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Hydrogen sorption properties of the nanocomposites Mg–Mg₂Ni_{1-x}Fe_x

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Abstract

The hydrogen sorption properties of the composites 85 wt.% Mg–15 wt.% Mg₂Ni_{1-x}Fe_x ($x=0, 0.1$ and 0.3) prepared by high-energy ball milling were studied. It was shown that the presence of a Mg₂Ni_{1-x}Fe_x additive significantly improved the kinetics of hydrogen absorption and desorption of magnesium, the absorption capacity remaining sufficiently high even at temperatures between 423 and 573 K. The catalytic effect of the Mg₂Ni_{1-x}Fe_x intermetallics was explained as due to the formation of a second hydride, Mg₂NiH₄, to the appearance during the mechanical alloying of defects facilitating the formation of hydride nuclei and to the presence of Ni and Fe clusters on the surface of nanocomposite particles.

Keywords: Hydrogen absorbing materials; Nanostructures; Mechanical alloying; Gas–solid reactions; X-ray diffraction

1. Introduction

One of the promising properties of magnesium and its alloys is the possibility of reversible formation of hydrides. Unfortunately, the high absorption capacity of magnesium (7.6 wt.% H₂) is attained after preliminary activation at high temperature and pressure. Its hydriding kinetics are poor below 600 K, which is also the minimum temperature needed for the dehydriding reaction. For that reason, a large number of investigations have been aimed at improving the hydriding–dehydriding kinetics of magnesium by preparing composites on its basis with an absorption capacity close to that of pure magnesium.

During the past years, high-energy ball milling has proved to be a suitable method for the preparation of such composites with improved hydrogen sorption properties. Ball-milling results in formation of a pure and reactive surface with dislocations and other defects [1–3]. The additives present in the composites along with magnesium very often play the role of catalysts in the hydriding and dehydriding processes. Thus, mechanical alloying is a simple way of introducing a catalyst into the reaction system [4,5].

Various substances have been used as additives to the magnesium nanocomposites obtained by ball milling. In a series of papers Mg is mechanically alloyed with some transition metals (Ce, Ti, Nb, Fe, Co, Ni) [6–10] or an intermetallic additive like MNi₅ (pure or partially substituted LaNi₅, MmNi₅ or YNi₅ [11–18]), FeTi_{1.2} [19], ZrNiCr [20], ZrNi_{1.6}Cr_{0.4} [20] and ZrFe_{1.4}Cr_{0.6} [21,22]. Nickel belongs to a special category as it forms with magnesium the intermetallic compound Mg₂Ni able to absorb hydrogen reversibly as a ternary hydride, Mg₂NiH₄. The possible important applications of hydrogen storage materials of the Mg–Ni system are the reason for a large number of papers dealing with them, the most important results having been summarized recently in a review of Orimo and Fujii [23].

Depending on the nature and quantity of the additive, its catalytic effect on hydriding and dehydriding of magnesium may be due to the appearance of: (i) new intermetallic phases; (ii) binary metal hydrides with a varying stoichiometry which may ‘pump’ hydrogen to the magnesium surface; and (iii) clusters of transition metals on the surface of Mg particles playing the role of active sites for dissociative chemisorption of hydrogen.

The present paper represents a continuation of the authors’ work on the hydrogen storage characteristics of magnesium mechanically alloyed with various additives [11,15,18,24]. As was pointed out above, Mg₂Ni absorbs

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hydrogen with formation of the ternary hydride Mg_2NiH_4 , which is accompanied by an increase in the volume. In the literature there is also information on the catalytic effect of iron clusters when they are present on the surface of the magnesium particles. In view of this it is of interest to establish how a magnesium composite containing Mg_2Ni or $\text{Mg}_2\text{Ni}_{1-x}\text{Fe}_x$ would behave during hydriding–dehydriding. A composite of that kind could combine the high hydrogen absorption capacity of magnesium with the lower dehydriding temperature of Mg_2Ni . On the other hand, the presence of iron in the composite should also have a favourable effect on the hydriding kinetics.

2. Experimental

Powdery magnesium, nickel and iron of 99.9% purity were used for the preparation of Mg_2Ni and $\text{Mg}_2\text{Ni}_{1-x}\text{Fe}_x$ ($x=0.1$ and 0.3). Mixtures having the corresponding composition were pelleted and heated under argon at 823 K for 120 h. The samples obtained were mechanically, ground with magnesium (85 wt.% Mg+15 wt.% $\text{Mg}_2\text{Ni}_{1-x}\text{Fe}_x$) in a Fritsch Pulverisette 5 planetary ball mill to obtain mechanically alloyed composites. The grinding proceeded under argon using stainless steel balls (diameter=10 mm) and container (volume \approx 75 cm³), the balls to sample weight ratio being 10:1. The rotation speed of the mill was 200 rpm and the milling time, 30 min.

The hydrogen absorption–desorption characteristics of the mechanically alloyed samples thus obtained were determined by the volumetric method described in Ref. [25]. The hydriding reaction proceeded at $T=373, 423,$

473 and 573 K and a pressure of 1 MPa. Hydrogen desorption was measured at $T=573$ K and $P=0.15$ MPa.

The phase composition of the initial intermetallics and the hydrided and dehydrided mechanically alloyed samples was controlled by X-ray phase analysis using $\text{Cu K}\alpha$ radiation.

With a view to checking the composition and homogeneity of $\text{Mg}_2\text{Ni}_{0.9}\text{Fe}_{0.1}$ and $\text{Mg}_2\text{Ni}_{0.7}\text{Fe}_{0.3}$ alloys, electron microprobe analyses were performed using a CAMECA SX-100 instrument.

3. Results and discussion

The X-ray phase analysis data of the obtained initial intermetallic phases show that the Mg_2Ni sample is almost single-phase. According to the results reported in [26], $\text{Mg}_2\text{Ni}_{1-x}\text{Fe}_x$ alloys having a Mg_2Ni -type structure with hexagonal symmetry exist at least up to $x=0.25$ if prepared by melting of the elements at 1173 K. In the present study preparation has occurred at 823 K and the X-ray patterns indicate a free iron content not only in the sample with nominal composition $\text{Mg}_2\text{Ni}_{0.7}\text{Fe}_{0.3}$, but also in $\text{Mg}_2\text{Ni}_{0.9}\text{Fe}_{0.1}$. The calculated values of the cell parameters ($a=5.20\text{--}5.21$ Å; $c=13.22\text{--}13.24$ Å) are close to those of pure Mg_2Ni .

Microprobe analysis of the $\text{Mg}_2\text{Ni}_{0.9}\text{Fe}_{0.1}$ sample reveals the presence of nickel and iron clusters. As can be seen in the backscattering electron microphotograph in Fig. 1, each cluster is surrounded by a ring containing Mg and Ni with a prevailing Ni-content and both the cluster and the ring are immersed in the matrix of a Mg_2Ni -type phase containing traces of Fe. The presence of nickel agglomer-

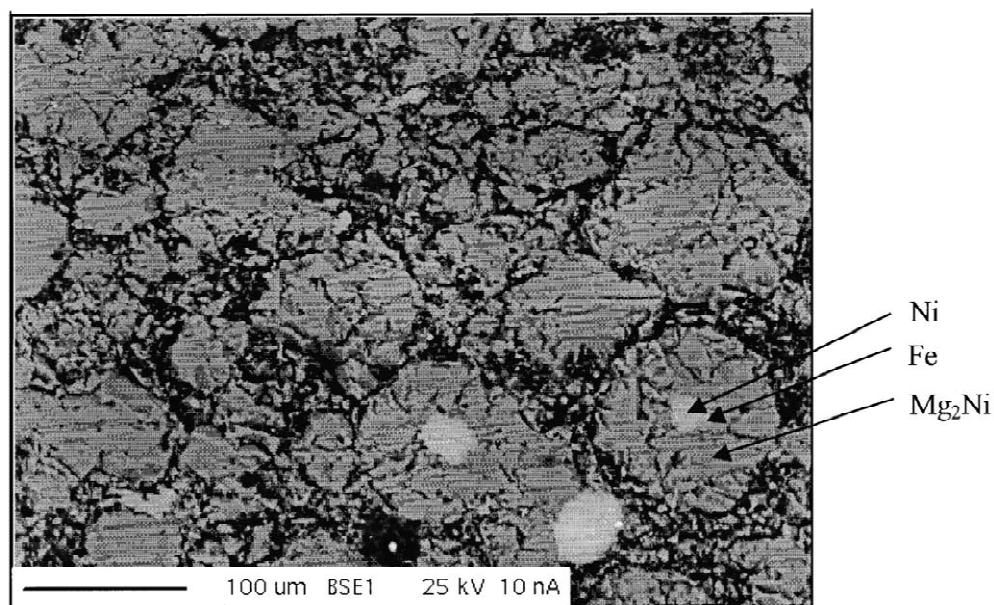


Fig. 1. Backscattering electron microphotograph of the $\text{Mg}_2\text{Ni}_{0.9}\text{Fe}_{0.1}$ sample showing the presence of: (i) Ni and Fe clusters (white phase); (ii) Mg_2Ni -type phase (grey phase).

ates indicates that the formation reaction of this phase has not proceeded to completion. In the case of $\text{Mg}_2\text{Ni}_{0.7}\text{Fe}_{0.3}$, the analysis shows the presence of Fe agglomerates and a small amount of Ni clusters along with the Mg_2Ni -type phase. This is visualized in the backscattering microphotograph in Fig. 2. Comparing data on both samples with Fe substitution one can conclude that in $\text{Mg}_2\text{Ni}_{0.7}\text{Fe}_{0.3}$ the formation of the Mg_2Ni phase has proceeded more completely than in the case of $\text{Mg}_2\text{Ni}_{0.9}\text{Fe}_{0.1}$.

The results of the first hydriding cycle of the composites with the nominal composition 85 wt.% Mg–15 wt.% $\text{Mg}_2\text{Ni}_{1-x}\text{Fe}_x$ are shown in Fig. 3. As it is evident from the figure, all the three composites reach a high absorption capacity without preliminary activation, which would have been necessary for magnesium, its alloys and the mechanically alloyed systems obtained on its basis.

Figs. 4–6 present the kinetic curves of hydriding at different temperatures and a pressure of 1 MPa. The relatively high hydrogen capacity reached at low hydriding temperatures (473 and 373 K), which is not observed with other magnesium composites containing intermetallics should be noted in this case. Obviously, the rate of absorption for the composites $\text{Mg}-\text{Mg}_2\text{Ni}_{1-x}\text{Fe}_x$ is appreciable even in the case when the driving force ($P_{\text{applied}} - P_{\text{eq}}$) is reduced. This fact may be important from the point of view of future application.

The kinetic curves of hydriding at 573 K for the three composites (Fig. 7) show no substantial difference in the proceeding of hydrogen absorption. However, the difference is distinct when comparing the results for 623 and 573 K (Figs. 8–10). With the three composites, hydriding at 573 K occurs at a higher rate than it does at 623 K. The

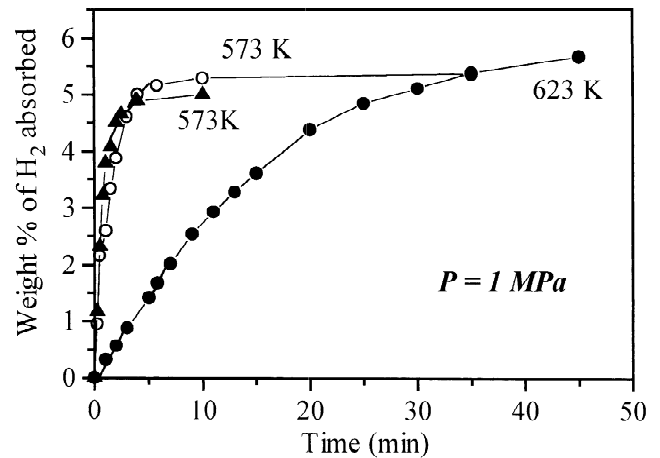


Fig. 3. Kinetic curves of hydriding during the first cycle of composites with nominal compositions: (●) 85 wt.% Mg–15 wt.% Mg_2Ni ; (○) 85 wt.% Mg–15 wt.% $\text{Mg}_2\text{Ni}_{0.9}\text{Fe}_{0.1}$; (▲) 85 wt.% Mg–15 wt.% $\text{Mg}_2\text{Ni}_{0.7}\text{Fe}_{0.3}$.

presence of Fe and the lower content of Mg_2Ni retard the hydriding process. This effect can be ascribed to the fact that at 573 K hydriding is accompanied by simultaneous formation of two hydrides, MgH_2 and Mg_2NiH_4 , whereas at 623 K it is MgH_2 only that appears. Taking into account that at 573 K the ternary hydride is formed more easily than the magnesium hydride, this means that the formation of the ternary hydride ends at the beginning of the process, and a large number of nuclei appear on the particle surfaces. This fact determines the higher rate of hydriding at the above temperature. At 623 K nuclei of magnesium hydride only are obtained, due to which the hydriding proceeds with a lower rate. The oxygen contamination could also play an important role.

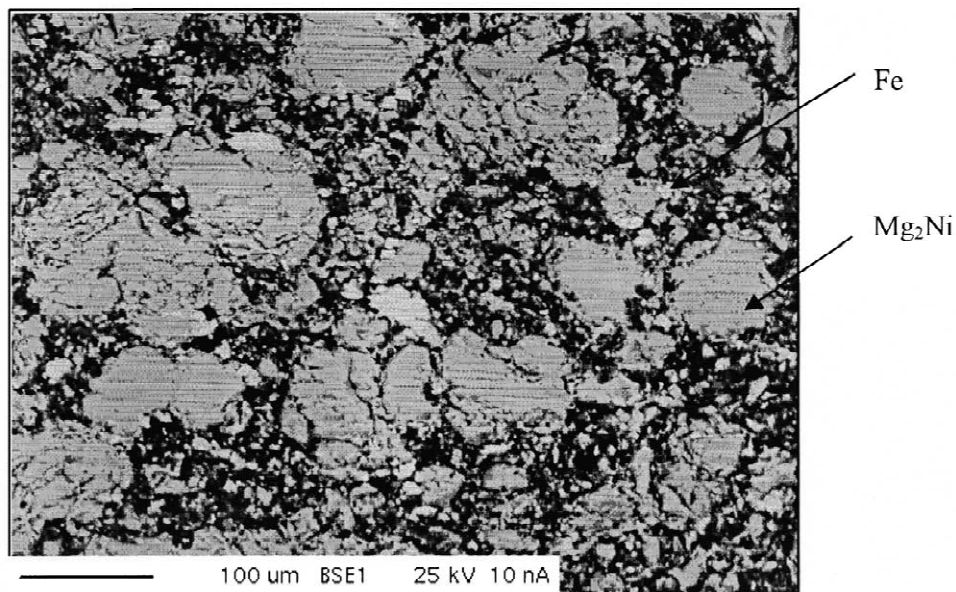


Fig. 2. Backscattering electron microphotograph of the $\text{Mg}_2\text{Ni}_{0.7}\text{Fe}_{0.3}$ sample showing the presence of: (i) Fe (and some Ni) clusters (white phase); (ii) Mg_2Ni -type phase (grey phase).

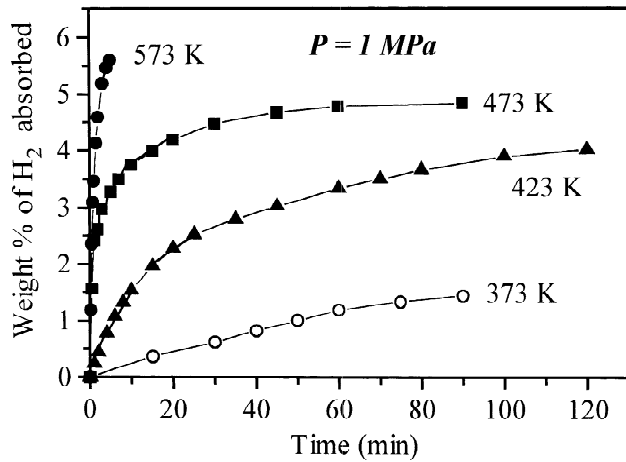


Fig. 4. Kinetic curves of hydriding of the composite 85 wt.% Mg-15 wt.% Mg₂Ni at different temperatures and $P=1$ MPa.

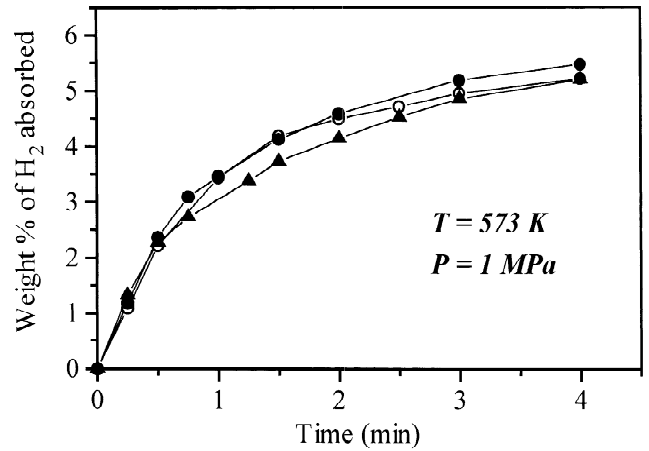


Fig. 7. Hydrogen absorption versus time behaviour during the beginning of the hydriding process of the composites 85 wt.% Mg-15 wt.% Mg₂Ni (●), 85 wt.% Mg-15 wt.% Mg₂Ni_{0.9}Fe_{0.1} (○) and 85 wt.% Mg-15 wt.% Mg₂Ni_{0.7}Fe_{0.3} (▲) at $T=573$ K and $P=1$ MPa.

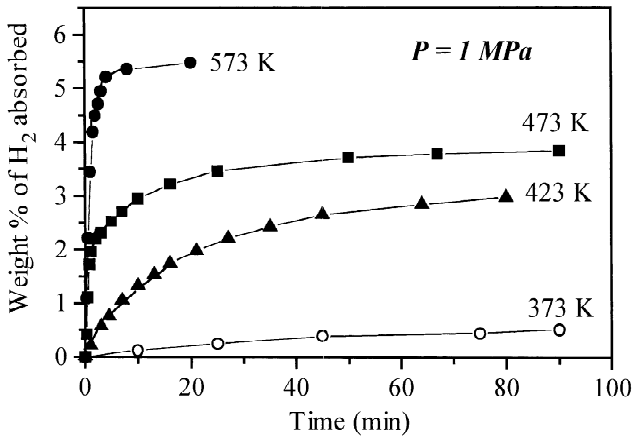


Fig. 5. Kinetic curves of hydriding of the composite 85 wt.% Mg-15 wt.% Mg₂Ni_{0.9}Fe_{0.1} at different temperatures and $P=1$ MPa.

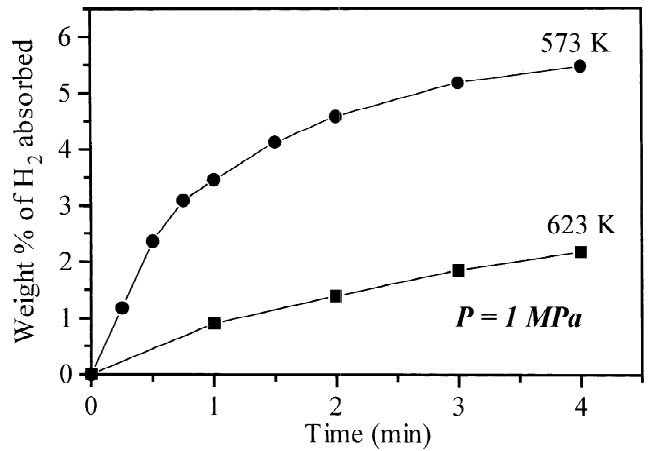


Fig. 8. Hydrogen absorption versus time behaviour during the beginning of the hydriding process of the composite 85 wt.% Mg-15 wt.% Mg₂Ni at temperatures of 573 and 623 K and a pressure of 1 MPa.

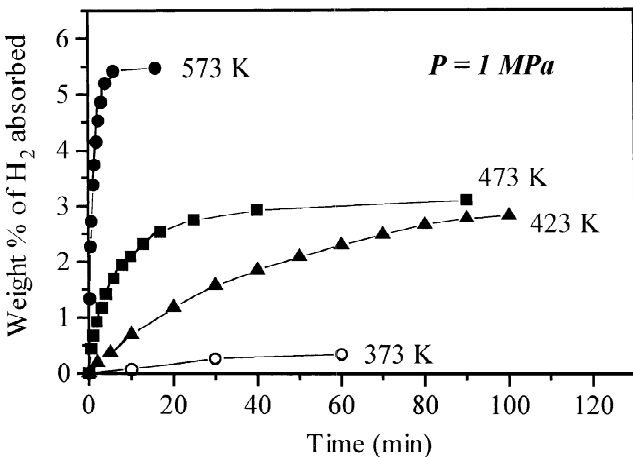


Fig. 6. Kinetic curves of hydriding of the composite 85 wt.% Mg-15 wt.% Mg₂Ni_{0.7}Fe_{0.3} at different temperatures and $P=1$ MPa.

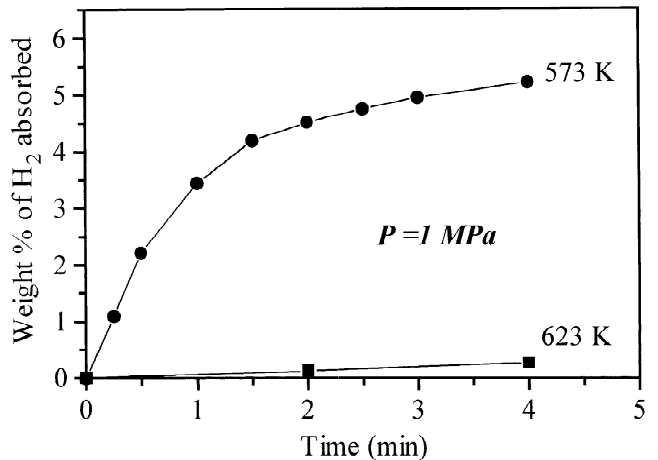


Fig. 9. Hydrogen absorption versus time behaviour during the beginning of the hydriding process of the composite 85 wt.% Mg-15 wt.% Mg₂Ni_{0.9}Fe_{0.1} at temperatures of 573 and 623 K and a pressure of 1 MPa.

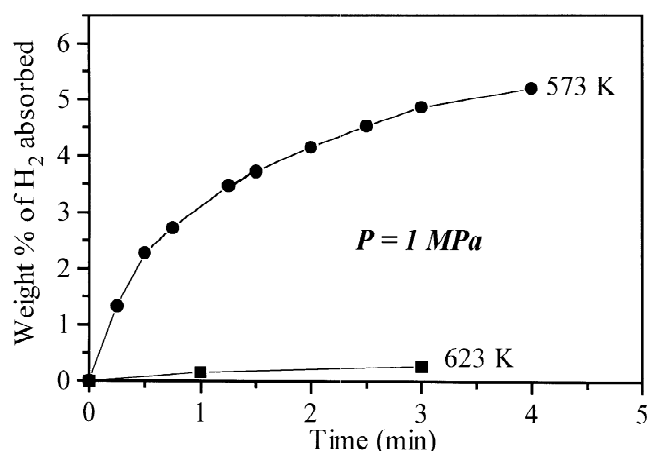


Fig. 10. Hydrogen absorption versus time behaviour during the beginning of the hydriding process of the composite 85 wt.% Mg-15 wt.% $Mg_2Ni_{0.7}Fe_{0.3}$ at temperatures of 573 and 623 K and a pressure of 1 MPa.

The high absorption capacity at lower hydriding temperatures and the improved hydriding kinetics at these temperatures are obviously a result of the catalytic action of $Mg_2Ni_{1-x}Fe_x$ in the composites. The presence of the intermetallics, which is associated with the formation of the ternary Mg_2NiH_4 leads to a larger interface that facilitates the nucleation and growth of the hydride layer. On the other hand, when hydriding and desorption take place at 573 K, superparamagnetic nickel and iron appear on the particle surfaces, which is evidenced by magnetic data. Segregated nickel on the Mg_2Ni surface has also been found by Schlapbach et al. [27]. The hydriding kinetics is additionally improved by the process of mechanical alloying where the appearing defects and dislocations help the nucleation. The simultaneous presence of all these factors is the probable reason for both the proceeding

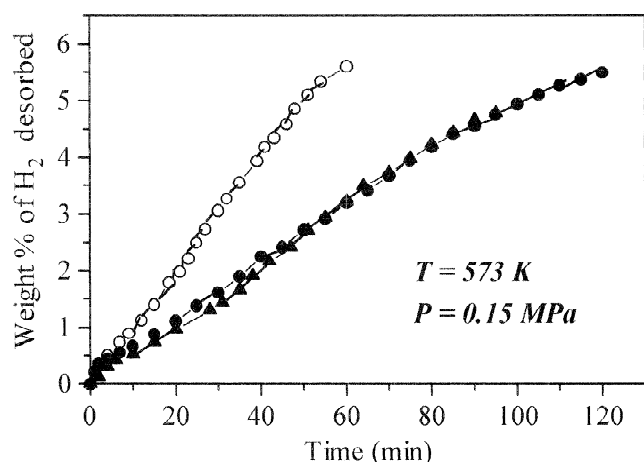


Fig. 11. Kinetic curves of dehydriding at $T=573$ K and $P=0.15$ MPa of composites with nominal compositions: (●) 85 wt.% Mg-15 wt.% Mg_2Ni ; (○) 85 wt.% Mg-15 wt.% $Mg_2Ni_{0.9}Fe$; (▲) 85 wt.% Mg-15 wt.% $Mg_2Ni_{0.7}Fe_{0.3}$.

of the reaction at lower temperatures and the better kinetic behaviour of the composites during hydrogen absorption.

The catalytic effect of the $Mg_2Ni_{1-x}Fe_x$ additive is more pronounced during hydriding of the composites than is the case of their dehydriding. This is illustrated by the kinetic curves of hydrogen desorption of the three composites at 573 K (Fig. 11). As it is evident from the figure, the presence of the catalytic additive is the reason for the higher rate of desorption which is usually relatively low for the magnesium systems at this temperature. The effect is most pronounced for the composite containing $Mg_2Ni_{0.9}Fe_{0.1}$.

4. Conclusion

The investigation of the absorption-desorption characteristics of mechanically alloyed nanocomposites of magnesium and $Mg_2Ni_{1-x}Fe_x$ intermetallics shows that the additives have a catalytic effect on the hydriding of magnesium which consists in:

- (i) attaining a high absorption capacity without preliminary activation;
- (ii) improving the hydriding kinetics at a temperature which is relatively low for magnesium-based systems;
- (iii) a sufficiently high absorption capacity at low hydriding temperatures;
- (iv) a reduced temperature of hydrogen desorption from the hydrided samples.

The catalytic effect observed is due to an increase in the Mg/hydride interface as a result of the formation of a second hydride (Mg_2NiH_4) in the system, to the mechanical alloying and the presence of Ni and Fe clusters on the surface of nanocomposite particles.

References

- [1] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, J. Alloys Comp. 217 (1995) 245.
- [2] H. Aoyagi, K. Aoki, T. Masumoto, J. Alloys Comp. 231 (1995) 804.
- [3] S. Orimo, K. Ikeda, H. Fujii, Y. Fujikawa, Y. Kitano, K. Yamamoto, Acta Mater. 45 (1997) 2271.
- [4] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen, R. Schulz, J. Alloys Comp. 217 (1995) 295.
- [5] K.J. Gross, P. Spatz, A. Züttel, L. Schlapbach, J. Alloys Comp. 261 (1997) 276.
- [6] E.Yu. Ivanov, I.G. Konstanchuk, A.A. Stepanov, V.V. Boldyrev, Dokl. Akad. Nauk SSSR 286 (1986) 385.
- [7] I.G. Konstanchuk, E.Yu. Ivanov, M. Pezat, B. Darriet, V.V. Boldyrev, P. Hagenmuller, J. Less-Common Met. 131 (1987) 181.
- [8] J.-L. Bobet, E. Akiba, B. Darriet, Int. J. Hydrogen Energy 26 (2001) 493.
- [9] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, Appl. Phys. A, Mater. Sci. Proc. 72 (2001) 157.
- [10] L.E.A. Berlouis, E. Cabrera, E. Hall-Barientos, P.J. Hall, S.B. Dodd, S. Morris, M.A. Imam, J. Mater. Res. 16 (2001) 45.

- [11] M. Terzieva, M. Khrussanova, P. Peshev, *J. Alloys Comp.* 267 (1998) 235.
- [12] G. Liang, S. Boily, J. Huot, A. Van Neste, R. Schulz, *J. Alloys Comp.* 267 (1998) 302.
- [13] G. Liang, S. Boily, J. Huot, A. Van Neste, R. Schulz, *J. Alloys Comp.* 268 (1998) 302.
- [14] G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schulz, *J. Alloys Comp.* 297 (2000) 261.
- [15] M. Terzieva, M. Khrussanova, P. Peshev, D. Radev, *Int. J. Hydrogen Energy* 20 (1995) 53.
- [16] S.S. Sai Raman, D.J. Davidson, O.N. Srivastava, *J. Alloys Comp.* 292 (1999) 202.
- [17] M. Zhu, Y. Gao, X.Z. Che, Y.Q. Yang, C.Y. Chung, *J. Alloys Comp.* 330–332 (2002) 708.
- [18] M. Khrussanova, J.-L. Bobet, M. Terzieva, B. Chevalier, D. Radev, P. Peshev, B. Darriet, *J. Alloys Comp.* 307 (2000) 283.
- [19] L. Guoxian, W. Erde, F. Shoushi, *J. Alloys Comp.* 223 (1995) 111.
- [20] J. Yang, M. Cuireanu, R. Roberge, *Mater. Lett.* 43 (2000) 234.
- [21] P. Wang, A. Wang, H. Zhang, B. Ding, Z. Hu, *J. Alloys Comp.* 297 (2000) 240.
- [22] P. Wang, H.F. Zhang, B.Z. Ding, Z.Q. Hu, *Acta Mater.* 49 (2001) 921.
- [23] S. Orimo, H. Fujii, *Appl. Phys. A, Mater. Sci. Proc.* 72 (2001) 167.
- [24] M. Khrussanova, E. Grigorova, I. Mitov, D. Radev, P. Peshev, *J. Alloys Comp.* 327 (2001) 230.
- [25] B. Tanguy, J.L. Soubeyroux, M. Pezat, J. Portier, P. Hagenmuller, *Mater. Res. Bull.* 11 (1976) 1441.
- [26] J.P. Darnaudery, B. Darriet, M. Pezat, *Int. J. Hydrogen Energy* 8 (1983) 705.
- [27] L. Schlapbach, D. Shaltiel, P. Oelhafen, *Mater. Res. Bull.* 14 (1979) 1235.