JOURNAL OF MATERIALS SCIENCE 28 (1993) 3457–3462

Synthesis, structural characterization and hydrogenation behaviour of the new hydrogen storage composite alloy La_2Mg_{17}–x wt% $LaNi_5$

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Alloys with the general formula La_2Mg_{17}–x wt% $LaNi_5$ ($x = 10$, 20, 30 and 40) have been synthesized and the hydrogen storage capacity of these new composite materials investigated. The materials were activated at temperatures of ~ 360 °C under a hydrogen pressure of ~ 33 kg cm^{-2}. Optimum storage capacity of 5.24% in terms of pressure and composition was observed for La_2Mg_{17}–10 wt% $LaNi_5$ at ~ 400 °C. This is one of the very highest hydrogen storage capacities known so far. The hydriding rate of La_2Mg_{17} in the presence of $LaNi_5$ is about 3–4 times that of La_2Mg_{17} alone. In order to elucidate the role of $LaNi_5$ in accelerating the hydrogen desorption rate of La_2Mg_{17}, the structural and microstructural characteristics of the composite material were carried out employing the XRD, SEM and EDAX techniques. The hydriding rate and hydrogen storage capacity are closely related to the microstructure and the types of phase present in the alloys.

1. Introduction

Investigations of new hydride materials which have the desired properties for hydrogen storage, e.g. higher storage capacity, lighter weight and faster kinetics, have become quite prominent in recent years. It is known that Mg has the highest hydrogen storage capacity (~ 7 wt %) but it has two significant disadvantages: (i) the Mg–H_2 reaction has poor kinetics and (ii) the resulting hydride is not reversible under ambient conditions [1]. In the search for viable storage materials, one therefore has recourse to Mg-based alloy systems. The magnesium–rare earths form one such system and high storage capacity alloys such as La_2Mg_{17} (~ 4 wt %) and $LaMg_{12}$ (~ 4.5 wt %) have indeed been found [2–6]. However, a significant disadvantage of these is the very slow absorption–desorption kinetics [7]. This is about ten times slower than that of the well-known hydrogen storage alloy $LaNi_5$. In order to improve the kinetics, we have undertaken studies on composite materials. There have been only a few investigations relating to the hydrogen storage characteristics of the mixed type of composite material [8–13]. In the present study, the hydriding behaviour of the new composite materials La_2Mg_{17}–x wt % $LaNi_5$ were investigated for various values of x ($x = 10$, 20, 30 and 40). For evaluation of hydrogen storage characteristics, the equilibrium pressure and composition relations for these materials were measured under three isothermal conditions (at 350, 375 and 400 °C). It has been found that the composite system La_2Mg_{17}–10 wt % $LaNi_5$ has the optimum storage capacity. A maximum hydrogen storage capacity of about 5.24% was easily obtainable for this material (La_2Mg_{17}–10 wt % $LaNi_5$). It may be pointed out that the hydrogen storage capacity of 5.24% is possibly the highest known so far. In comparison, the best-known reproducible high storage capacity is 3.8% for Mg_2Ni. In addition to this, the as-synthesized alloy La_2Mg_{17}–x wt % $LaNi_5$ shows about 3–4 times faster kinetics than that exhibited by La_2Mg_{17} alone. In order to understand the effect of $LaNi_5$ addition on the hydrogen storage capacity and the kinetics, structural/microstructural characterization and chemical analysis of these composite materials have been undertaken. These revealed that La_2Mg_{17} is the majority phase and Ni, $MgNi_2$ and $LaNi_3$ are the minority phases present in the composite alloy. Free Ni together with Ni-containing phases are expected to play an important role in the acceleration of hydriding kinetics.

2. Experimental procedure

At first the native ingredient La_2Mg_{17} was synthesized through a solid-state diffusion process, by taking stoichiometric quantities of the highly pure constituent elements lanthanum (99.9%) and magnesium (99.99%), pressed in the pellet form. A somewhat new synthesis route encompassing encapsulation of subliming Mg by La from all sides has been adopted by us [14]. The superiority of this method is that when the pellets are melted, practically no magnesium escapes. The pellets were melted in a pre-baked quartz tube under an argon atmosphere with the help of a radio-frequency induction furnace (12 kW). To avoid contamination of the flux ingredients (particularly magnesium), water was circulated in the outer jacket. Then the as-prepared intermetallic, which presumably possesses very

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nearly the envisaged stoichiometry, was quenched to room temperature. In the next step, the composite alloys La_2Mg_{17}–x wt % $LaNi_5$ with $x = 10$, 20, 30 and 40 were synthesized. Pre-synthesized $LaNi_5$ (Ergenics) which was characterized through X-ray diffraction (XRD) was employed for synthesis of the composite materials. Pellets of homogeneous mixtures of La_2Mg_{17} and $LaNi_5$ in the proper stoichiometric ratios were melted in the r.f. induction furnace under an Ar atmosphere with the experimental set-up already mentioned.

The as-synthesized composite materials were characterized through XRD. A Philips wide-angle X-ray powder diffractometer PW-1710 was used for this purpose. Transverse sections of the specimens were cut and polished by standard metallographic techniques and the compositions of the as-synthesized alloys were determined by PV-9900 equipment for energy-dispersive analysis of X-rays (EDAX) attached to a Philips EM-CM-12 electron microscope.

The hydrogen storage characteristics were evaluated through evaluation of pressure–composition isotherms of the as-prepared composite alloys. The P–C–T characteristics were monitored by a volumetric method after preliminary outgassing of the reactor vessel, employing the set-up described elsewhere [15]. The as-synthesized samples were activated by applying a hydrogen pressure of ~ 33 kg cm^{-2} and heating at 360 ± 10 °C for about 6 h. The pressure changes were continuously monitored at high temperature to determine the dehydriding characteristics during the desorption process.

3. Results and discussion

The dehydriding behaviour of the composite alloy La_2Mg_{17}–x wt % $LaNi_5$ was measured for several values of x (10, 20, 30, 40) at a temperature ranging from 350 to 400 °C. Fig. 1a–d show the kinetic curves of dehydrogenation at different temperatures and at a pressure (P) of 4 kg cm^{-2} for La_2Mg_{17}–x wt % $LaNi_5$ with $x = 10$, 20, 30 and 40, respectively. These results indicate that desorption is strongly affected by temperature. The initial release of hydrogen from the materials was linear with time and decreased at longer times. It was found that addition of $LaNi_5$ to La_2Mg_{17} accelerated the hydriding rate by about 3–4 times in comparison with La_2Mg_{17} alone. The curves exhibited by Fig. 1a–d suggest that the highest hydrogen storage capacity corresponds to $x = 10$, i.e. La_2Mg_{17}–10% $LaNi_5$.

In order to verify this and to make an estimate of the hydrogen storage capacity, the pressure composition isotherms of La_2Mg_{17}–x wt % $LaNi_5$ for various values of x were evaluated. Representative P–C isotherms for the as-prepared composite alloys are shown in Fig. 2a–d for $x = 10$, 20, 30 and 40, respectively. It is clear from the P–C isotherms that the maximum weight percentage of hydrogen desorbed from the material is 5.24 for $x = 10$ (at 400 ± 10 °C). In all cases, clear-cut plateaux were observed. As seen from the figures, dissociation pressure–composition isotherms vary considerably according to the amount of $LaNi_5$ which is added to La_2Mg_{17}. Obviously, the desorption rate depends on the temperature and pressure under which the alloy has been hydrided. It was noticed that after ten hydrogenation–dehydrogenation cycles, the sample corresponded to a fine particle-size powder. It was also observed that interaction with hydrogen of the composite alloys La_2Mg_{17}–x wt % $LaNi_5$ led to decomposition into hydride phases of La and Mg, even at 125 °C for $x = 40$ to 325 °C for $x = 10$. The temperature at which hydrogen absorption took place became lower with increasing $LaNi_5$ content in the composite alloy.

In order to understand the role of $LaNi_5$ addition, which significantly accelerated the hydrogen desorption rate of La_2Mg_{17}, structural/microstructural and chemical analysis of the phases of the composite alloys were carried out using XRD, SEM and EDAX techniques. It was found that the hydriding rate and hydrogen storage capacity were closely related to the

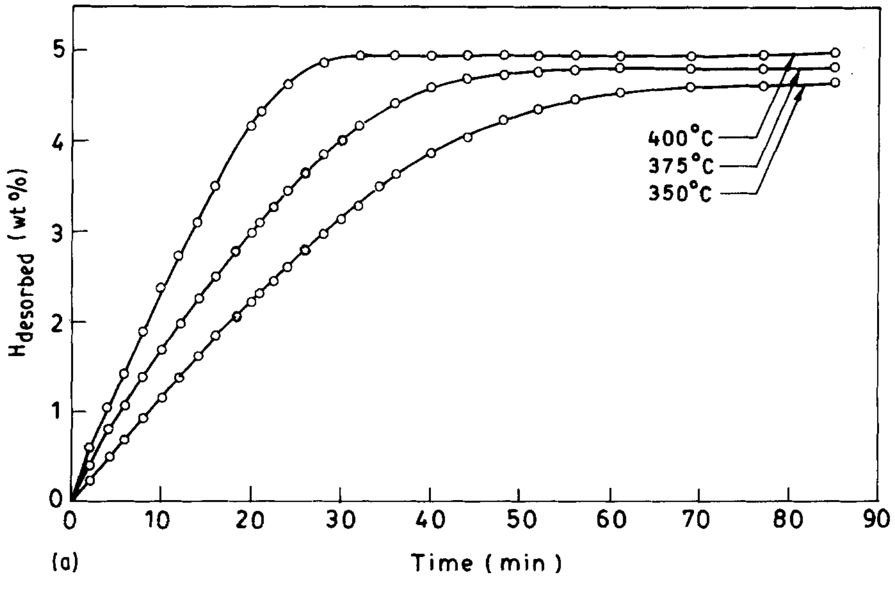
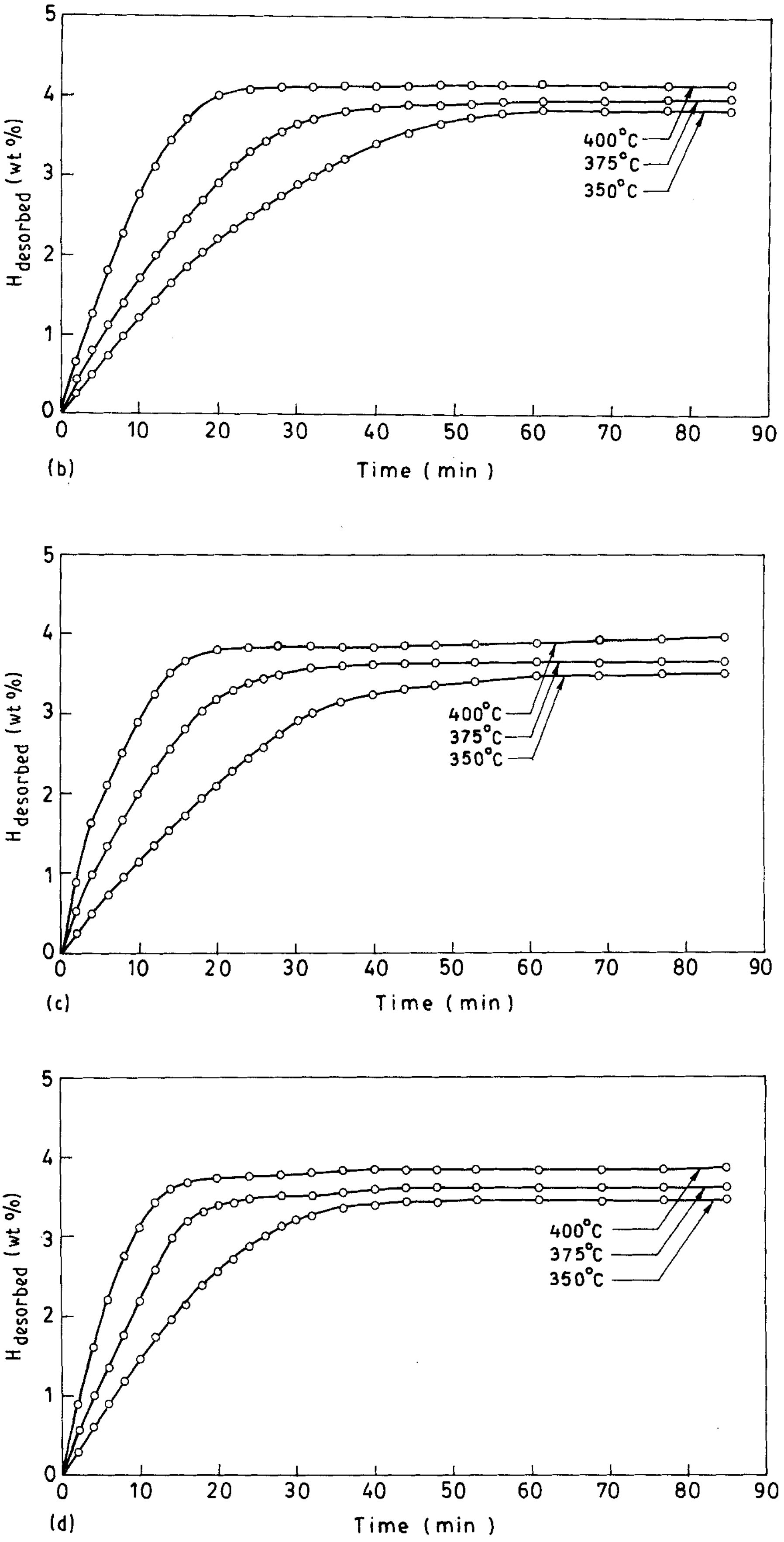


Figure 1 Kinetic curves of hydrogen desorption at $P = 4$ kg cm^{-2} and different temperatures for the alloys La_2Mg_{17}–x wt % $LaNi_5$ with $x =$ (a) 10, (b) 20, (c) 30 and (d) 40.



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microstructure and types of phase present in the alloys. Fig. 3a and b show representative X-ray diffraction patterns of as-synthesized La_2Mg_{17}–x wt % $LaNi_5$ for $x = 10$ and 40, respectively. These results revealed that the dominant phase present in the composite alloys was La_2Mg_{17}. However, minority phases $MgNi_2$, $LaNi_3$ and Ni were also found to be present (see Fig. 3a and b). It is expected that an important

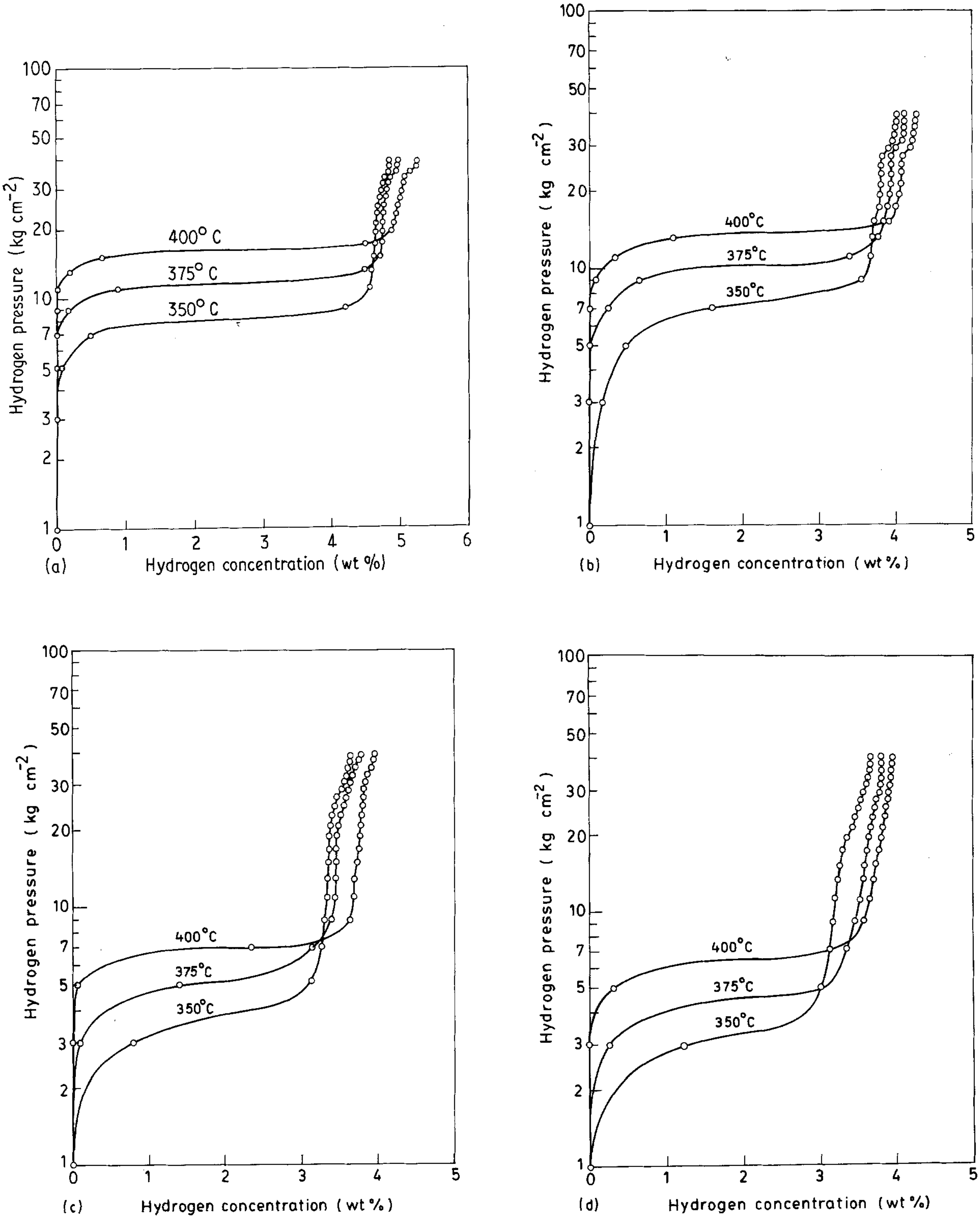

Figure 2 Pressure–composition isotherms of the composite alloys La_2Mg_{17}–x wt % $LaNi_5$ with x = (a) 10, (b) 20, (c) 30 and (d) 40.

parameter influencing hydrogenation–dehydrogenation is the surface Ni in contact with La_2Mg_{17} and other Ni-bearing phases. Free Ni was present in the as-synthesized composite alloys for all values of x. As is known, Ni on the surface decreases the activation energy of dissociation of hydrogen molecules. The hydriding rate and storage capacity are probably dependent on the Ni-bearing phases which form sites favourable to hydride nucleation, and may also serve as channels by which the hydrogen would enter and come out of the bulk of the main phase. The rapidity with which the composite alloys absorb and desorb hydrogen seems to suggest that the additional phases, particularly those embodying Ni, may also affect the kinetics and play a crucial role in the acceleration of hydriding rates of composite alloys. This conclusion is indirectly confirmed by experimental data on desorption from the hydrided composite alloys.

In order to elucidate the influence of $LaNi_5$ on the hydrogenation–dehydrogenation characteristics of La_2Mg_{17} intermetallic, scanning electron microscopy as well as EDAX analysis of the La_2Mg_{17}–x wt %

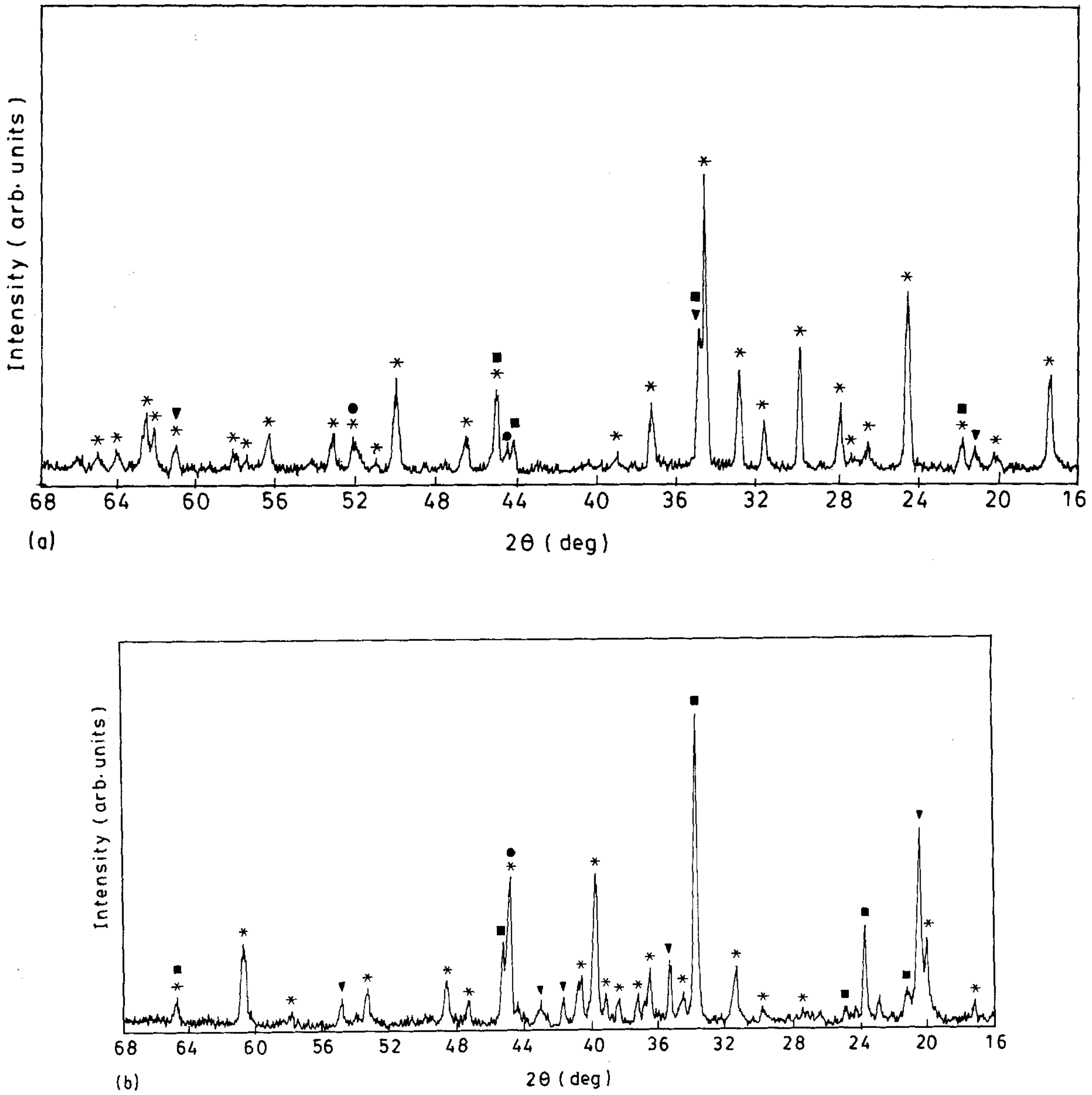

Figure 3 X-ray diffraction patterns of the as-synthesized composite alloys (a) La_2Mg_{17}–10 wt % $LaNi_5$ and (b) La_2Mg_{17}–40 wt % $LaNi_5$. Different phases are outlined: (✱) La_2Mg_{17}, (▼) $LaNi_3$, (■) $MgNi_2$, (●) Ni.

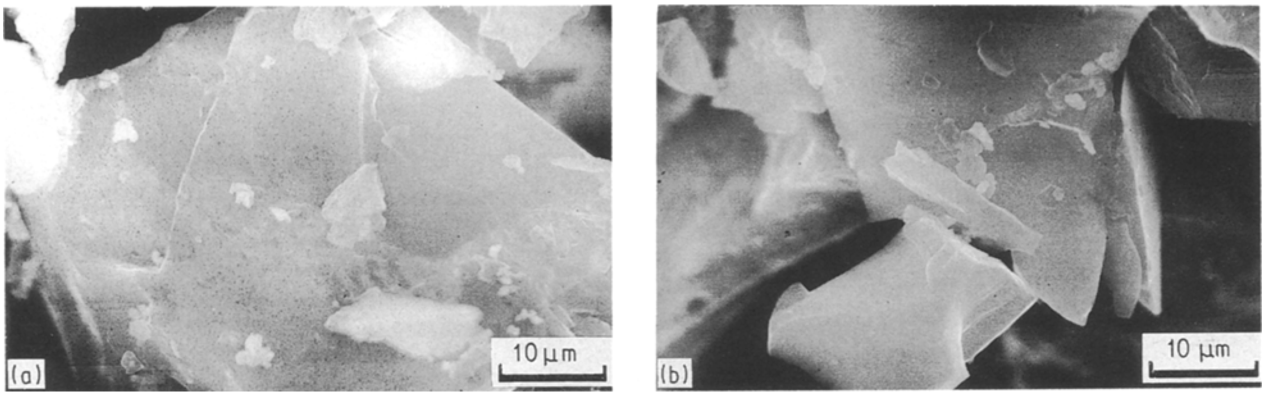

Figure 4 Scanning electron micrographs of the as-synthesized composite alloys (a) La_2Mg_{17}–10 wt % $LaNi_5$ and (b) La_2Mg_{17}–40 wt % $LaNi_5$.

$LaNi_5$ alloys from various cross-sections of the material were undertaken. Fig. 4a and b show scanning electron micrographs of the as-prepared composite alloy La_2Mg_{17}–x wt % $LaNi_5$ for $x = 10$ and 40, respectively. The micrographs demonstrate the multiphasic nature of the material, which is in conformity with the XRD results already described. The dominant microstructural feature corresponds to the La_2Mg_{17} matrix (represented by larger crystallites) and the smaller precipitate-like particles correspond

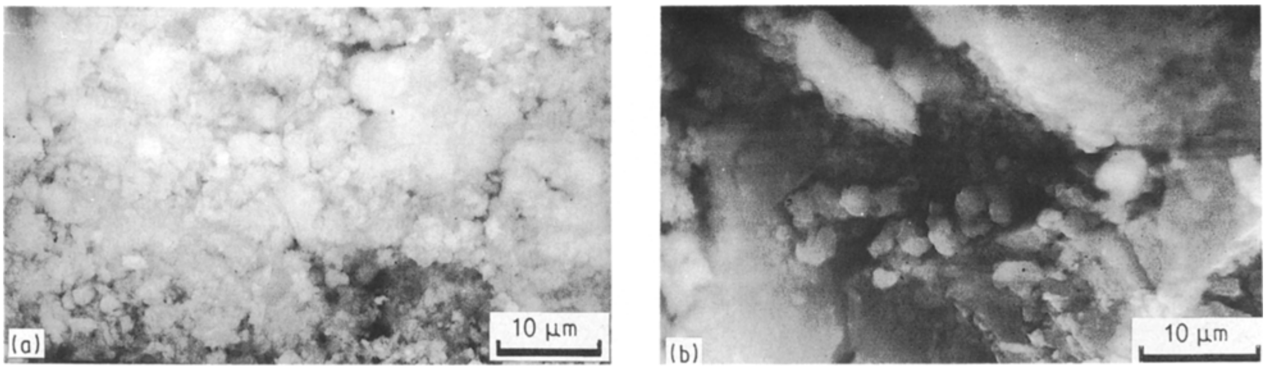

Figure 5 Scanning electron micrographs of the dehydrogenated composite alloys (a) La_2Mg_{17}–10 wt % $LaNi_5$ and (b) La_2Mg_{17}–40 wt % $LaNi_5$, after ten absorption–desorption cycles.

to minority phases like $MgNi_2$, $LaNi_3$ and free Ni. The presence of free Ni, either embodied in the $MgNi_2$ or in the free form, presumably accelerates the hydrogen absorption–desorption, leading to the better kinetics observed for the composite alloys La_2Mg_{17}–x wt % $LaNi_5$. The difference in the hydriding characteristics of the composite alloys for various values of x is considered to be due to differences in the amounts and types of the phases present in the alloys. A comparison of the surface for as-prepared and dehydrogenated composite alloys La_2Mg_{17}–x wt % $LaNi_5$ ($x = 10$ and 40) is given in Fig. 4a and b and Fig. 5a and b, respectively. It can be seen that whereas in both the cases hydrogenation produces fracture and breakage of the surface into small domains, this tendency is more pronounced for $x = 10$ than for $x = 40$.

4. Conclusion

The aim of this study was to increase the hydriding and dehydriding rates for La_2Mg_{17} intermetallic. With this in view, we have investigated the synthesis, structural characterization and hydrogenation behaviour of the new composite material La_2Mg_{17}–x wt % $LaNi_5$ (x = 10, 20, 30 and 40). These alloys react with hydrogen at 360 ± 10 °C and they have nearly the same hydriding rate. The as-synthesized composite alloy La_2Mg_{17}–10 wt % $LaNi_5$ shows the highest hydrogen desorption capacity (5.24%). In contrast to the presently known high hydrogen storage capacity of 3.8% for Mg_2Ni, the present capacity of 5.2% is higher by about 36%. These results show that the dehydriding rate of La_2Mg_{17} increases in the presence of $LaNi_5$. The dependence of hydriding parameters of these composite alloys on the phase composition and microstructure has been elucidated. The increase in the hydrogenation rate appears to be produced by a catalytic effect of the minority phases $MgNi_2$ and $LaNi_3$, in addition to free Ni on the surface and in the bulk. The active Ni precipitates presumably split H_2 into H (atomic hydrogen). The hydrogen then reacts with the La_2Mg_{17} phase which is the hydrogen acceptor to form the hydrides. The reverse reaction takes place on dehydrogenation. These results suggest that the activation energy depends strongly on the surface structure of the as-synthesized material.

Acknowledgements

The authors are grateful to the Department of Non-Conventional Energy Sources and the Council of Scientific and Industrial Research for financial support. The authors are grateful to Professor. A. Balchin (UK), Dr K. Sapru (USA), Professor M. V. C. Sastri (Madras, India) and Dr K. V. C. Rao (Hyderabad, India) for helpful discussions.

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Received 6 January
and accepted 17 November 1992