



Short communication

Alloying of Mg/Mg₂Ni eutectic by chosen non-hydride forming elements: Relation between segregation of the third element and hydride storage capacity

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ABSTRACT

Eutectic mixture Mg–11.3 at.% Ni was modified by elements X from the 13th (Al, Ga, In) and 14th group (Si, Ge, Sn and Pb). Phase analysis and distribution of X between primary solid solution Mg–Ni–X and Mg₂Ni–X compound was carried out in stabilization annealed samples before hydrogen charging and in hydrided state. In the both states, it was found that X prefers Mg₂Ni–X to Mg–Ni–X solid solution, and that the preference is stronger in the hydrided state. The effect is more pronounced for elements X from the 13th group. Suggested explanation was based on influence of X on the formation enthalpy of hydrides. It was observed that In increases the hydrogen storage capacity of the eutectic mixture. The most likely explanation is based on a strong segregation of In to phase Mg₂Ni–X, and on a weak tendency of In to form phases with Mg and Ni.

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1. Introduction

Hydrides of Mg-based alloys are promising hydrogen storage materials (HSMs) [1,2]. Pure Mg is very effective hydrogen absorber, since it absorbs theoretically 7.6 wt.% H₂ forming β-MgH₂. Its desorption kinetics, however, does not meet requirements of technical practice, first of all due to a low rate of hydrogen desorption.

Possible ways are sought how to find and activate easy channels for hydrogen atoms to enter the storage phases during hydrogen charging and to leave them during the hydrogen discharging. Much effort has been devoted, e.g., to elucidation of the mechanism of catalysis and to investigation of optimal structure of Mg-based HSM. It was found that admixture of Ni facilitates the hydrogen charging and discharging characteristics of Mg [3–8]. The base binary alloy Mg–Ni was modified by hydride forming elements and their affect upon the density of valence electrons between the Mg–H and Ni–H atoms was reported [9,10]. Attraction of bonding electrons by the additive atoms weakens the bonds between Mg and H and between Ni and H and cause destabilization of the Mg- and Ni-hydrides, which results in desired decrease of hydriding/dehydriding temperatures.

From this point of view, it may seem surprising that elements with weaker bonding with H compared to the bond strength between Mg and hydrogen or even non-hydride forming elements show a beneficial effect upon the hydrogen desorption rate

[9,11–24]. Influence of new phases formed by additives on the hydriding/dehydriding properties are studied in papers [12,25].

In the present paper, addition of substitution elements X from the 13th (X¹³: Al, Ga, In) and the 14th group (X¹⁴: Si, Ge, Sn, Pb) to Mg–Mg₂Ni eutectic was systematically studied and relative preference of X either to Mg-rich primary solid solution Mg–Ni–X (referred to as (Mg) hereafter) or to intermetallic phase Mg₂Ni–X (referred to as phase I) was obtained. None of the elements X forms stable solid hydrides. The hydrides of X¹³ are usually called *polymeric*, since they make chains (X¹³H₃)_x [26,27]. The stability of covalent hydrides X¹⁴ H₄ is also low and decreases going down the row in the periodic table.

2. Experimental

Experimental alloys were prepared by induction melting of pure elements (purity better than 99.99 at.%) and casting in copper mould under the protective atmosphere of pure Ar (purity 99.9999 vol.%). Mass of each batch was about 300 g. Mg and Ni (purity 99.98 at.% and 99.96 at.%, respectively) and components X = Al, Ga, In, Si, Ge, Sn, and Pb were used to preparation of 7 ternary alloys Mg–8.5 at.% Ni–2.8 at.% X. Phase composition was checked by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Principal phases present in the alloys after stabilization anneals 630 K for 18 h in pure Ar were (Mg) and phase I that catalyze the hydrogen desorption from (Mg) [28]. The temperature of the stabilization anneal 630 K was chosen high enough to reach the structure stabilization within a few hours and, at the same time, to low enough to suppress the evaporation of Mg. In the cast alloys investigated in the present work, the phase I solidifies as a component of

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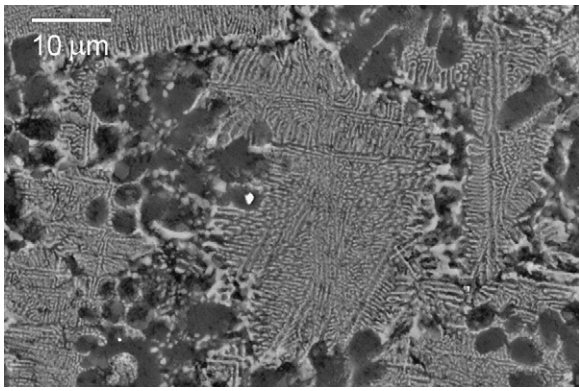


Fig. 1. SEM micrograph of Mg–Ni–Ga after anneal 630 K/18 h/Ar. Dark – (Mg), light – I.

a fine lamellar eutectic (Mg)+I. The structure after the stabilization anneal is exemplified in Fig. 1 for X=Ga. It is illustrated that dark primary (Mg) particles, of which the size is up to about 5 μm, are aggregated to colonies with diameter in the order of tens of μm. They are surrounded by eutectic mixture (Mg)+I.

Samples in the form of 0.7 mm thick foils were subjected to hydrogen charging in pure hydrogen (purity 99.9999 vol.%, pressure 30 bar) at constant temperature 620 K for 14 days. Measurement of hydrogen storage capacity was performed by precise weighing with samples of total mass of about 5 g. Further experimental details were described elsewhere [29].

Phases in Mg–Ni–X alloys were identified by XRD using of X’Pert Pro MPD device (PANanalytical B.V., Almelo, the Netherlands; Co K_α radiation was registered) and HighScore Plus software. The phase analysis was carried out in two states of experimental alloys: after stabilization anneal (state A), and after stabilization anneal and hydrogen charging (state B). Scanning electron microscopy (SEM JEOL JSM 6460 + EDAX Oxford instruments analyzer) was used for measurement of chemical composition of phases in states A and B.

3. Results and discussion

3.1. Phase analysis

All samples were composed mainly of two majority phases, (Mg) and I. Minority phases found in the Mg–Ni–X alloys are listed in Table 1. Some of them were found also in papers [21,22,30–32] devoted to study of similar alloy systems. Volume fraction of Mg₂Ni₃Si and Mg₂Ge was about 10%; volume fraction of other phases was about 5 vol.%. For XRD pattern, see Figs. 2–5.

Al and Ga show a strong tendency to form precipitates NiX; Si, Ge and Pb form particles of Zintl phases Mg₂X. Al, Si and Sn form ternary compounds with Mg and Ni. A kind of a ternary phase (denoted as T in Table 1 and Figs. 2–5) was identified also in XRD

Table 1
Phases detected in Mg–Ni–X by XRD and SEM. Two principal phases (Mg) and phase I, are not listed in table.

Group	X	XRD	SEM
13	Al	NiAl, Mg ₃ Ni ₂ Al ^a	NiAl
	Ga	MgGa ₂ , NiGa, T ^b	–
	In	–	–
14	Si	Mg ₂ Si, Mg ₂ Ni ₃ Si, T ^b	Mg ₂ Ni ₃ Si
	Ge	Mg ₂ Ge, GeO ₂ , Mg(OH) ₂ , T ^b	Mg ₂ Ge
	Sn	Mg ₇₉ Ni ₁₃ Sn ₈ , SnO, T ^b	Mg ₇₉ Ni ₁₃ Sn ₈
	Pb	Mg ₂ Pb, Pb, PbO, Pb ₃ O ₄ , Mg(OH) ₂ , T ^b	–

^a [30].

^b Ternary phase [21,22,30].

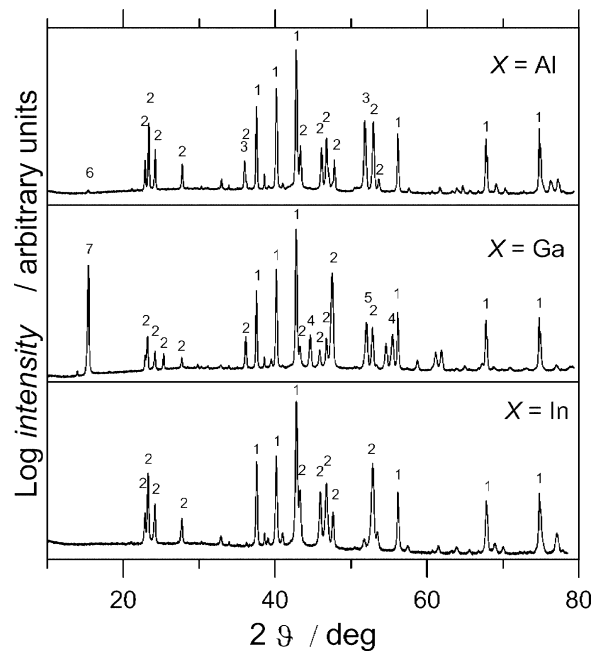


Fig. 2. XRD pattern of Mg–Ni–X¹³ in state A. 1 – (Mg), 2 – I, 3 – NiAl, 4 – MgGa₂, 5 – GaNi, 6 – Mg₃Ni₂Al, 7 – T.

pattern for X=Ga, and for X¹⁴. It is likely that this phase is isostructural with the cubic phase Mg₃Ni₂X described in [30] for X=Al and Ti and in Refs. [21,22] as a component in the multiphase structure observed in alloys Mg–Ni–Ge.

Alloy Mg–Ni–Pb is susceptible to form oxides in both A and B states. In alloys Mg–Ni–Pb and Mg–Ni–Ge, traces of hydroxide Mg(OH)₂ were identified in the XRD pattern – see in Figs. 4 and 5. It is worth of noting that no minority phase was found in alloy Mg–Ni–In – in this alloy, all atoms of In enter either the phase (Mg) or the phase I.

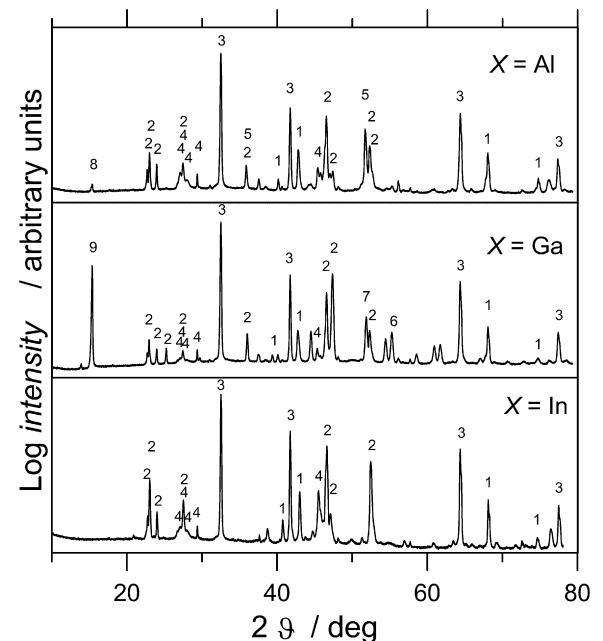


Fig. 3. XRD pattern of Mg–Ni–X¹³ in state B. 1 – (Mg), 2 – I, 3 – MgH₂, 4 – Mg₂NiH₄, 5 – NiAl, 6 – MgGa₂, 7 – GaNi, 8 – Mg₃Ni₂Al, 9 – T.

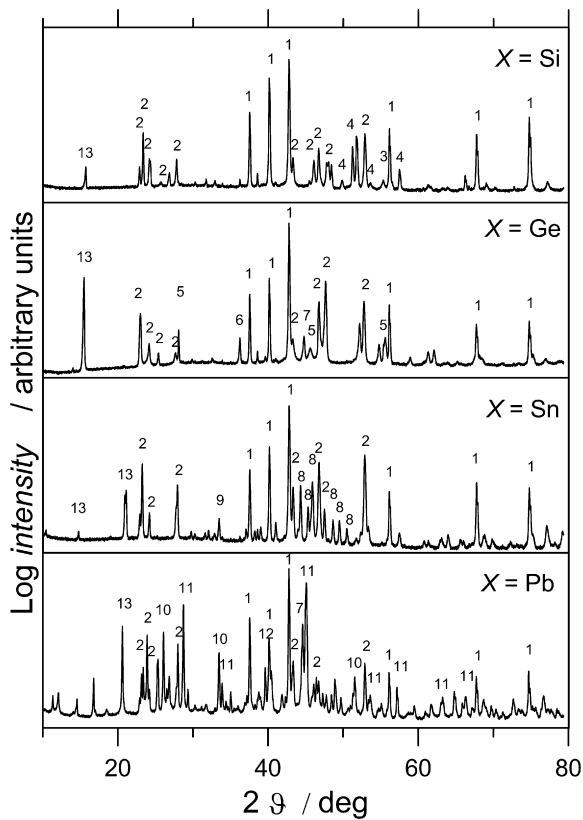


Fig. 4. XRD pattern of Mg–Ni– X^{14} in state A. 1 – (Mg), 2 – *I*, 3 – Mg_2Si , 4 – Mg_2Ni_3Si , 5 – Mg_2Ge , 6 – GeO_2 , 7 – $Mg(OH)_2$, 8 – $Mg_{79}Ni_{13}Sn_8$, 9 – SnO, 10 – Mg_2Pb , 11 – PbO, 12 – Pb_3O_4 , 13 – *T*.

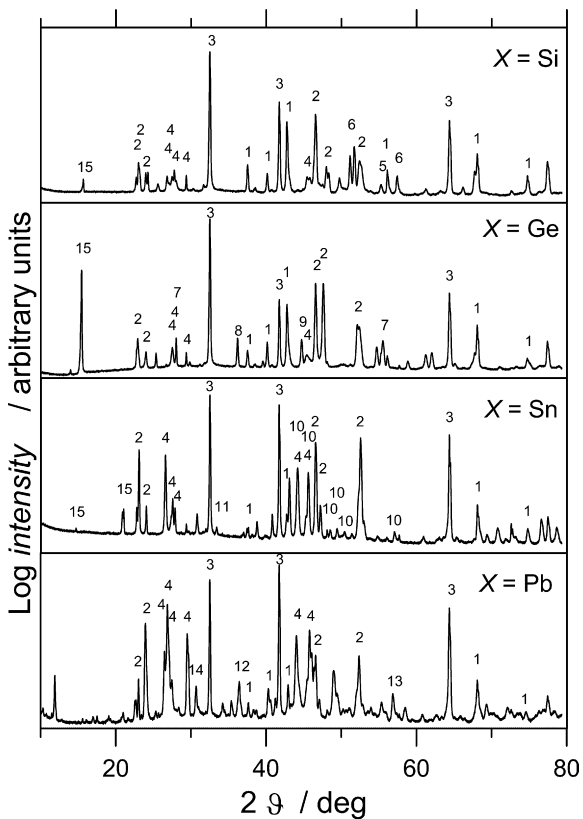


Fig. 5. XRD pattern of Mg–Ni– X^{14} in state B. 1 – (Mg), 2 – *I*, 3 – MgH_2 , 4 – Mg_2NiH_4 , 5 – Mg_2Si , 6 – Mg_2Ni_3Si , 7 – Mg_2Ge , 8 – GeO_2 , 9 – $Mg(OH)_2$, 10 – $Mg_{79}Ni_{13}Sn_8$, 11 – SnO, 12 – Pb, 13 – PbO, 14 – Pb_3O_4 , 15 – *T*.

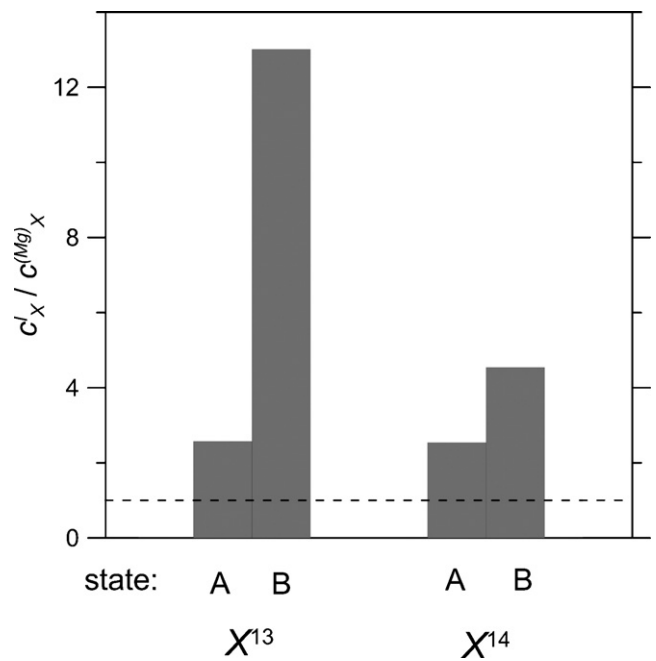


Fig. 6. Average concentration ratio of X in phase *I* and (Mg), respectively, measured for elements from group 13 and 14 in states A and B. Dashed line: $(c_X / c^{(Mg)}_X) = 1$ – no preference in distribution of X .

3.2. Interaction of minority phases with hydrogen

Comparing X-ray diffraction pattern in states without and with hydrogen (cf. Figs. 2 and 3 and Figs. 4 and 5, respectively), it was found that – except for phases in alloy Mg–Ni–Pb – the minority phases do not interact with hydrogen in a significant extent. This is in agreement with very low hydrogen solubility in NiAl reported in Ref. [33] and with results on decomposition of Zintl phases in hydrogen [25]. Since elements X form no stable hydrides X_pH_q and no stable complex hydrides of $Mg_pNi_qX_rH_s$ were experimentally observed and reported in the literature, the only way how minority phases could interact with hydrogen would be their transformation into simpler hydrides $Mg_pNi_qH_s$ or Mg_pH_s and into X , similarly as it was found for binary phase Mg_2Si in [25]. However, no peak of pure X was observed in hydrogenated state B, which implies that the minority phases in studied alloys do not take part significantly in hydrogen charging of alloys Mg–Ni– X .

The only exception is alloy Mg–Ni–Pb, where partial decomposition of oxides, hydroxide $Mg(OH)_2$ and Zintl phase Mg_2Pb was observed during hydrogenation. In this case, the decomposition was accompanied by appearance a diffraction peak for pure Pb in state B – see Fig. 5. Different behavior of alloy Mg–Ni–Pb compared to behavior of other studied alloys is most likely caused by the lowest bonding strength between Mg and Pb [34] and by the lowest standard free energy of interaction of Pb with oxygen [35,36].

3.3. Concentration of X in (Mg) and *I*

Concentration of X in majority phases (Mg) and *I*, c'_X and $c^{(Mg)}_X$, respectively, was measured by SEM-EDAX in state A and state B. In state A, it was observed that X prefers slightly phase *I* to phase (Mg). The preference can be illustrated by concentration ratio $c'_X / c^{(Mg)}_X$, which value is higher than unity if the binding of X to the phase *I* is stronger than the binding of X to phase (Mg) and lower than unity in the reverse situation. In Fig. 6, mean values of concentration ratio are plotted for X^{13} and X^{14} . Hydrogen charging changes the elements distribution, which is more obvious for elements X^{13} than for elements X^{14} : concentration ratio increases significantly

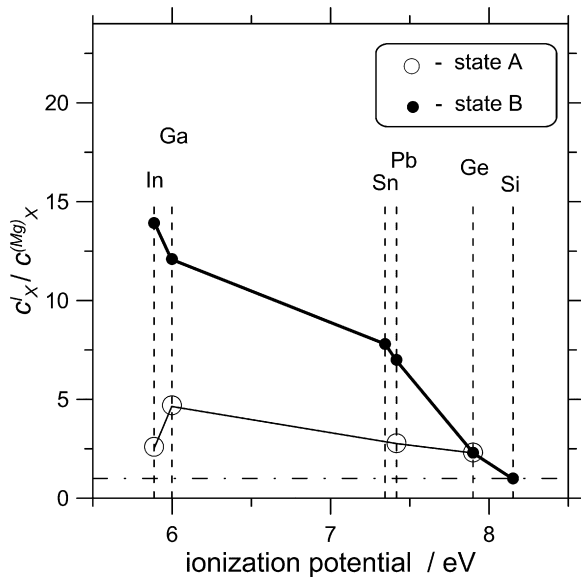


Fig. 7. Correlation between $c'_X/c^{(Mg)}_X$ and ionization potential of X. Thin line – $c'_X/c^{(Mg)}_X$ in state A, thick line – $c'_X/c^{(Mg)}_X$ in state B. Dash-dot line: $(c'_X/c^{(Mg)}_X) = 1$ – no preference in distribution of X.

during hydrogen charging (state B). The observation can be rationalized by differently strong influence of individual element X upon the formation of hydrides: Hydrogenation leads to a recrystallization of both phases and to a formation of new hydrides structures. Hence, the changed concentration of X in *I* and in (Mg) in state B may be related to a change of respective formation enthalpies ΔH_f . The change of ΔH_f calculated for Mg_2Ni with and without Al during hydrogenation was reported in [31,37]. Effect of Al upon the formation enthalpy of MgH_2 was studied in [38]. Unfortunately, relevant data on ΔH_f for other elements X in MgH_2 and Mg_2NiH_4 are not available in the literature.

It is known [39–41] that stability of hydrides (enthalpy of hydride decomposition is equal to the negative of ΔH_f) depends on the enthalpy of ionization of components. We have made an attempt to systemize present results and plotted measured values of concentration ratio ($c'_X/c^{(Mg)}_X$) as a function of ionization potential of X. It is obvious in Fig. 7 that elements X¹³ with lower ionization potential show significant preference to Mg_2NiH_4 . Values for Al in both states and for Si, Sn in state A are not plotted due to the tendency to form minority phases. Al atoms, e.g., enter NiAl precipitates rather than majority phases. Hence, the alloy Mg–Ni–Al behaves as being without any admixture element ($c'_{Al} \sim c^{(Mg)}_{Al} \ll 1$).

3.4. Correlation between segregation of X and hydrogen storage capacity

It was reported in [38,42] that alloying effects that influence parameters of hydride formation may be correlated with a change in hydrogen storage properties. In Fig. 8, overall gravimetric hydrogen storage capacity *m* of the heterogeneous alloy system Mg/ Mg_2Ni –X is plotted as a function of concentration ratio ($c'_X/c^{(Mg)}_X$). It can be seen that there is a monotonous relationship between *m* and $c'_X/c^{(Mg)}_X$. Al is not plotted since it enters neither of the two principal phases, therefore storage capacity of Mg–Ni–Al was found close to that for eutectic binary alloy Mg–Ni.

It is known that hydrided phase *I* shows a very effective catalytic effect on the hydrogen desorption from phase (Mg) [43]. This may be, most likely, the cause of significant relationship between the observed preference of X to phase *I* ($c'_X/c^{(Mg)}_X > 1$) in state B and hydrogen storage capacity *m*. It is obvious in Fig. 8 that In shows the strongest preference to the phase *I*. Moreover it forms

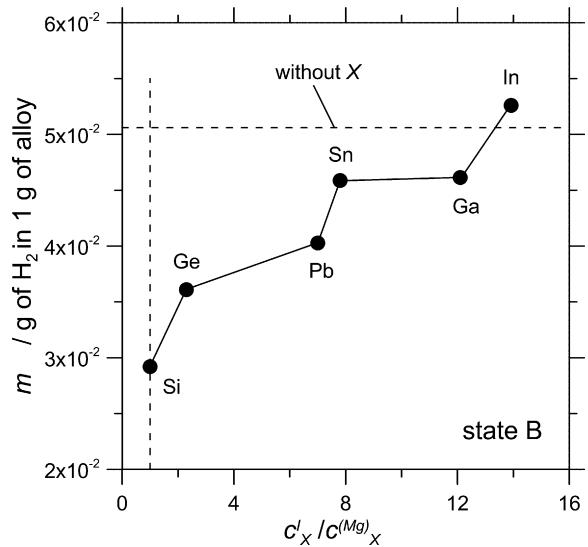


Fig. 8. Correlation between hydrogen storage capacity *m* of Mg–Ni–X alloys and preference of X to phase *I* scaled by the ratio $c'_X/c^{(Mg)}_X$. Dashed horizontal – practically attainable hydrogen storage capacity measured in non-alloyed binary alloy Mg–Ni, dashed vertical – $(c'_X/c^{(Mg)}_X) = 1$ (no preference in distribution of X).

no minority ternary phases with Mg and Ni (Table 1), which means that no In atoms enter phases that do not participate the hydride charging/discharging process. It can be seen in Fig. 8 that In is very efficient in increasing the hydrogen storage capacity – the value of *m* found for X=In is higher than practically attainable value measured for non-alloyed eutectic Mg–11.3 at.% Ni. However, the mechanism controlling the influence of elements X in the phase *I* upon the hydrogen storage capacity *m* is unclear at present and should be discovered in next studies.

4. Conclusions

In the present paper, structure and chemical composition of cast and stabilized Mg–8.5 at.% Ni–2.8 at.% X alloys (X – elements of 13th and 14th group) was investigated. Primary solid solution (Mg) and eutectic mixture (Mg) + *I* were the principal structural components. Except for In, all alloying elements X form minority phases (listed in Table 1). Volume fraction of Mg_2Ni_3Si and Mg_2Ge was about 10 vol.%, in other cases the fraction was close to 5 vol.%.

All experimental alloys were studied in two states: after stabilization anneal 630 K/18 h/Ar (state A) and after stabilization anneal and hydrogen charging (state B). All detected phases were identified in XRD spectra, chemical composition of some minority phases with Al, Si, Ge and Sn were also verified by SEM. It was found that – with the exception of phases with Pb – none of observed minority phases reacts in a significant extent with hydrogen. Consequently, these phases play no role in hydrogen charging/discharging behavior of studied alloys.

Relative concentration of X in *I* and (Mg) was obtained by SEM. It was found that X shows a slight preference to phase *I* in state A and much more pronounced preference to phase *I* in state B. This tendency is especially strong in case of elements from 13th group. It was found that concentration ratio ($c'_X/c^{(Mg)}_X$) decreases with increasing ionization potential of X.

It was obtained that the stronger is the preference of X to phase *I*, the higher is the hydrogen storage capacity of alloy Mg–Ni–X. For X=In, the hydrogen storage capacity is higher than the capacity of un-alloyed binary eutectic alloy Mg–Ni. Exclusive behavior of In may be a consequence of a strong segregation of In to phase *I* and of a high efficiency of alloying effect – no minority phase is formed by In.

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References

- [1] B. Sakintuna, F. Lamari-Darkrim, M. Hirscher, *Int. J. Hydrogen Energy* 32 (2007) 1121–1140.
- [2] I.P. Jain, Ch. Lal, A. Jain, *Int. J. Hydrogen Energy* 35 (2010) 5133–5144.
- [3] Y. He, J. Fan, Y. Zhao, *Int. J. Hydrogen Energy* 35 (2010) 4162–4170.
- [4] N. Mahmoudi, A. Kafrou, A. Simchi, *J. Power Sources* 196 (2011) 4604–4608.
- [5] M.Q. Fan, S.-S. Liu, Y. Zhang, J. Zhang, L.-X. Sun, F. Xu, *Energy* 35 (2010) 3417–3421.
- [6] D. Vojtech, P. Novak, J. Cizkovsky, V. Knotek, F. Prusa, *J. Phys. Chem. Solids* 68 (2007) 813–817.
- [7] K. Crosby, X. Wan, L.L. Shaw, *J. Power Sources* 195 (2010) 7380–7385.
- [8] A. Revesz, D. Fatay, *J. Power Sources* 195 (2010) 6997–7002.
- [9] K. Nakatsuka, M. Yoshino, H. Yukawa, M. Morinaga, *J. Alloys Compd.* 293–295 (1999) 222–226.
- [10] N. Novakovic, J. Grbovic-Novakovic, L. Matovic, M. Manasievic, I. Radislavjevic, B. Paskas-Mamula, N. Ivanovic, *Int. J. Hydrogen Energy* 35 (2010) 598–608.
- [11] J. Prigent, M. Gupta, *J. Alloys Compd.* 446–447 (2007) 90–95.
- [12] M. Tanniru, D.K. Slattery, F. Ebrahimi, *Int. J. Hydrogen Energy* 35 (2010) 3555–3564.
- [13] N. Terashita, M. Takahashi, K. Kobayashi, T. Sasai, E. Akiba, *J. Alloys Compd.* 293 (1999) 541–545.
- [14] J.J. Vajo, F. Mertens, C.C. Ahn, R.C. Browman Jr., B. Fultz, *J. Phys. Chem. B* 108 (2004) 13977–13983.
- [15] K. Komiya, N. Morisaku, Y. Shinzato, K. Ikeda, S. Orimo, Y. Ohki, K. Tatsumi, H. Yukawa, M. Morinaga, *J. Alloys Compd.* 446–447 (2007) 237–241.
- [16] G.I. Duarte, L.A.C. Bustamante, P.E.V. de Miranda, *Scripta Mater.* 56 (2007) 789–792.
- [17] Q. Li, K.-C. Chou, Q. Lin, L.-J. Jiang, F. Yhan, *Int. J. Hydrogen Energy* 29 (2004) 1383–1388.
- [18] T. Sato, H. Blomqvist, D. Noreus, *J. Alloys Compd.* 356–357 (2003) 494–496.
- [19] S. Doppiu, P. Solsona, T. Spassov, G. Barkhordarian, M. Dornheim, T. Klassen, S. Surinach, M.D. Baro, *J. Alloys Compd.* 404–406 (2005) 27–30.
- [20] Q. Li, Q. Lin, K.-C. Chou, L. Jiang, *J. Mater. Sci.* 39 (2004) 61–65.
- [21] F.C. Gennari, G. Urretavizcaya, J.J.A. Gamboa, G. Meyer, *J. Alloys Compd.* 354 (2003) 187–192.
- [22] F.C. Gennari, G. Urretavizcaya, G. Meyer, *J. Alloys Compd.* 356–357 (2003) 588–592.
- [23] F.C. Gennari, F.J. Castro, G. Urretavizcaya, G. Meyer, *J. Alloys Compd.* 334 (2002) 277–284.
- [24] H. Imamura, K. Yoshihara, M. Yoa, I. Kitayawa, Y. Sakata, S. Ooshima, *Int. J. Hydrogen Energy* 32 (2007) 4191–4194.
- [25] R. Janot, F. Cuevas, M. Latroche, A. Percheron-Guegan, *Intermetallics* 14 (2006) 163–169.
- [26] G. Brendel, *Ullmanns Encyklopaedie der technischen Chemie*, vol. 13, Verlag Chemie, Weinheim, New York, 1977, p. 109.
- [27] G. Wulfsberg, *Principles of Descriptive Inorganic Chemistry*, University Science Books, Sausalito, CA, 1991, 94965, p. 343.
- [28] R.B. Schwartz, *MRS Bull.* 24 (1999) 40–44.
- [29] J. Cermak, L. Kral, *Acta Mater.* 56 (2008) 2677–2686.
- [30] L. Guanglie, C. Linshen, W. Lianbang, Y. Huantang, *J. Alloys Compd.* 321 (2001) L1–L4.
- [31] J. Zhang, Y.N. Huang, P. Peng, C. Mao, Y.M. Shao, D.W. Zhou, *Int. J. Hydrogen Energy* 36 (2011) 5375–5382.
- [32] Y.K. Song, R.A. Varin, *Metall. Mater. Trans. A* 32A (2001) 5–18.
- [33] Z.R. Xu, R.B. McLellan, *Acta Mater.* 46 (1998) 2877–2880.
- [34] L.N. Larikov, *Difusion*, in: J.H. Westbrook, R.L. Fleischer (Eds.), *Intermetallic Compounds*, vol. 1, J. Willey&Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1995, pp. 757–770.
- [35] N. Birks, F.S. Pettit, G.H. Meier, *Introduction to the High-Temperature Oxidation of Metals*, 2nd ed., Cambridge Univ. Press, Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo, 2006, pp 22–24.
- [36] http://www.webelements.com/oxygen/bond_enthalpies.html.
- [37] J. Zhuang, J.M. Hastings, L.M. Corliss, R. Bau, C.Y. Wei, R.O. Moyer, *J. Solid State Chem.* 40 (1981) 352–360 (quoted from: J. Zhang, D. Zhou, J. Liu, *Trans. Non-ferrous Met. Soc. Chin.* 19 (2009) 205–209).
- [38] C.X. Shang, M. Bououdina, Y. Song, Z.X. Guo, *Int. J. Hydrogen Energy* 29 (2004) 73–80.
- [39] S.F. Parker, *Coord. Chem. Rev.* 254 (2010) 215–234.
- [40] W. Grochala, P.P. Edwards, *Chem. Rev.* 104 (2004) 1283–1315.
- [41] R.O. Moyer Jr., S.M. Antao, B.H. Toby, F.G. Morin, D.F.R. Gilson, *J. Alloys Compd.* 460 (2008) 138–141.
- [42] S.V. Alapati, J.K. Johnson, D.S. Sholl, *J. Phys. Chem. C* 111 (2007) 1584–1591.
- [43] J. Cermak, B. David, *Int. J. Hydrogen Energy* (2011), doi:10.1016/j.ijhydene.2011.07.133.