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SIZE-DEPENDENT EFFECTS

Hydriding properties of the nanocomposite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ obtained by ball milling

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Abstract The hydrogen sorption properties of the nanocomposite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ obtained by mechanical alloying in inert atmosphere were investigated. Absorption measurements were performed under a hydrogen pressure P = 1 MPa at temperartures ranging from 373 to 573 K, while desorption studies proceeded at P = 0.15 MPa and temperatures of 573 and 553 K. The addition of the intermetallic compound $Mg_2Ni_{0.8}Co0_{0.2}$ was shown to improve the hydriding kinetics of magnesium. The composite exhibited a high hydrogen capacity which did not decrease even after a large number of absorption–desorption cycles. Comparison of the hydriding kinetics of the intermetallic compounds Mg_2Ni and $Mg_2Ni_{0.8}Co_{0.2}$ indicated facilitation of the process by the presence of cobalt in the alloy. Magnetic measurement data on $Mg_2Ni_{0.8}Co_{0.2}$ showed formation of superparamagnetic precipitations of nickel and cobalt playing the role of active centres for dissociative chemisorption of hydrogen. The behaviour of the composite was explained by the catalytic effect of the intermetallic $Mg_2Ni_{0.8}Co0_{0.2,}$ the existence of Ni and Co clusters on the surface and the process of mechanical alloying.

Introduction

Due to its high absorption capacity, magnesium is considered as one of the most promising materials for hydrogen storage. Unfortunately, this capacity is attained after preliminary activation at high temperatures and pressures, the hydriding kinetics being poor below 600 K. For that reason, a large number of investigations [1–10] have been aimed at improving the hydriding–dehydriding kinetics of magnesium by preparing, mostly with the use of high-energy ball milling, of magnesium-based composites containing several metals, metal oxides and intermetallics. Data from the literature show very favourable results when an intermetallic compound containing a 3d-metal is added to magnesium [8–12]. In this case, the hydriding process is considerably accelerated, the hydrogen absorption capacity remaining high.

Previous results exhibited that a pronounced catalytic effect was shown with additives of the intermetallics $Mg_2Ni_{1-x}Me_x$ in cases when Me = Fe or Co [11, 12]. The presence on the sample surfaces of 3d-metal clusters facilitating dissociative hydrogen chemisorption was the possible reason for this effect.

In the above studies it was shown that the most promising materials for hydrogen storage were the nanocomposites 85 wt.% Mg–15 wt.% $Mg_2Ni_{1-x}Co_x$ with $x = 0.1$ and 0.3. A sample of this type with $x = 0.2$ was investigated in the present work. In addition to further elucidation of the additive catalytic effect on the absorption–desorption properties of magnesium in the composite, the investigation was also aimed at obtaining information on how far the registered high absorption capacity of these composites is preserved after a large number of absorption–desorption cycles.

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This is very important if magnesium is to be used as a hydrogen storage material.

Experimental

Powdery magnesium, nickel and cobalt with a 99.9% purity were used for the preparation of the intermetallic compound $Mg_2Ni_{0.8}Co_{0.2}$. Pellets of an intimate mixture corresponding to the above composition were heated at 823 K for 120 h. The composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ was obtained by mechanical grinding in a Fritsch Pulverisette 5 planetary ball mill. The milling was performed under argon using stainless steel balls (diameter = 10 mm) and container (volume about 75 cm^3), the balls to sample ratio being 10:1. The rotation speed of the mill was 200 rpm and the grinding duration, 30 min.

The hydrogen absorption–desorption characteristics of the composite were determined by the volumetric method described in Ref. [13]. Hydriding was studied at T = 373, 423, 473 and 573 K under a pressure of 1 MPa, while the desorption of hydrogen was measured at P = 0.15 MPa and temperatures of 553 and 573 K.

The phase compositions of the intermetallic compound obtained and the hydrided and dehydrided composite samples were checked by X-ray phase analysis using CuKα radiation.

Magnetic susceptibility measurements of hydrided and dehydrided samples of $Mg_2Ni_{0.8}Co_{0.2}$ were performed by the Faraday method.

The specific surface area alteration of samples subjected to a large number of absorption–desorption cycles was controlled by adsorption of nitrogen.

Results and discussion

Hydriding kinetics

X-ray phase analysis of the $Mg_2Ni_{0.8}Co_{0.2}$ sample obtained as described above showed that the formation of the main phase of a Mg_2Ni-type during the synthesis was accompanied by the appearance of a parasitic impurity of the intermetallic compound $MgNi_2$. The X-ray diffraction pattern in Fig. 1 also reveals the presence of a certain amount of nonbonded cobalt. Darnaudery et al. [14] has established that with a large number of metals, among them with cobalt, the intermetallics remain single-phase with a Mg_2Ni-type structure up to $x = 0.25$ when prepared by melting of the elements at 1,173 K. In this study the synthesis has been carried out at 823 K and this is probably the reason for the presence of free cobalt in the product.

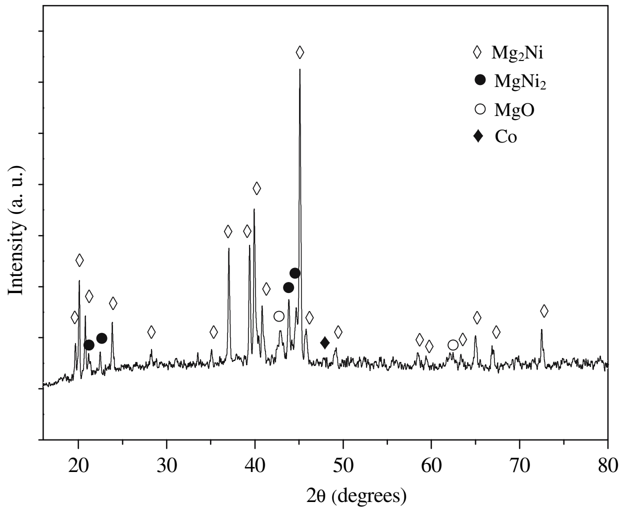

Fig. 1 X-ray diffraction pattern of the alloy with the nominal composition $Mg_2Ni_{0.8}Co_{0.2}$

The calculated values of the cell parameters of the phase with the nominal composition $Mg_2Ni_{0.8}Co_{0.2}$ are $a = 5.21$ Å and $c = 13.26$ Å. The parameters are very close to those of pure Mg_2Ni ($a = 5.21$ Å and $c = 13.23$ Å), which is not surprising, taking into account the closeness of the Ni and Co atomic radii ($R_{Ni} = 1.246$ Å and $R_{Co} = 1.252$ Å).

Figure 2 shows the kinetic curves of hydrogen absorption for the composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ at different temperatures and a pressure of 1 MPa. It is evident that, similarly to the previously studied magnesium composites with intermetallic compounds $Mg_2Ni_{1-x}Co_x$ having different compositions [12], here again, there is a significant absorption at relatively low temperatures.

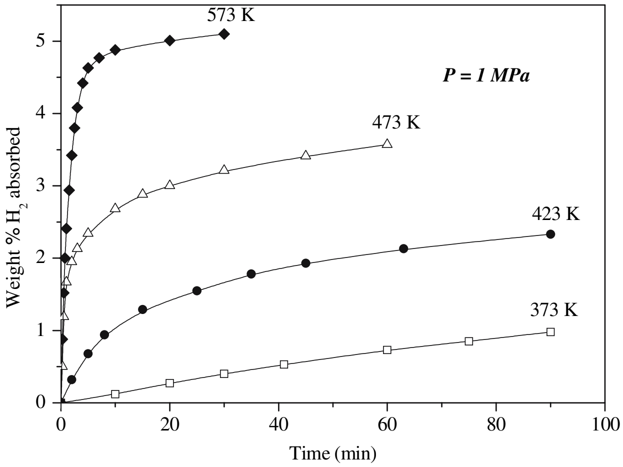

Fig. 2 Kinetic curves of hydriding of the composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ at different temperatures and P = 1 MPa

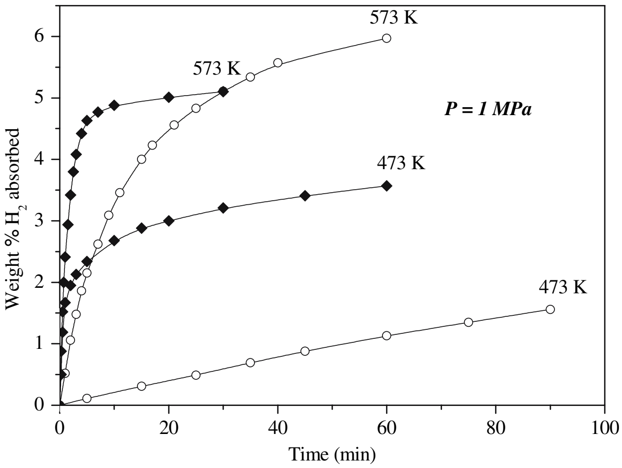

Fig. 3 Kinetic curves of hydriding at P = 1 MPa and T = 473 and 573 K, respectively, of: (○) pure magnesium; (♦) 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ composite

The effect of the intermetallic phase $Mg_2Ni_{0.8}Co_{0.2}$ on the hydriding kinetics of magnesium is illustrated in Fig. 3 where the relationships between the absorbed hydrogen amount and the duration of hydriding of pure magnesium and of a composite sample at a pressure of 1 MPa and temperatures of 573 and 473 K are given. The absorption capacity of the composite remains rather high and is attained in an incomparably shorter hydriding time. The curves presenting hydriding at 473 K clearly show the advantages of the composite as compared to pure magnesium.

The experimental values of the time needed for absorption of 20–80% of the whole possible hydrogen amount can be used to calculate the mean hydrogen absorption rate as proposed by Dehouche et al. [15]. Thus, this rate (1.33 wt.% H_2/min at 573 K) is very close to the value (1.36 wt.% H_2/min) registered with the composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.9}Co_{0.1}$ which has the best absorption–desorption characteristics among the magnesium composites with $Mg_2Ni_{1-x}Co_x$ intermetallics studied by the authors so far [12].

In a previous paper [16], the addition of the pure intermetallic phase Mg_2Ni was also shown to affect favourably the hydriding kinetics of magnesium in its composites obtained by mechanical alloying. This effect was smaller than that observed when part of the nickel in the additive is replaced by cobalt. It was assumed that the better kinetic characteristics should be associated with the presence of cobalt on the surface of the substituted samples, this increasing the catalytic effect of the intermetallic compound. Comparison of the kinetic curves during the first hydriding cycle of the two additives shown in Fig. 4 indirectly supports this supposition. Magnetic measurements on hydrided and dehydrided $Mg_2Ni_{0.8}Co_{0.2}$ were carried out with a view to its experimental confirmation.

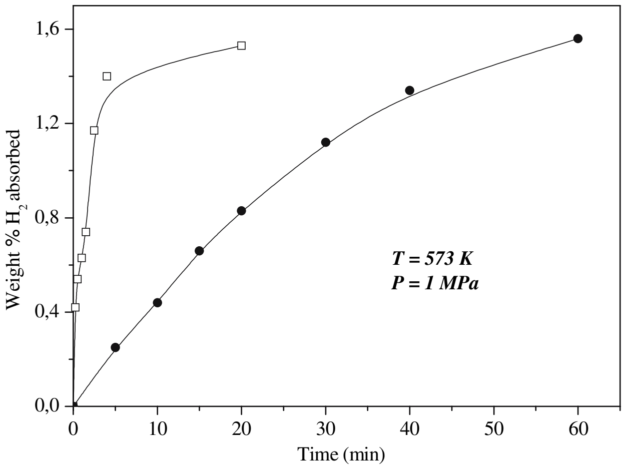

Fig. 4 Kinetic curves of hydriding at P = 1 MPa and T = 573 K of: (●) Mg_2Ni; (□) $Mg_2Ni_{0.8}Co_{0.2}$

It is worth noting that using magnetic susceptibility measurements, Siegmann et al. [17] established already in 1978 that during hydriding, precipitations of metallic Ni appeared on the surface of the $LaNi_5$ alloy. Dissociative chemisorption of H_2 was found to proceed on them, thus transforming them into sites supplying highly reactive hydrogen. More recently magnetic measurements and XPS analyses proved the existence of superparamagnetic 3d-metal precipitations on the surface of Mg_2Ni [18, 19], FeTi [19] as well as V–Ti–Ni and V–Ti–Fe alloys [20].

The data obtained in the present study by magnetic measurements on samples of hydrided and dehydrided $Mg_2Ni_{0.8}Co_{0.2}$ are given in Figs. 5 and 6. The initial intermetallic compound is strongly ferromagnetic, due

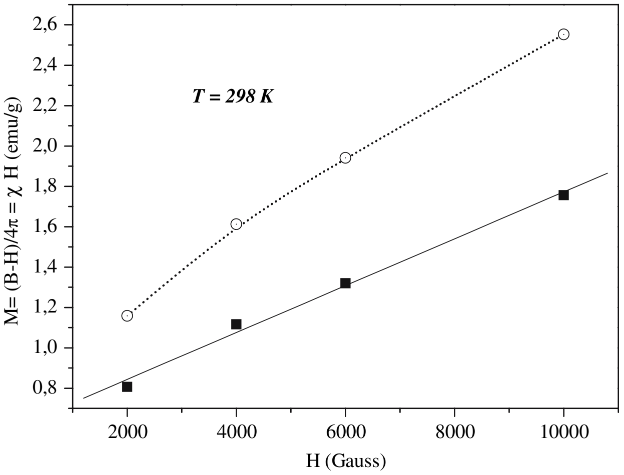

Fig. 5 Magnetization versus magnetic field dependences for: (■) hydrided $Mg_2Ni_{0.8}Co_{0.2}$; (○) dehydrided $Mg_2Ni_{0.8}Co_{0.2}$

to which no data on it are presented. The absence of a nonlinear dependence between the magnetization and the magnetic field (Fig. 5) which is more obvious with the dehydrided sample than the hydrided one, indicates that the dehydrided sample contains a larger number superparamagnetic clusters. The lower experimental values of the magnetization and the magnetic susceptibility after hydriding can be explained by the fact that part of these superparamagnetic particles participate in the hydriding process at sites of dissociative hydrogen chemisorption. From Fig. 6, it is clear that the values of χ for the hydrided and dehydrided intermetallic at H = 2,000 G and different temperatures show that after hydriding the amount of the active sites decreases. It is enough to compare, by way of example, the χ-values at room temperature, which are 4.7×10^{-4} and 6.8×10^{-4} emu/g for the hydrided and dehydrided samples, respectively.

Hydrogen absorption–desorption cycling of the composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$

The absorption properties of the composite under consideration were also investigated during cycling. Data were obtained on the hydrogen absorption capacity after 70 cycles at T = 573 K and P = 1 MPa. Figure 7 illustrates the results obtained after 60 and 4 min hydriding. With a hydriding duration of 4 min the absorption capacity of the composite shows only a weak trend to increasing with the number of cycles. The capacity remains practically constant and high irrespective of the number of cycles in cases when the sample is hydrided for 1 h.

The behaviour demonstrated by the composite after many cycles is probably associated with a change in its dispersion. Specific surface area data show that during the cycling the initial sample decrepitates and the surface becomes three times larger: from about 2 m^2/g to about 6 m^2/g. This result is, however, due to several factors which have different and often opposite effects on the size of the interface: (i) oxidation of the surface by the oxygen impurity present in the hydrogen which blocks part of the magnesium and affects the surface accessible to the reaction; (ii) splitting of the oxide layer, leading to the appearance of a new interface; (iii) sintering of the sample, this resulting in a decreased interface.

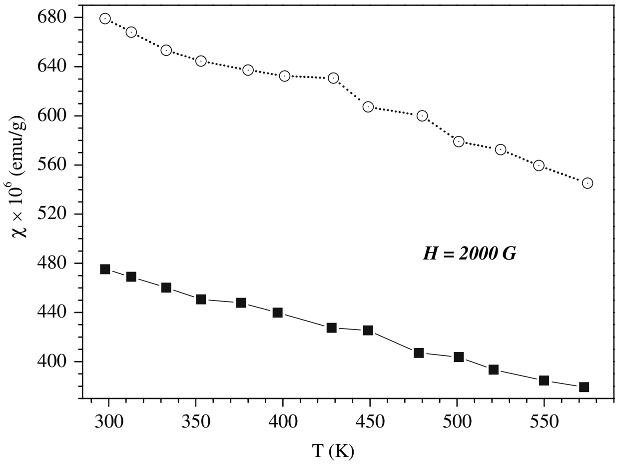

Fig. 6 Magnetic susceptibility versus temperature dependences for: (■) hydrided $Mg_2Ni_{0.8}Co_{0.2}$; (○) dehydrided $Mg_2Ni_{0.8}Co_{0.2}$

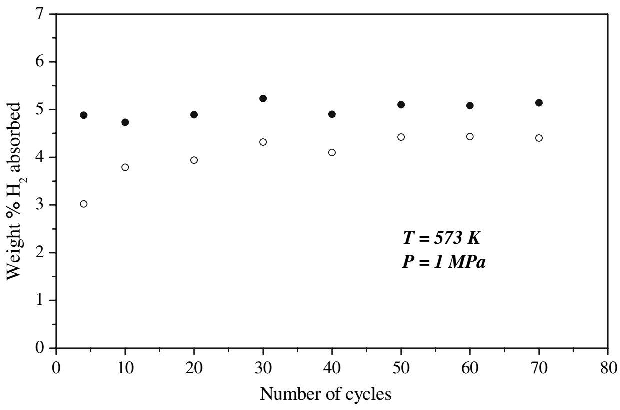

Fig. 7 Absorption capacity change of the composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ with the number of hydrogen absorption–desorption cycles (○) 4 min hydriding; (•) 60 min hydriding

On the other hand, the absorption process, especially in the beginning of hydriding, is strongly affected by the presence of active sites of dissociative chemisorption of hydrogen, this being the rate controlling step [21, 22]. Boudart et al. [23] established that the MgO formed on the surface of magnesium-containing systems may cause the appearance of paramagnetic defects able to capture protons, thus facilitating hydrogen chemisorption. During the continuous oxidation of the composite under consideration by the oxygen present in hydrogen, after a number of cycles the concentration of such defects on the sample surface could reach a sufficient value. These paramagnetic sites along with the available nickel and cobalt precipitations probably also play a definite catalytic role during the hydriding of the composite.

Dehydriding of the composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$

The desorption of hydrogen from the composite investigated at 573 and 553 K is illustrated by the kinetic dependences in Fig. 8. When dehydriding

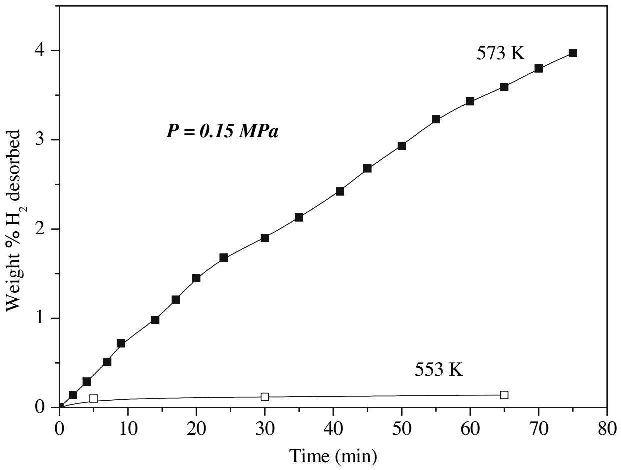

Fig. 8 Kinetic curves of dehydriding of the composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ at P = 0.15 MPa and temperatures of 553 K (□) and 573 K (■), respectively

proceeds at 573 K, the time measured, $\tau_{1/2}$ (min), for which desorption of half of the hydrogen absorbed at this temperature occurs, is 43 min. This value is commensurable with the value $\tau_{1/2}$ = 50 min determined in a previous paper [12] for the composite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.9}Co_{0.1}$. A temperature drop of only 20 K, down to 553 K deteriorates considerably the hydrogen desorption from the sample investigated. This is probably associated with an enhanced stability of the hydride of the $Mg_2Ni_{0.8}Co_{0.2}$ alloy which has been found for a close alloy composition ($Mg_2Ni_{0.75}Co_{0.25}$) by Darnaudery et al. [14].

Conclusion

In the present paper the nanocomposite 85 wt.% Mg–15 wt.% $Mg_2Ni_{0.8}Co_{0.2}$ was shown to be a promising material for hydrogen storage, showing good hydriding. At relatively low temperatures it reaches high absorption capacity values which are preserved for many absorption–desorption cycles. The behaviour demonstrated by the composite was attributed to the catalytic role of the intermetallic phase $Mg_2Ni_{0.8}Co_{0.2}$ and the formation of superparamagnetic precipitations of Ni and Co on the sample surfaces which favour the dissociative chemisorption of hydrogen as well as to the preparation method of the composite.

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