Hydrogenation properties of Mg_2AlNi_2 and mechanical alloying in the Mg–Al–Ni system

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ABSTRACT

Samples with Mg_mAlNi_n composition (m, $n \leq 3$) were synthesized by ball milling in form of crystalline nanoparticles, and were found to be a single phase with partially disordered CsCl-type cubic structure. For compositions with large m and small n, minor quantities of Mg and Mg_2Ni are segregated. XRD Rietveld refinements indicate that the two $Pm\bar{3}m$ sublattices basically have (Mg, Al) and (Mg, Al, Ni) occupations, respectively. Hydrogenation experiments on the Mg_2AlNi_2 sample by the PCI technique showed a reversible absorption/desorption of 1.4 wt% H_2 with formation/decomposition of the MgH_2 and Mg_2NiH_4 hydrides. The van't Hoff plot gives $\Delta_r H = 67.7$ kJ mol^{-1} (enthalpy of dehydrogenation), and $T_0 = 524$ K (temperature of dehydrogenation at $p = 0.1$ MPa). A kinetic study of the gas release at 535 K showed a satisfactory behaviour, with a first fast step followed by a slower one in both the absorption and desorption processes.

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1. Introduction

Despite its well known weak points, magnesium hydride is still often considered to be the best hydrogen storage material which is presently available. Many efforts were made in the last years to improve its performance by lowering the decomposition temperature and/or improving the corresponding kinetics. In most cases, doping or alloying of elemental Mg with very minor quantities of other metals, oxides or different compounds was attempted; positive results were often obtained as far as the kinetics, but not thermodynamics, of the $MgH_2 \rightarrow Mg + H_2$ reaction is concerned [1–3].

The way leading to true Mg-containing inter-metallic compounds or alloys was comparatively less explored. Although the storage capacity may be expected to decrease drastically on reducing the Mg contents of the system, significant improvements could be achieved with a lower dehydrogenation temperature. Within this line of research, the Mg–Ni and Mg–Al binary systems were investigated. The first one, which provides the important hydrogenation reaction $Mg_2Ni + 2H_2 \rightarrow Mg_2NiH_4$, is also attractive because of the well known catalytic properties of Ni [3]. Nanocrystalline $Mg + Mg_2Ni$ composites were thus claimed to improve the hydrogenation kinetics of both components [4]. The Mg–Al system aroused interest in the hope that, owing to the quite unstable

Al–H bonding in aluminium hydride [5], a mixed Mg–Al hydride with intermediate bond strength between MgH_2 and AlH_3 could be formed. This was not found to occur; yet the $Mg_{17}Al_{12}$ binary compound proved to hydride reversibly with formation of MgH_2 and Al [6–8].

Concerning the Mg–Al–Ni ternary composition, some studies were performed by doping Mg_2Ni with very minor Al quantities [9–11], and an improvement of the desorption kinetics was generally observed. The $Mg_{1-x}Al_xNi$ [12] and $Mg_{2-x}Al_xNi$ [13–16] systems were explored within the $x \leq 0.5$ compositional range, but in most cases the reaction with hydrogen was characterized only partially or was not considered at all. In particular, the Mg_3AlNi_2 compound turned out to present different cubic phases according to the preparation method: a $Fd\bar{3}m$ $NiTi_2$-type crystal structure, when synthesized by conventional heat treatments [13,15,16], and a $Pm\bar{3}m$ CsCl-type structure when prepared by ball milling [14]. Also the ball milled $MgAlNi_2$ compound showed the CsCl-type phase [12]. The hydrogenation capacity proved to decrease substantially with the increase of the Al contents, but the equilibrium temperature of dehydrogenation at/or above room pressure was not studied.

We thus started an investigation of a broader compositional area within the Mg–Al–Ni ternary system, along the Mg_mAlNi_n lines with m, $n = 1, 2, 3$. The first aim was to synthesize samples with several compositions by mechanical alloying, in order to obtain nanocrystalline materials with best performance for the hydrogenation reaction. Secondly, we wanted to understand in what conditions single-phase or poly-phase materials are obtained, and to characterize their crystallographic features. The last goal was to

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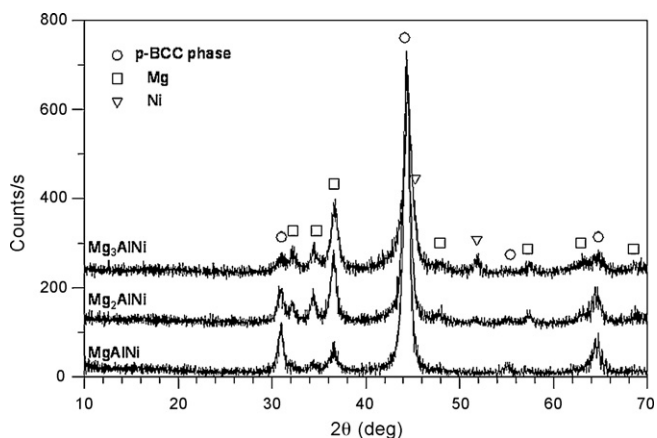E-mail address: catti@mater.unimib.it (M. Catti).

Fig. 1. Powder XRD patterns (CuKα radiation) of the Mg$_m$AlNi samples with $m = 1$–3. The main phase is a pseudo-body-centered-cubic ($Pm\bar{3}m$ space group) AlNi-type solid solution.

Fig. 2. Powder XRD patterns (CuKα radiation) of the Mg$_m$AlNi$_2$ samples with $m = 1$–3.

assess the thermodynamic and kinetic behaviour of some of these samples with respect to hydrogen absorption/desorption. In particular, we intended to clearly identify the active chemical species in the hydride formation, and to elucidate their effects on the temperature of dehydrogenation of the material at pressures not lower than 0.1 MPa.

2. Experimental

The materials were prepared by mechanical alloying in Retsch PM100 planetary and a Spex 8000 high-energy ball mills (Ar atmosphere), with milling times varying from 30 to 100 h, and ball-to-powder-mass-ratios of 10:1. Reagent-grade pure metals were used as starting materials, and all samples were always handled in a glove-box filled with purified argon. The progress of the mechanochemical reaction was periodically checked by X-ray powder diffraction (XRD) in the course of the milling. The reaction was considered to be ended when no appreciable XRD change appeared on further milling. A Bruker D8 Advance powder diffractometer, with CuKα radiation ($\lambda = 1.5418$ Å) and secondary-beam monochromator, was used for the X-ray characterization. Microstructural analyses were performed by means of a Scanning Electron Microscope (SEM: Tescan Vega Ts 5136) with an energy-dispersive X-ray spectrometer (EDX: EDAX Genesis 4000).

Thermodynamic and kinetic measurements of the hydrogenation/dehydrogenation reactions were done by the method of pressure-composition-isotherm (PCI), employing an automatic Sievert-type apparatus of the Advanced Materials Corporation. The sample of 0.5 g was loaded into the 5 cc reactor located in a furnace with temperature control. After evacuation, hydrogen gas of high purity was introduced at increasing pressures.

3. Results and discussion

3.1. Synthesis and XRD characterization of the Mg–Al–Ni alloys

Samples were synthesized (Spex 8000, 30 h milling time) with the 1:1, 1:2, and 1:3 Al/Ni molar ratios; for each of them, the Mg/Al ratio was increased from 1:1 to 3:1. In case of the Mg$_2$AlNi$_2$ composition, for which detailed hydrogenation measurements are reported below, other samples were also prepared by 100 h milling (Retsch equipment). As main feature, the final XRD pattern of all samples showed four broad peaks of the CsCl-type $Pm\bar{3}m$ cubic structure in the $2\theta \leq 70°$ range (Figs. 1–3): (1 0 0), (1 1 0), (1 1 1), and (2 0 0) at increasing angles. The same structure is observed for the AlNi alloy, with $a = 2.882$ Å. The (1 0 0) and (1 1 1) reflexions, distinguishing the $Pm\bar{3}m$ from the $Im\bar{3}m$ space group (BCC lattice), appear to be comparatively weak in all diffractograms. Thus, the main phase present in all samples looks like a partially ordered solid solution with AlNi-type structure; if the two atomic sites at $x = 0$, $y = 0$, $z = 0$ and 1/2, 1/2, 1/2 had the same average chemical composition, a true BCC lattice would be attained. In particular, as the intensity of Bragg peaks can be hardly affected by the Mg/Al dis-
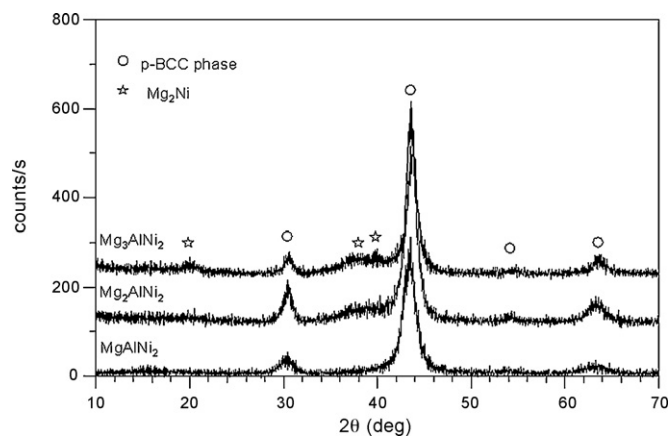
tribution in view of the close scattering powers of such atoms, we can conclude that some disordering of (Mg, Al) vs. Ni should occur in at least one of the two sites of the CsCl-like structure, at variance with the full order observed in the AlNi alloy. A progressive separation of Mg out of the pseudo-BCC solid solution appears clearly to occur as m increases along each Mg$_m$AlNi$_n$ series (Figs. 1–3). In addition to elemental Mg, also Mg$_2$Ni and Ni may separate for the compositions richest in Mg (Table 1). We also prepared samples with Mg/Al ratio of 4:1; in this case larger quantities of the same phases were observed in addition to the p-BCC solid solution, and results are not reported here.

Rietveld profile refinements of the collected XRD powder patterns were performed by the FULLPROF code [17]. Taking into account the poor quality of the data (small scattered intensity and few very broad Bragg peaks), due to low crystallinity of the nanoparticles, it was not possible to distinguish between Mg and Al atoms. The starting structure was then modelled with a full Mg atom in the 0, 0, 0 site and a mixture of Mg and Ni consistent with the sample nominal composition in the 1/2, 1/2, 1/2 site, considering Al equivalent to Mg. The Mg/Ni fraction was refined on each site, but the quantity of Ni in 0, 0, 0 never attained 10%, so that in most cases the starting composition was finally kept fixed. A pseudo-Voigt function was used for the Bragg peak profile, and the background was treated by interpolation through a number of selected points in the pattern. For the samples of the Mg$_m$AlNi series, with larger amounts of impurities (Fig. 1), Mg was included as a second phase in the refinement. Convergence was attained with average R_p and R_{wp} values of 0.13 and 0.18. The unit-cell parameters are reported in Table 1. The uncertainty is estimated to be of the order of 0.01 Å from results on different samples with the same composition. A
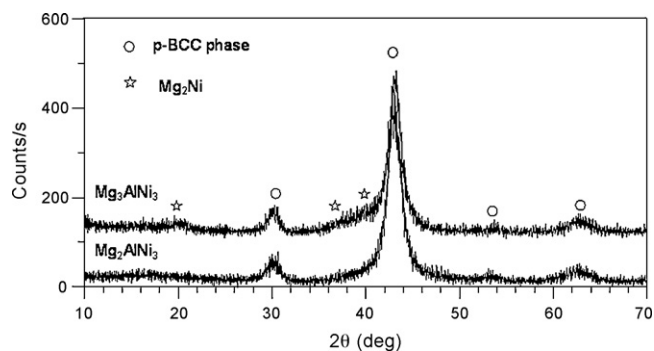

Fig. 3. Powder XRD patterns (CuKα radiation) of the Mg$_m$AlNi$_3$ samples with $m = 2$–3.