6.03±0.01 Å			6.36±0.06 Å		
After [10]	$a=4.883$ Å			$a=5.714$ Å			$a=6.049$ Å			$a=6.388$ Å		

metal, 10 steel balls (diameter 10 mm), hydrogen pressure between 5 and 7 bars.

The vial is then placed on a planetary mill (Retsch PM 400). An initial low rotation rate (around 50 rpm) is kept for 15 min in order to avoid a too-large spread-out of the alkali metal on the wall and cover of the vial. During that period, a small quantity of hydride is formed, which presents two interesting features: firstly there is a modification of the surface tension of the metal and secondly the hydride acts as a catalyst for further hydridation. After that initial period, the rotation is progressively increased (in 2 h) up to 250 rpm and that rate is kept for 12 h. At this step of the synthesis, the hydride is a greyish powder which contains small quantities of free metal finely divided. It is thus necessary, before the opening of the vial, to place it in an oven at 120°C for 1 h. The dispersed metal is rapidly transformed in a pure MH hydride with a M/H ratio equal to  $1 \pm 0.02$  as determined by chemical analysis (reaction with water and acidimetry coupled with the hydrogen evolved volume). One has to note that the XRD performed on the greyish powder exhibits a pure MH diagram, which means that the free metal is actually very finely dispersed and, in that case, the eye is a better tool than X-rays.

### 3. Results

The X-rays patterns of the hydrides obtained by this method are shown in Fig. 1. The peaks are sharp, indicating a good crystalline organization of the powder. On the other hand, the peaks correspond to a FCC cubic unit cell with the Miller indices of the same parity and the intensities fit well with that calculated for the cubic unit cells, space group  $Fm\bar{3}m$ , (see Table 1).

The results concerning the X-ray reflections relative to the hydrides NaH, KH, RbH and CsH are represented in

Table 1. First of all, the  $a$  parameters calculated from the  $d_{hkl}$  distances are in good agreement with those given in the literature [10], the only observed reflections are those for which all Miller indices are of the same parity, characteristic of FCC symmetry.

The experimental intensities fit fairly well with that calculated on the basis of a  $Fm\bar{3}m$  unit cell with M in position  $4a$  and H in position  $4b$ , except for RbH which presents a large discrepancy between calculated and experimental intensity values. This fact can be easily explained by the experimental conditions: the wavelength (MoK $\alpha$ ) provokes an intense fluorescence with rubidium. On the other hand, with the copper wavelength, the absorption is too high even with a small diameter capillary. However, the interplanar distances are correct even under that condition.

### 4. Conclusion

Ball milling under hydrogen pressure constitutes an easy and reproducible method for the preparation of large quantities of pure alkali metal hydrides. The moderate rotation rate and the quite low hardness of the reactants are such that the risk of contamination of the hydride by metallic impurities coming from the shocks between balls and vial wall remains very small. This process can easily be adapted for industrial applications since we are already able to synthesize at once in 16 h up to 16 g of NaH or 89 g of CsH at the laboratory scale.

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