JOURNAL OF MATERIALS SCIENCE **39** (2004) 1557–1562

The reaction of hydrogen with Mg-Cd alloys prepared by mechanical alloying

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In this paper, we present the hydrogen storage properties of Mg-Cd alloys prepared by ball milling. Mechanical alloying of a mixture of Mg and Cd elemental powders containing up to 20 at.%Cd leads to a magnesium solid solution. The lattice spacings of the hcp Mg phase shrink with dissolution of cadmium atoms in Mg. The mechanically alloyed pure Mg-Cd alloys are very difficult to activate for hydrogen absorption. However, if vanadium and graphite additives are added, a Mg(Cd)-V-C nanocomposite forms after ball milling and the activation then becomes very easy. The hydrogen absorption/desorption kinetics are very fast. The plateau pressure and slope of hydrogen absorption/desorption increase, while the hydrogen storage capacity decreases with increasing cadmium content.

1. Introduction

Magnesium hydride is considered as a potential hydrogen storage material for several applications because of its high storage capacity and low cost. However, practical applications of magnesium and its alloys for hydrogen storage are limited by the slow hydrogen sorption kinetics and by the high dissociation temperature of MgH_2 [1–3]. Numerous studies show that the hydrogen sorption kinetics of magnesium can be greatly improved by: (i) alloying with other elements to form Mg solid solution [1, 4, 5]; (ii) mixing or alloying with catalytic transition elements, such as Ni, Co, Ti, Fe, and with intermetallic compounds e.g. $LaNi_5$, FeTi, $ZrFe_{1.4}Cr_{0.6}$ to form composites [6–17], (iii) surface coating or doping with Ni and Pd [18], surface treatment by organic compound [19, 20], milling with graphite and organic compound [21], lixivation [22]; and (iv) mechanical grinding which creates lattice defects and small grain size [23–26]. Recently, the problem of slow hydrogen sorption kinetics has been basically solved by mechanical milling of MgH_2 with transition metal additives [25, 27] or oxides [28]. For example, the MgH_2-5 at.%V composite desorbs at 473 K (under vacuum) and re-absorbs hydrogen rapidly even at room temperature [27].

The high thermodynamic stability of MgH_2 remains the last obstacle for applications. Research conducted in the last few decades showed that the plateau pressure of magnesium hydride does not change by forming composites, by surface treatment, by adding catalysts, or by forming a nanostructure unless true magnesium alloys such as Mg_2Ni, Mg_2Cu, Mg_2Al_3 are formed [2, 3, 6, 25, 28].

Some reports have claimed that the plateau pressure of MgH_2 can be changed by forming multiphase alloys, for example, in the Mg-Al-Y, Mg-Li-Ni-Zn [29], Mg-FeTi(Mn) [30], and in the recent Mg-Zn-Y [24] system. The changes in plateau pressures were explained by the complex multiphase nature of the composites [24, 30], however, the real physical reasons behind have not been understood or reported.

Magnesium forms solid solution and compounds with few elements under equilibrium states. Non-equilibrium processing methods, such as mechanical alloying, rapid quenching can produce new magnesium alloys and new structures, such as amorphous phases, extended solid solutions, and non-stoichiometric intermetallic compounds which may alter the thermodynamic properties. However, none of these new alloys and structures are stable at elevated temperature e.g., 300°C, which is needed for activation of most air exposed Mg-based alloys. The multi-component single phase (usually amorphous phase) transforms to the conventional equilibrium multi-phase composites after activation, and the end result is: improved kinetics and no destabilization of the magnesium hydride [31–36]. If the as-prepared alloy can be hydrogenated *in situ* without exposition to air (this was the case for Mg/Pd sputtered film [37]), novel properties may be obtained.

In this work, we investigate the Mg-Cd system, since Cd is the only element which can form a complete mutual solid solution with Mg under equilibrium state. Cadmium as an alloying element in magnesium has been investigated by Douglass [1], however the Mg-1 at.%Cd alloy that was made showed very sluggish hydrogen desorption kinetics, and was rejected at the

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very beginning. Therefore, no thermodynamic properties were reported.

2. Experimental

Mg (99.9% pure) and Cd (99.9 wt% pure, −325 mesh) were mixed and then mechanically alloyed in a Spex 8000 ball mill under the protection of argon. A hardened steel crucible and three steel balls of 12.7 mm in diameter were used for milling. The ball to powder weight ratio was 10:1. Vanadium catalyst (2.5 at.%) was added to the powders after that the Mg(Cd) solid solution was formed, and then, ball milled for an additional 20 h in order to distribute the catalyst. In addition, graphite (2 wt%) was also added as anti-sticking agent and for activation purpose [38].

X-ray diffraction analysis of the mechanically alloyed powders was performed on a Siemens D-500 X-ray diffractometer with Cu K_α radiation. The crystallite size was determined from X-ray peak broadening by using the Williamson-Hall method, and the lattice parameters were determined from the X-ray peak positions by least square method [39]. The hydrogen storage properties of the mechanically milled powders were evaluated by using an automated Sievert's apparatus. The mechanically alloyed powders were put into the reactor, evacuated for 20 min, then heated to 573 K to do the first absorption under a hydrogen pressure of 1.0 MPa. Hydrogen desorption was performed under vacuum with a large volume, so that the pressure buildup during desorption is small (0.007 MPa).

3. Results and discussion

Fig. 1 shows the X-ray diffraction spectra of the Mg-10Cd and Mg-20Cd (in atomic percent) powders after 20 h of mechanical alloying. The spectrum of pure Mg is also given for comparison. It can be seen that the X-ray diffraction peaks of the Mg phase shift to high angles, and the diffraction peaks of cadmium disappear in the mechanically alloyed Mg-Cd alloys. This indicates that the cadmium has been dissolved in the hcp magnesium phase. Since the atomic size of Cd is smaller than that of Mg, the dissolution of cadmium atoms in the hcp Mg phase causes shrinking of the lattice spacing. The very broad diffraction peaks indicate that the grain size is small for the as-milled powders. The crystallite size has been determined to be 39 ± 8 and 37 ± 6 nm for Mg-10Cd and Mg-20Cd respectively from peak broadening using the Williamson-Hall method [39].

The vanadium and graphite additives do not react with Mg or Cd upon 20 h of mechanical alloying. The XRD spectra of the as-milled Mg-Cd-V-C powders only show the shifted Mg peaks and a very broad small vanadium peak. Since the carbon content is very low, no diffraction peak from graphite is observed. The addition of vanadium and graphite do not change the lattice parameter of Mg, as confirmed by ball milling Mg-V, Mg-C and Mg-V-C separately. There is no solid solution of V and C in Mg obtained under the present mechanical alloying conditions.

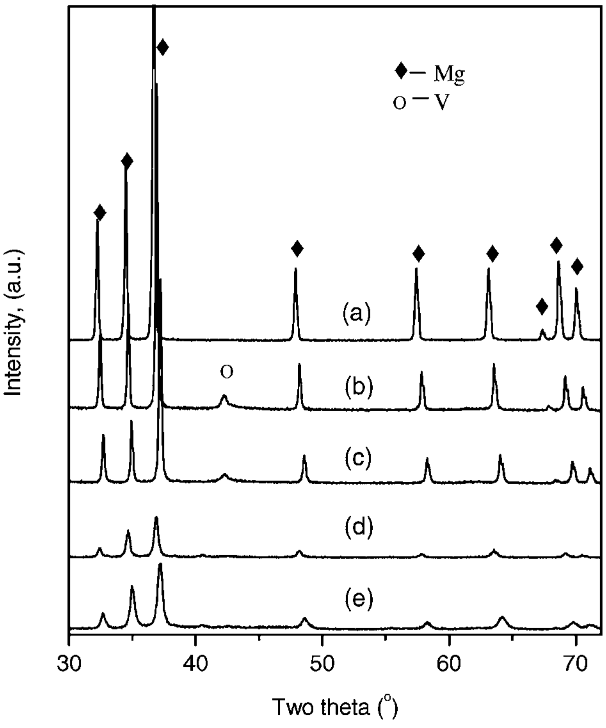

Figure 1 XRD spectra of the Mg-Cd alloys after mechanical alloying and hydriding/dehydriding (HD): (a) as-milled pure Mg, (b) Mg-10Cd-V-C, after HD, (c) Mg-20Cd-V-C, after HD, (d) as-milled Mg-10Cd and (e) as-milled Mg-20Cd.

At equilibrium, an ordered MgCd compound exists below 526 K in the composition range of 40–60 at.%Mg. At lower temperatures, an additional order phase Mg_3Cd forms on the Mg rich side [40]. Therefore, there should be a Mg_3Cd phase present in the Mg-20Cd sample at room temperature under equilibrium conditions. However, no such phase was formed during mechanical alloying.

After several cycles of hydrogen absorption/desorption at 350°C during 24 h, grain growth of the Mg(Cd)-V-C composite is observed. Fig. 1 shows the XRD spectra of the Mg(Cd)-V-C composites (the V and C contents are specified in the experimental) after hydrogen desorption at 350°C and quenched at a cooling rate of 2°C/min down to room temperature. We clearly observe that the diffraction peaks are sharper in comparison to that of the as-milled powders. The grain size increases to 64 ± 6 and 80 ± 20 nm for Mg-10Cd-V-C and Mg-20Cd-V-C powders respectively. The peak position of Mg(Cd) does not change, indicating that the cadmium remains in solution in the hcp Mg. This is not surprising because magnesium and cadmium show continuous mutual solubility in the hcp (Mg, Cd) phase at elevated temperatures. Rapid cooling after hydrogen desorption suppresses the phase separation (precipitation of the Mg_3Cd phase from the supersaturated hcp Mg(Cd) solid solution). After hydrogen desorption, the diffraction peak of vanadium at $2\theta = 42.17°$ can be clearly seen. No other phase is present on the XRD spectra. Since the mixing heats of V-Cd and V-Mg are positive [41], no reactions between V and Cd or V and Mg are expected. Although vanadium has a strong tendency to react with graphite to form vanadium carbide VC, no such phase was observed after 20 hydrogen absorption/desorption cycles.

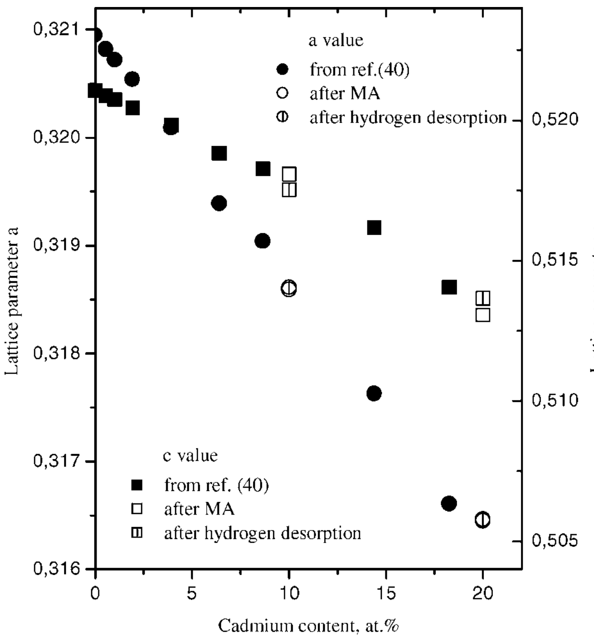

Figure 2 Lattice parameters of the HCP Mg(Cd) phase as a function of Cd content.

The lattice parameters "a" and "c" of the hcp Mg phase are shown in Fig. 2. The values from literature [40] are also given. It can be seen that the lattice spacings of Mg do shrink when Cd dissolves in the hcp-Mg lattice. Based on the trend of the lattice parameters versus Cd content in Fig. 2, we believe that cadmium is completely dissolved in the Mg lattice for Mg-10Cd and Mg-20Cd samples after mechanical alloying. After hydrogen desorption of the hydrogenated sample, the lattice parameters of the hcp Mg(Cd) phase are basically the same as those of the as-milled alloys.

The room temperature X-ray diffraction spectra of the hydrogenated samples are shown in Fig. 3. In the case of Mg-10Cd, beside the MgH_2 phase, a Mg_3Cd phase is present. In the case of Mg-20Cd, a MgCd intermetallic compound forms. It is not clear when the phase separation occurred. It could be during hydrogenation at high temperatures or during cooling after hydrogenation. The lattice parameters of MgH_2 in the hydrogenated samples at room temperature are exactly the same as that of pure MgH_2 given in the literature [40] indicating that the MgH_2 is very stoichiometric, no $Mg(Cd)H_2$ phase is obtained at room temperature.

The pure Mg(Cd) alloys without V and C additives could not be activated at 623 K under a hydrogen pressure of 1.5 MPa in 24 h. The Mg(Cd)-V-C composite absorbs hydrogen rapidly even in the first cycle upon exposure to 1.0 MPa of hydrogen at 573 K. No incubation period is observed on the first hydrogen absorption curve as shown in Fig. 4. The first hydrogen absorption of Mg-20Cd-V-C is faster than that of Mg-5Cd-V-C. It can be fully hydrided in 1000 s in the first cycle. The absorption/desorption kinetics improves with cycling in the initial 5 cycles, and then remains stable. After this activation period, the composite can be fully hydrided in 500 s. The variation in Cd content does not lead to significant changes of the hydrogen absorption kinetics.

The hydrogen desorption kinetics are very fast also for the vanadium catalyzed Mg(Cd) solid solution alloys. The hydrogen desorption curves are shown in Fig. 5. The desorption kinetics improves with increasing Cd content. For the case of Mg-20Cd-V-C, the hydrogen desorption is completed in 100 s. This is almost 2 times faster than that of MgH_2-5V reported previously [27].

The thermodynamic properties of the composites changes with Cd content. Fig. 6 shows the pressure-composition isotherms (PCI) of Mg-Cd alloys with various Cd contents. The hydrogen absorption/desorption plateau pressures increase, the plateau length becomes shorter, and the slope becomes bigger with increasing

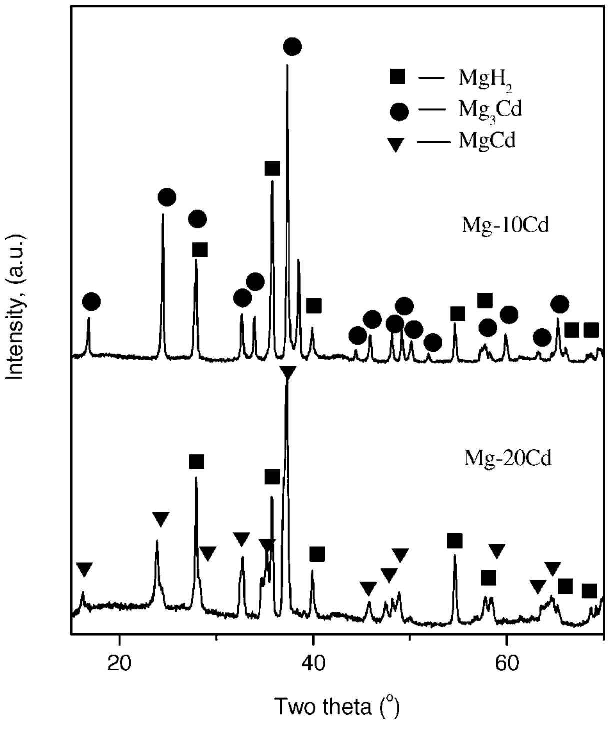

Figure 3 The X-ray spectra of the hydrogenated Mg(Cd) alloys.

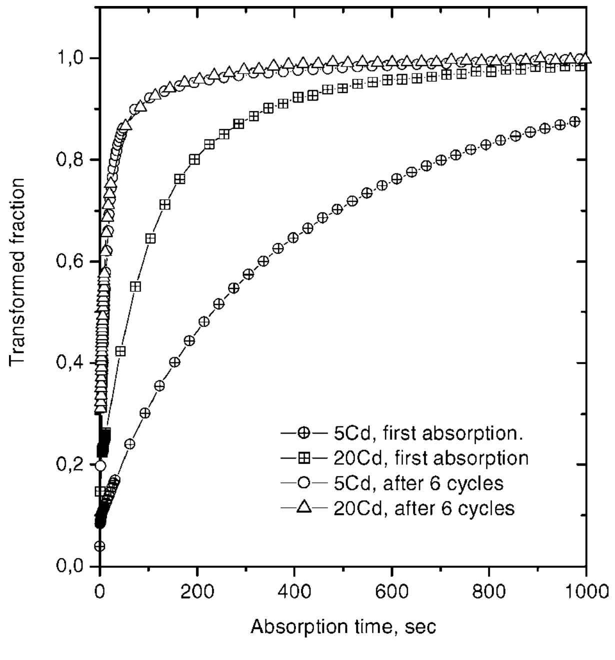

Figure 4 Hydrogen absorption curves of the Mg(Cd)-V-C composites at 573 K under a pressure of 1.0 MPa.

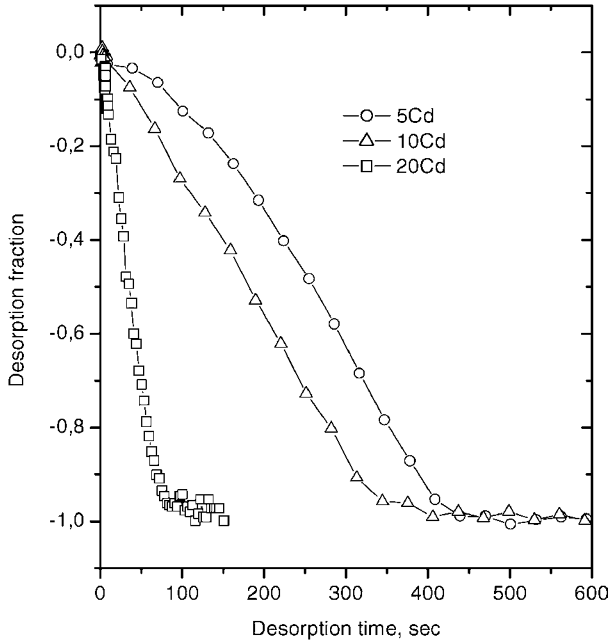

Figure 5 Hydrogen desorption curves of the Mg(Cd)-V-C composites at 573 K against a pressure of 0.015 MPa.

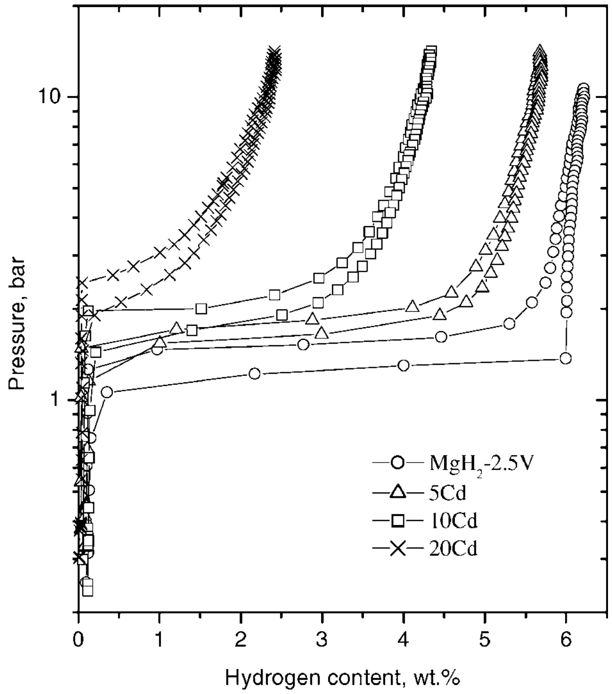

Figure 6 PCT curves of Mg(Cd)-V-C composites at 573 K.

Cd content. For the case of Mg-20Cd-V-C, a very sloping PCI curve is observed. As well documented in the literatures [42–44], pure Mg shows very flat plateau on hydrogen absorption and desorption. Sometimes, a sloping absorption plateau arises, due to the slow absorption kinetics, however, the desorption plateau is fairly flat [42].

The $Mg(Cd)_x$ solid solution may decompose upon hydrogenation according to the equation:

$$MgCd_x + H_2 \rightarrow MgH_2 + xCd$$

The equilibrium hydrogen pressure P will be given by $P = P_{Mg}(-\frac{\overline{\Delta G_{Mg}}}{RT})$, where P_{Mg} is the pressure in equilibrium with pure Mg and MgH_2. $\overline{\Delta G}_{Mg}$ is the relative partial molar free energy of Mg in the $MgCd_x$ alloy. Since $\overline{\Delta G}_{Mg}$ is negative for $MgCd_x$ alloy, the hydrogen absorption/desorption plateau pressure of $MgCd_x$ alloys is higher that that of MgH_2.

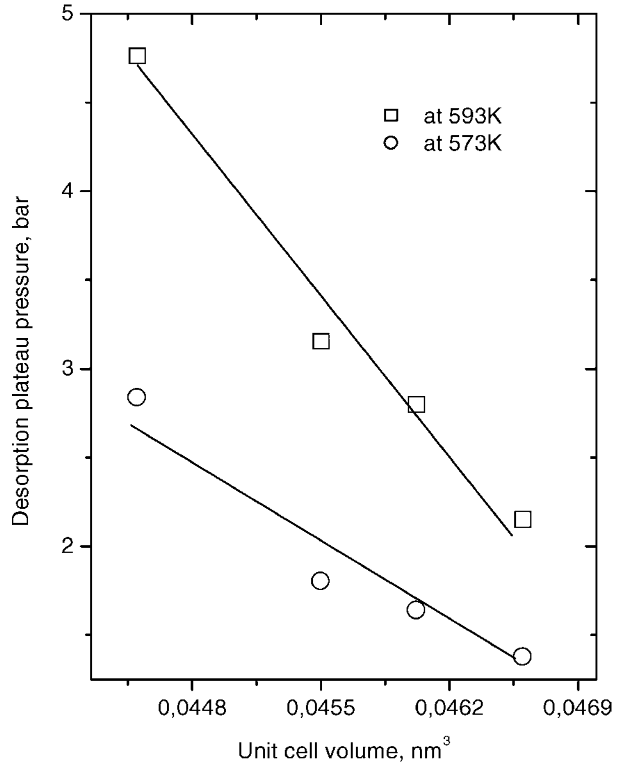

Figure 7 Desorption plateau pressure versus unit cell volume of Mg(Cd) alloys.

The empirical rule of hydride stability for intermetallic compounds, such as AB_5 and AB_2, shows that the hydride stability is lower when the unit cell volume of the compound is smaller [45, 46]. This rule is valid for the interstitial hydrides in which the metallic bonding plays an important rule [47]. In the case of magnesium hydride, a high proportion of ionic and covalent bonding is expected [48]. The empirical rule in this case may not be valid. However, plots of the desorption plateau pressures at the midpoint of the PCI curves versus the unit cell volumes of the Mg(Cd) solid solutions show approximately straight lines in Fig. 7; the smaller the unit cell volume is, the higher is the desorption plateau pressure. Our recent experiments on other systems including Mg-In, Mg-Al, Mg-Zn and Mg-Ag indicate that the empirical rule of hydride stability does not hold, small unit cell volume of Mg solid solution does not necessarily give high plateau pressure [49].

Fig. 8 shows the PCI (pressure-composition-isotherm) curves at various temperatures for Mg-10Cd-V-C sample. The hysteresis of hydrogen absorption/desorption becomes smaller with increasing temperature. The relationship of plateau (at the midpoint of the plateau) pressures with temperature are shown in Fig. 9. Since a bigger hysteresis is observed at lower temperatures, the calculation of the thermodynamic parameters (reaction enthalpy and entropy) is not accurate. A rough calculation indicates that the enthalpy of hydrogen desorption is reduced to 71 kJ/mol for Mg-5Cd-V-C from 75 kJ/mol for pure magnesium hydride.

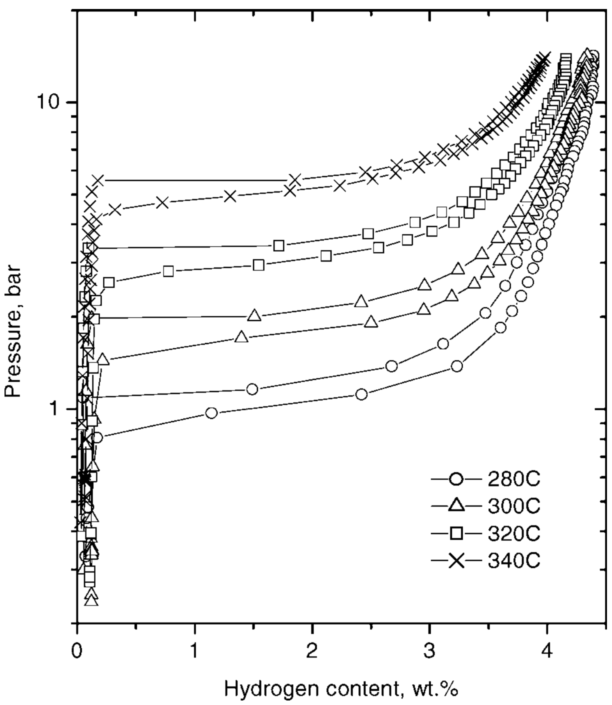

Figure 8 PCT curves of Mg-10Cd-V-C composite at various temperatures.

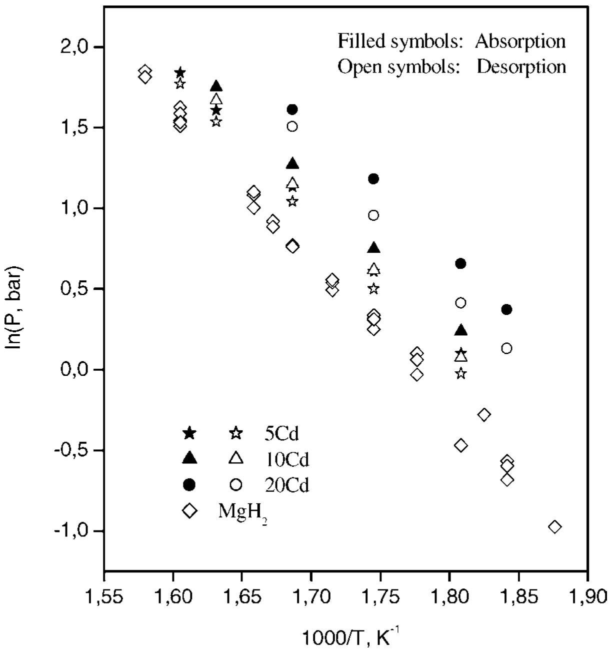

Figure 9 Variations of plateau pressures (at the midpoint of plateaus) with inverse temperatures for MgH_2 and Mg(Cd)-V-C alloys.

The reaction enthalpy varies with the hydrogen content across the plateau, as reported in the $ZrMn_{2+x}$ system [50], the details will be discussed in an upcoming report.

4. Conclusions

Cadmium can be dissolved in hcp-Mg to form a solid solution containing up to 20 at.% Cd at room temperature by mechanical alloying. The unit cell volume of hcp Mg(Cd) solid solution decreases with increasing Cd content.

The Mg(Cd) solid solution with V and C additives absorbs hydrogen easily in the first cycle. The hydrogen absorption/desorption is fairly fast after activation. Vanadium catalyst and the graphite additive do not react with Mg and Cd, and therefore, the alloy structure and hydrogen absorption/desorption kinetics remain stable after exposure to high temperatures.

The dissolution of Cd atoms in the hcp Mg phase results in a shrinking of the lattice spacings. The hydrogen absorption/desorption plateau pressure and slope increase, but hydrogen storage capacity decreases with increasing Cd content.

Acknowledgement

The authors would like to thank Dr. J. Huot for technical assistance.

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Received 21 July
and accepted 13 November 2003