Preparation and hydriding properties of magnesiumcontaining hydrogen storage materials chemically deposited from a homogeneous phase

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Abstract

Use of the dissolution of magnesium metal in liquid ammonia enabled novel magnesiumcontaining hydrogen storage materials to be prepared. The dispersion of magnesium atoms in ammonia matrices at 77 K using a metal vapour technique gave rise to a homogeneous solution of dissolved magnesium metal in liquid ammonia. Hydrogen storage materials prepared using the solvent power of ammonia are of two types. (i) Magnesium was crystallized out of the solution of dissolved magnesium in liquid ammonia; the crystallization was carried out in the presence or absence of catalytically active nickel powders (respectively Mg--Ni or Mg); (ii) Magnesium was highly dispersed on an active carbon (AC) support by impregnating the AC with the solution (referred to as Mg/AC). Using AC on which catalytically active nickel had been previously supported, the preparation of samples was further extended to include binary systems (Mg-Ni/AC). These samples were investigated in connection with the preparation methods. The magnesium samples were extremely active toward hydrogen absorption. For the Mg--Ni and Mg-Ni/AC samples an increase in nickel markedly accelerated the initial hydriding rates of the parent magnesium metal.

1. Introduction

There is considerable potential for and intrinsic interest in magnesium and magnesium-based alloys as rechargeable hydrogen storage materials [1, 2]. In earlier publications [3] we described the hydriding properties of magnesium systems chemically modified with organic compounds. In particular, small, solvated magnesium particles formed by vapour deposition of metal atoms in low-temperature organic matrices can be used effectively for hydriding [4–8].

More recent work has shown that extremely active and novel magnesiumcontaining hydrogen storage materials can be obtained from the solution of magnesium metal in liquid ammonia [9]. The studies in our laboratory are aimed at addressing this issue in two ways.

(i) Finely divided magnesium is crystallized out of a homogeneous solution of magnesium in liquid ammonia. If this procedure is conducted in the presence of catalytically active metals, the preparation of samples is extended to include binary systems.

(ii) By impregnating a solid carrier of high surface area with the solution of dissolved magnesium in liquid ammonia, magnesium particles are highly dispersed on the carrier. In this case, using a previously activated metalsupporting solid carrier, the system can also be developed to prepare magnesium-containing binary systems. This method of preparation of hydrogen storage materials makes it possible to form them into any shape.

We used nickel as a counterpart in the binary system; nickel is thus available to cleave the hydrogen bond, which is an essential step enabling hydrogen to enter the host metal. Further, active carbon (AC) was available as an inert support with a high surface area to stabilize the small, active magnesium particles. The preparation and hydriding properties of various magnesium samples (Mg, Mg–Ni, Mg/AC and Mg–Ni/AC) obtained using the solvent power of ammonia were investigated.

2. Experimental details

2.1. Materials

Magnesium (purity 99.95%) was obtained from Furukawa Magnesium Co. Ltd. Ammonia (purity greater than 99.9%), produced by Iwatani Ind. Ltd., was dried through calcium oxide and subsequently through a sodium hydroxide column. Nickel powders were prepared by an incipient wetness technique; Ni(NO₃)₂.6H₂O was decomposed in a solution of ammonium hydroxide, forming precipitates of hydroxide. The resulting precipitates were filtered off, washed thoroughly with distilled water, dried and finally reduced with hydrogen at 573 K. Active carbon (AC, 1040 m² g⁻¹) was purchased from Nakarai Chemicals Ltd., and was subjected to evacuation at 573 K for 10 h prior to use. For the AC-supported nickel (Ni/AC), the AC was impregnated with aqueous nickel(II) nitrate and the resulting slurry was dried, calcined and reduced with hydrogen at 573 K for 5 h. The nickel loading of Ni/AC was 0.1–5 wt.% of the total sample weight.

2.2. Sample preparation and procedures

The experimental requirements for the preparation of a homogeneous solution of magnesium in liquid ammonia are a furnace (tungsten wire coil basket, Japan Lamp Industrial) for generating the magnesium vapour inside a Pyrex-glass vacuum system (jar shaped, internal diameter 62 mm, length 175 mm) and a cold surface onto which the metal vapour can be deposited. The apparatus employed here was similar to previous apparatus which has been described elsewhere in detail [8]. According to the type of sample, one of two procedures was followed.

(i) After evacuation of the reaction system (to approximately 10^{-5} Torr), magnesium was vaporized into an ammonia matrix (approximately 60 cm³) which had been condensed as a layer on the wall of the cooled (77 K)

reactor. The magnesium metal vapour was dispersed into ammonia matrices on the inner surface of the reactor which was cooled with liquid nitrogen, yielding a dark blue solid. On completion of the low-temperature deposition, the reactor was warmed to 198 K with stirring and the excess ammonia was pumped off leaving active magnesium powder. The preparation of the Mg–Ni sample was carried out in a similar way, except that the magnesium vapour was dispersed into low-temperature ammonia matrices in the presence of nickel powder.

(ii) The preparation of Mg/AC was similar to that described above. AC, which had been previously evacuated at 573 K for 10 h, was added to a solution of dissolved magnesium in liquid ammonia at 198 K. During vigorous stirring the dark blue colour of the solution gradually disappeared as a result of the deposition of magnesium onto the surface of the AC support. To prepare Mg–Ni/AC, nickel-supporting AC (Ni/AC) was used instead of AC.

All sample preparation steps were carried out in an atmosphere of dry argon, otherwise the sample becomes unreactive. Hydrogen absorption measurements were made using glass volumetric equipment and a high vacuum system. Prior to the measurements the samples were evacuated at 473-593 K for 2 h.

3. Results and discussion

3.1. Reaction of magnesium with ammonia

Studies on the dissolution of magnesium in ammonia have produced inconsistencies [10]. Magnesium dissolves in liquid ammonia to yield a blue homogeneous solution containing the ammoniated electron [11] when vaporized into ammonia matrices at 77 K. However, with several different forms of normal magnesium (chips, powder and filings), no reaction occurred. The reaction mixture of magnesium and ammonia is a dark blue colour, apparently as a result of a charge transfer complex similar to the complexes reported by Skell and Girad [12] for magnesium atoms with ammonia. It has been shown that alkali metals dissolve in liquid ammonia to form similar blue solutions which are characteristic of the solvated electron [11]. This is also the case for the present magnesium–ammonia system.

During the warm-up, with ammonia evaporating from the solution, the residue returned to metallic magnesium with hexagonal structure, which was confirmed by X-ray diffraction (XRD). However, the features of the magnesium precipitated out were dependent on the experimental conditions. As shown in the XRD spectra in Fig. 1, when ammonia was removed from the solution at a temperature below about 230 K, active magnesium in a finely divided state was reversibly regenerated, but thermal treatment at elevated temperatures resulted partly in the formation of crystalline Mg_3N_2 . For the metal–ammonia system, it has been shown that solutions of europium and ytterbium metal in liquid ammonia decomposed to form the diamide, $Eu(NH_2)_2$ and Yb(NH₂)₂, exclusively at 223 K, followed by thermal degradation of the amide at 513–523 K to give the nitride [13, 14]. However, it was found



Fig. 1. X-ray diffraction spectra (Cu K α radiation) of the samples crystallized out of the solution of dissolved magnesium in liquid ammonia at 230 K (bottom curve) and 473 K (top curve).

that on addition of anhydrous tetrahydrofuran to the solution of dissolved magnesium in liquid ammonia, the formation of Mg_3N_2 was depressed even under thermal treatment at elevated temperatures. Powder X-ray studies yielded an estimate of the size of magnesium crystallites of 17–23 nm. The solution of magnesium metals in liquid ammonia and decomposition might be described by the following equations:

$$Mg + nNH_3 \rightleftharpoons Mg^{2+} + 2e(NH_3)_n^{-}$$
 (1)

$$e(NH_3)_n^- + NH_3 \longrightarrow NH_2^- + \frac{1}{2}H_2$$
(2)

$$Mg^{2+} + 2NH_2^- \longrightarrow Mg(NH_2)_2$$
 (3)

$$Mg(NH_2)_2 \longrightarrow \frac{1}{3}Mg_3N_2 + \frac{4}{3}NH_3$$
(4)

Equation (1) represents the dissolution of the metal in liquid ammonia, which is the same as for alkali metals. The residue after evaporating was mainly magnesium owing to retardation of reactions (2), (3) and (4) at lower temperatures. Extended standing or heating at high temperatures would produce the amide $Mg(NH_2)_2$ (not observed here) and then the nitride Mg_3N_2 . It has been shown that other metal-ammonia systems, as well as magnesium-ammonia, exhibit essentially similar behaviour [11].

For the Mg–Ni samples, there was no indication of Mg₂Ni or MgNi₂ alloys by XRD. For the Mg/AC and Mg–Ni/AC, XRD studies were used to determine the nature of the samples formed during magnesium deposition. The reaction of dissolved magnesium in liquid ammonia with the AC support was accompanied by fading of the blue colour of the solution. This is probably an indication of the deposition of magnesium onto the AC surface by the reverse of reaction (1). For the samples thus prepared, no diffraction peaks assigned to magnesium were observed within the loading range examined; a high dispersion of magnesium on AC and Ni/AC is probably achieved by this technique. Further, XRD patterns showed negligible changes after the evacuation treatment, even at higher temperatures (473-593 K).

3.2. Hydrogen absorption of magnesium-containing systems

Magnesium particles crystallized out of a homogeneous solution of magnesium metal in liquid ammonia were used as an active hydrogen absorber. Magnesium was also used efficiently when deposited onto the inert solid support. The variation of hydrogen absorption with time, evaluated using volumetric equipment, is illustrated in Fig. 2. Both Mg and Mg/AC samples exhibited solvent power for hydrogen even at 473 K when exposed to high-purity hydrogen at 400 Torr. In preliminary experiments, the rate of hydrogen uptake was almost proportional to the hydrogen pressure under initial conditions. The samples containing nickel (Mg–Ni and Mg–Ni/AC) showed greater ability of hydrogen uptake under similar conditions. In particular, magnesium deposited onto AC with 1 wt.% Ni gave yields of $\alpha \approx 0.5$ after a reaction time of 2 h, where α is the fraction of magnesium metal reacted with hydrogen.

The effects of the addition of nickel on the activity were apparent; in the presence of small amounts of nickel the initial hydriding rates were markedly accelerated. We have found previously that for solvated magnesium particles (Mg–THF) prepared by metal vaporizing into a tetrahydrofuran (THF) matrix, the surface processes during the first step are important in determining the hydriding character of the magnesium [5–8]. For Mg–Ni–THF, the initial hydriding of magnesium is controlled by the extent of nickel



Fig. 2. Hydrogen absorption of various magnesium-containing samples at 473 K: (a) Mg and Mg-Ni; (b) Mg/AC and Mg-Ni/AC. Each sample was evacuated at 573 K for 2 h and then exposed to hydrogen gas at 400 Torr.

dispersion on the magnesium surface. Recently, Krozer and Kazemo [15] demonstrated that when a palladium layer is deposited onto the thin, ultrahigh vacuum evaporated magnesium, the reaction of magnesium with hydrogen is possible at much lower pressures and temperatures than previously reported. It was found that for both Mg–Ni and Mg–Ni/AC, the amount of nickel metal incorporated was important in determining the hydriding rates of magnesium. For Mg–Ni, an increase in nickel content (0, 8.3 and 10.0 wt.%) enhanced the initial hydriding; the dispersed nickel in intimate contact with magnesium catalytically and effectively activates the hydrogen to react with magnesium particles. The active nickel precipitates can catalyse the $H_2 \rightleftharpoons 2H$ reaction, and spill atomic hydrogen over to the magnesium phase as hydrogen acceptors to form the hydride. For Mg–Ni/AC, nickel previously supported on AC has been described [9].

The evacuation temperatures of these samples affect the hydriding properties. For the as-prepared samples, the kinetics of hydrogen absorption were very slow at 473 K and 400 Torr, but enhanced markedly when the sample was evacuated at elevated temperatures (473–593 K). The initial rates of hydriding increased by over an order of magnitude. This is probably due to the release of strongly adsorbed residual ammonia from the surface and/or, in particular for the Mg–Ni binary system, the reconstruction of surface morphology with an increase in evacuation temperatures. More recently, we described the rearrangement of surface structure induced by thermal treatment of the Eu–Ag and Yb–Ag systems which were also prepared by the reaction of dissolved lanthanide metal in liquid ammonia with silver powders [16].

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