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Nanocrystalline metal hydrides

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Abstract

Nanocrystalline hydrides are a new class of material in which outstanding hydrogen sorption may be obtained by proper engineering of the microstructure and surface. In this paper the thermodynamics and kinetics of hydride formation in a nanocrystalline alloy are presented. The role of grain size, grain boundaries, internal strain and chemical disorder is discussed, as is the effect of catalyst particles at the surface of the metal. Powders of nanocrystalline alloys, modified with a catalyst, readily absorb hydrogen, with no need for prior activation, in strong contrast to conventional hydrides. The materials show substantially enhanced absorption and desorption kinetics, even at relatively low temperatures. Examples of various nanocrystalline metal hydrides are given, based on Mg, Mg_2Ni, FeTi and $LaNi_5$.

Keywords: Nanocrystal; Metastable; Kinetics; Disorder; Strain; Grain size

1. Introduction

In spite of many advantages, metal hydrides have had until now only limited success as storage devices for hydrogen [1]. Most hydrides have a rather low storage capacity by weight (1–2 wt.%), and those few with a higher capacity (e.g. Mg_2NiH_4—3.6 wt.%, MgH_2—7.6 wt.%) have so far been usable only at high temperatures (300 °C or higher) and have shown very poor absorption/desorption kinetics. Most of the materials are highly reactive and easily form surface oxides and hydroxides, which inhibit the uptake of hydrogen. Typically metal hydrides require activation, which usually comprises a slow and complicated annealing process at high temperature and at high hydrogen pressure. These drawbacks have limited the practical use of metal hydrides.

In recent years many new developments have occurred in metal hydrides, from the introduction of new, nonconventional methods of fabrication, surface treatment, or by the discoveries of new hydride phases [2–8]. In this paper we shall review nanocrystalline metal hydrides, which offer a breakthrough in prospects for practical application. Their excellent properties (significantly exceeding traditional hydrides) are a result of the combined engineering of many factors: alloy composition, surface properties, microstructure, grain size etc. In the development of nanocrystalline hydrides, the goal is not only to improve operational properties of the existing hydrides, but also (more importantly) to create a new generation of materials, with the properties being designed and controlled to fulfil the particular demands of different applications.

Hydrogenation, i.e. formation of metal hydrides by absorption of hydrogen, is determined by both the thermodynamics and kinetics of the reaction. We shall describe the basic mechanisms which control these two aspects, and also show possible ways of exploiting them in order to improve properties of metal hydrides.

2. Thermodynamic properties

The equilibrium state of metal–hydrogen systems is determined by thermodynamic functions such as the free energy or chemical potential. However, real materials rarely attain the equilibrium state. Some materials are by definition not thermodynamically stable, for example amorphous alloys or crystalline metastable phases. Additionally, most materials are far from the ideal, because they contain grain boundaries, defects, impurities, disorder or strain. Real materials (although very often exhibiting stable and reproducible behaviour in practical applications) cannot be fully described by the basic thermodynamic functions, so that *p–c* isotherms for these materials often differ significantly from theoretical expectations. In the following sections we will discuss a variety of factors which substan-

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tially modify the p–c isotherms, and indicate their significance for the development of new materials.

2.1. Metastable atomic arrangements

As was pointed out above, some materials are stable in a practical sense while being metastable in terms of thermodynamics. Amongst them are, for instance, amorphous structures, typically produced by non-equilibrium processing such as rapid solidification or mechanical alloying. A glassy structure differs from the equilibrium, crystalline state essentially in the local configuration of atoms. The lack of a crystallographically defined structural unit results in a distribution of local atomic positions in the structure of the glass. As a consequence, a wide distribution of the available sites for hydrogen occurs [9–11]. Therefore, the hydrogenation behaviour of the amorphous structure is totally different than that of the thermodynamically stable, crystalline material, although both materials may have identical composition. An example of such a change in p–c isotherms is presented in Fig. 1 for FeTi, where the plateau (characteristic for the crystalline hydride) totally disappears for the amorphous material [12,13]. This example clearly illustrates the sensitivity of the p–c isotherms to the local atomic configuration.

Nanocrystalline metals (with grain size of less than about 50 nm) are different in microstructure from both polycrystalline and amorphous materials. In the case of very small grains the amount of atoms located within or close to grain boundaries becomes significant [14]. One of the most important questions is how this factor may affect the hydrogenation properties of the material. Fig. 2 shows absorption p–c isotherms for two nanocrystalline FeTi materials, prepared by ball-milling under different conditions. Both alloys are in a structurally relaxed state, i.e. with no residual strain (as determined by x-ray analysis) or chemical disorder. The grain size in both alloys is comparable (larger in the case of alloy A, but for both below 10 nm). The p–c isotherms of both nanocrystalline alloys differ significantly from the polycrystalline FeTi with an enhancement of solid state solubility (seen previously for nanocrystalline Pd [15,16]), and in one case, a lowering of the plateau pressure. The differences in the p–c isotherms between the two nanocrystalline alloys can be attributed to their microstructure. In contrast to alloy A, some recognizable amount of amorphous phase can be detected by x-ray diffraction in the structure of alloy B, and transmission electron microscopy indicated that the amorphous phase is located within the grain boundaries, as shown in Fig. 3 [17–19]. Numerical evaluation (based on the deconvolution of the respective x-ray reflections) suggest that the amount of amorphous phase in this material is equal to about 30% [19]. Therefore, this particular example of nanocrystalline FeTi may be treated in some sense as a two-phase material. The p–c isotherm reflects two com-

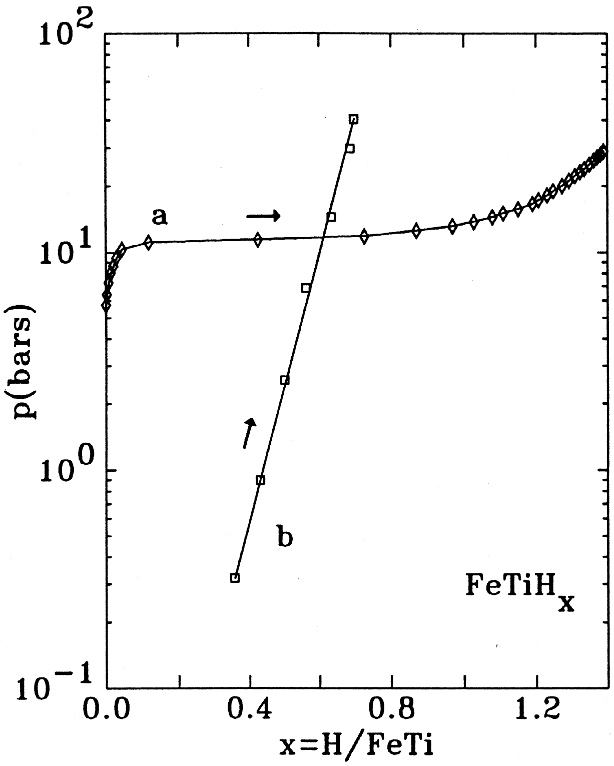

Fig. 1. Pressure–composition isotherms for absorption at room temperature for polycrystalline FeTi, and for amorphous FeTi.

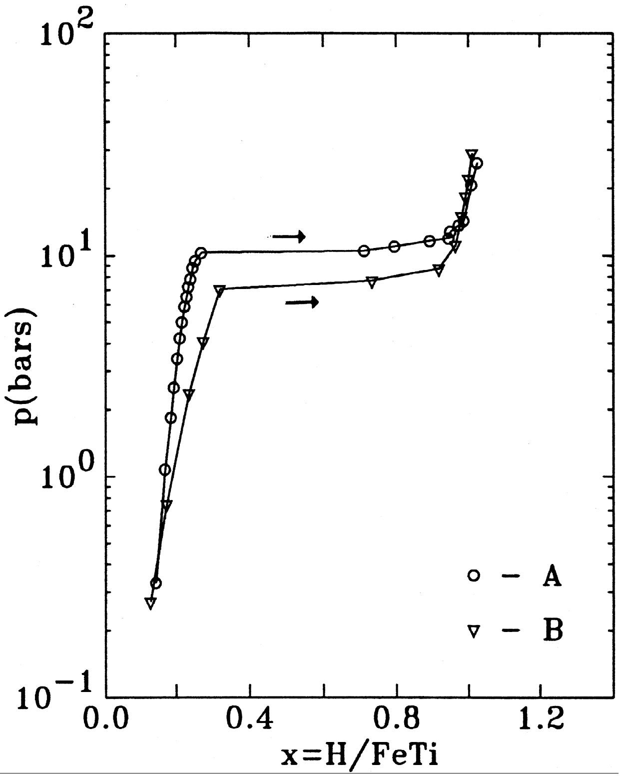

Fig. 2. Pressure–composition isotherms for absorption at room temperature for nanocrystalline FeTi (A) and nanocrystalline FeTi with amorphized grain-boundary phase (B).

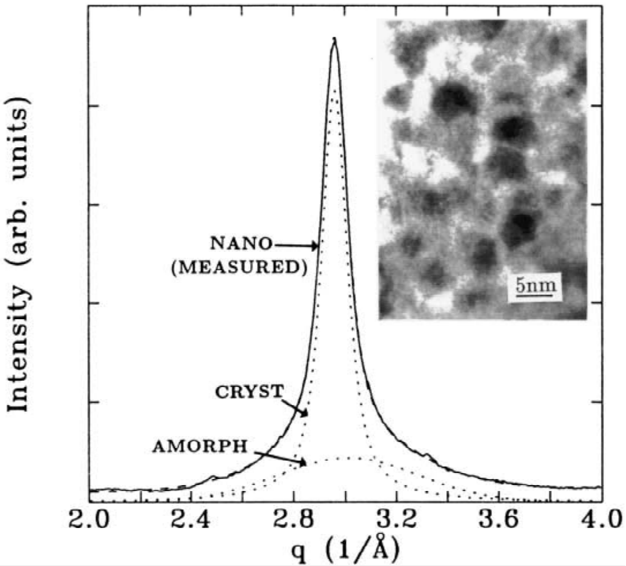

Fig. 3. X-ray structure factor for nanocrystalline FeTi showing deconvolution into amorphous and nanocrystalline phases [19]. Insert shows TEM micrograph of the same sample.

ponents: an enhanced range of solid-state solubility (which represents filling with hydrogen of the easily accessible sites in the amorphous grain boundaries [20]) and the formation of the crystalline hydride, which corresponds to the plateau. In the case of the partially amorphized alloy, the solid state solubility is further increased (as compared to the alloy without amorphous phase) and the plateau pressure is lower. This result may be explained by an interaction between the amorphous regions of grain boundaries and the nano-grains. The amorphous region is hydrogenated first, expands and so puts the encased nanograins under pressure, thus lowering the apparent plateau pressure. These phenomena are analyzed in detail (including the theoretical model and respective calculations) in Refs. [19,21].

From the above it can be seen that the characteristics of hydrogenation for nanocrystalline materials may depend essentially on the details of their microstructure, and on the other hand, the microstructure can easily be controlled by the fabrication process. In FeTi (and other systems, as for example Mg_2Ni) it is possible to obtain different degrees of grain-boundary amorphization, by changing the ball-milling conditions and purity of the ball-milling atmosphere [13]. Most nanocrystalline materials with a controlled degree of amorphization exhibit reproducible and stable *p–c* isotherms, provided they are not heated above 450 °C–500 °C, when grain growth may be initiated.

In conclusion, it has been shown that *p–c* isotherms for a given alloy can be effectively modified by the formation of metastable structures (e.g. amorphous structure). These structures can be obtained by means of a local change in the stable atomic positions into the metastable configurations, without changing local composition. Further modification may involve altering the relative amounts of the metastable and stable configurations (e.g. different degree of amorphization). As a consequence, the limits of solid state solubility in the *p–c* isotherm can be significantly extended and also the plateau pressure may be to some extent shifted.

2.2. Alloy composition

The chemical composition of the metal alloy is one of the most important factors in the metal–hydrogen system. The equilibrium conditions are reflected in the phase diagram, which dictates the respective phase composition under given temperature and pressure. Introducing metastable phases may result in a totally different behaviour of the alloy. In addition to metastable local atomic configurations (e.g. amorphous structure, as discussed in the previous section), metastable phases can be formed by altering the alloy composition, while preserving the crystallographic structure of the stable phase—in other words by forming supersaturated solutions. Unconventional methods of alloy fabrication (as for example rapid solidification or ball-milling) allow one to extend the solid state solubility of metals beyond the limits of stable phases. For example, at equilibrium the intermetallic compound FeTi exhibits a very limited solubility range, and any excess of iron or

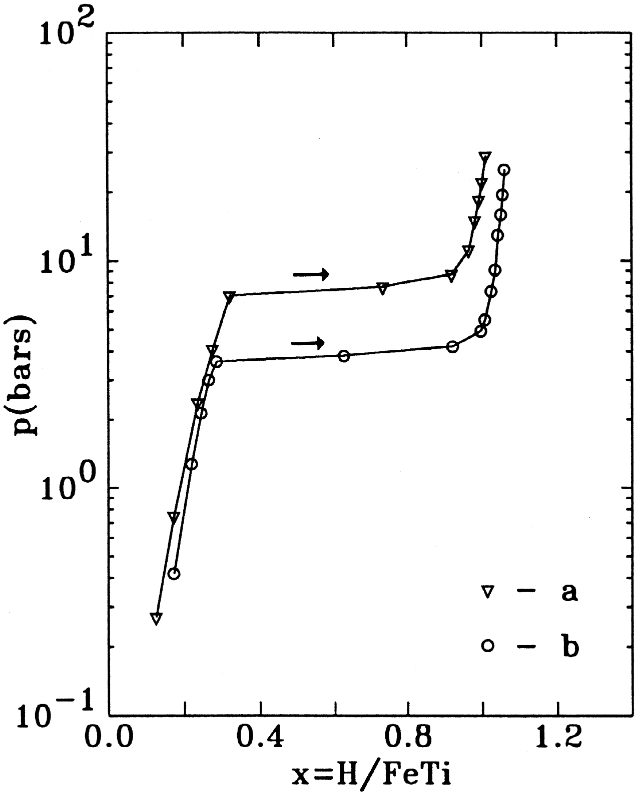

Fig. 4. Pressure–composition isotherms for absorption at room temperature for nanocrystalline FeTi(B)—(curve a) and nanocrystalline $Fe_{46}Ti_{54}$ (curve b).

titanium in the alloy results in the precipitation of additional phases. It is possible however, to extend the solubility range by using ball-milling [13]. Fig. 4 shows an example of a nanocrystalline FeTi supersaturated with Ti (by 4 at.%), in comparison to the stoichiometric alloy. Both materials have a grain size of less than 10 nm and exhibit enhanced solid-state solubility, which is a result of the nanocrystalline microstructure and the presence of grain boundaries. However, the essential difference between the two alloys is shown by the plateau pressure. The excess of Ti atoms in the FeTi structure results in a decrease of plateau pressure, as compared to the stoichiometric composition. It is noteworthy that the plateau remains flat and well defined in contrast to the behaviour for the system with a two-phase structure corresponding to a mixture of equilibrium phases, where the plateau is ''inclined'' [22]. Moreover, the nanocrystalline supersaturated alloy is in practice reasonably stable, i.e. there is no detectable precipitation of the excess Ti upon absorption and desorption. It should be noticed that the above example of the increase of plateau pressure due to alloying is not a universal feature. In other nanocrystalline alloys plateau pressure may be significantly increased, as for example by the addition of Cu to nanocrystalline Mg_2Ni [23]. Mg-based alloys (which are some of the most interesting for applications) behave in radically different ways depending on the addition. Some additions decrease plateau pressure, but most of them increase it (in some cases significantly), as it will be presented in upcoming papers.

2.3. Grain size and grain boundaries

In this section nanocrystalline alloys with no detectable amorphization will be described, i.e. alloys where no amorphous phase can be unambiguously detected by x-ray diffraction. TEM observations indicate that the grain boundaries are in this case narrower and better defined as compared to the structures which involve amorphization (in both cases no thinning of the TEM samples was applied in order to avoid thinning artifacts, and the observations were performed on thin edges of the samples). Fig. 5 shows a high-resolution TEM (HRTEM) micrograph of the grain boundary in nanocrystalline Mg_2Ni. In these alloys grain boundaries appear to be the high-angle boundaries. Since the contribution of grain boundaries obviously increases with the decrease of the grain size, for grains smaller than 20–30 nm the total amount of grain boundaries in the microstructure becomes very significant. For all nanocrystalline hydrides investigated (in the structurally relaxed state i.e. after proper annealing which eliminates the effects of strain and disorder, as is discussed in section 1d) the effect of grain boundaries does not dramatically change the shape of the *p–c* isotherms, apart from the enlarged solid state solubility already remarked upon. However, the effect of grain size becomes more visible in the van't Hoff plots, which show the correlation between plateau pressure and temperature. Fig. 6 shows a comparison of the van't Hoff plot for Mg with nanocrystalline structure, with the plot for conventional magnesium. The van't Hoff plot for nanocrystalline Mg is steeper. On the other hand, published results for nanocrystalline palladium do not indicate any significant difference in the enthalpy and entropy of hydrogenation, as compared to the polycrystalline material [24]. However, the reported measurements were performed for low temperatures only (below 100 °C), and as can be seen in Fig. 6, at lower temperatures the difference may be not obvious.

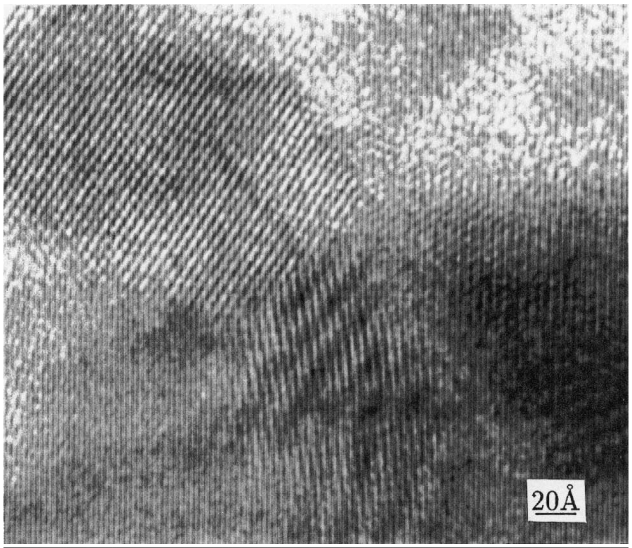

Fig. 5. HREM micrograph of the microstructure of nanocrystalline Mg_2Ni.

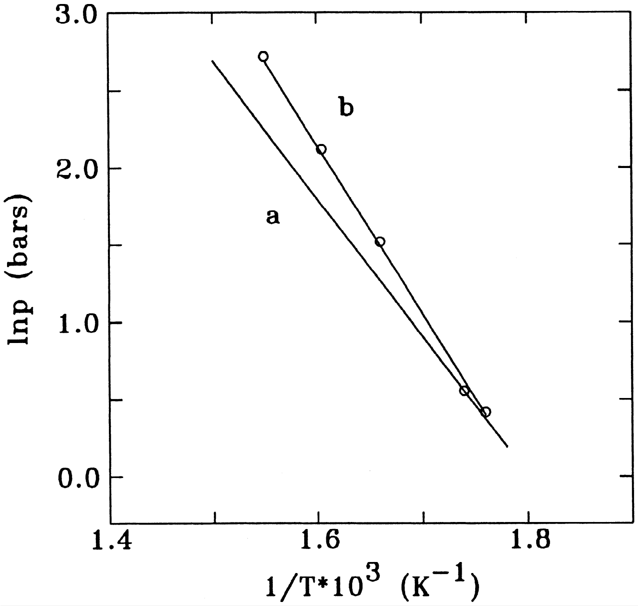

Fig. 6. Van't Hoff plot for magnesium (a) [2] and for nanocrystalline magnesium (b).

One possible explanation of the increased slope of the van't Hoff plot, which we have seen also in some other nanocrystalline hydrides [25], is that there is a higher binding energy of hydrogen in the nanocrystalline alloy. Since the plateau pressure taken for the van't Hoff plot corresponds to the hydrogenation of the nano-grains (and the solubility region to the grain boundaries), the increased binding energy should be attributed to the grains only, and not to the grain boundaries. Increased binding energy in nano-crystals may be explained for instance by assuming that nano-grains may not contain dislocations (as discussed in Ref. [26]), or may alternatively reflect other special defects with high binding energy. It is interesting to note that preliminary calorimetric measurements (DSC) indicate that the enthalpy of decomposition of the nanocrystalline hydride is indeed higher than that for the polycrystalline alloy. The effect of microstructure (and especially of the grain size and grain boundaries) on the van't Hoff plot is an interesting and open question, which still requires more study.

2.4. Strain and disorder

In addition to the above factors, the process of hydrogenation is very sensitive to imperfections, always present in real, non-equilibrium materials: defects, chemical disorder and strain. p–c–T characteristics may be altered substantially for materials containing significant amount of strain and disorder, as it was previously suggested in various papers [27,28]. However, direct experimental studies of these problems are often impossible, because most materials have to be activated (annealed at high temperature) prior to hydrogenation. The activation temperature usually exceeds the temperature at which chemical ordering and strain relief occurs, therefore inducing relaxation. By eliminating the need for activation (as is the case with nanocrystalline powders with a catalyst, described below in the section on kinetics) we can study for the first time unambiguously the effects of structural relaxation on hydrogenation. In Fig. 7 we show such effects in nanocrystalline FeTi, made by ball-milling. Ball-milling can introduce a significant amount of strain, disorder and defects into the material. Sensitivity of metal hydrides to these imperfections is reflected in the p–c isotherms. As shown in Fig. 7, the p–c isotherm for the nanocrystalline FeTi in the as-produced state differs drastically from the isotherms after annealing. These changes are indeed a result of relaxation, because careful structural investigation shows that there are no observable other changes in the microstructure such as grain growth or phase transformation. The p–c isotherm for the as-ball-milled state exhibit no plateau at all (curve a), because of the internal strain and chemical disorder, as discussed in detail in [29]. As seen in Fig. 7, a gradual change of the p–c isotherms is observed with annealing, until finally, after long annealing at 400 °C, a well defined plateau, characteristic for the fully relaxed material, is measured.

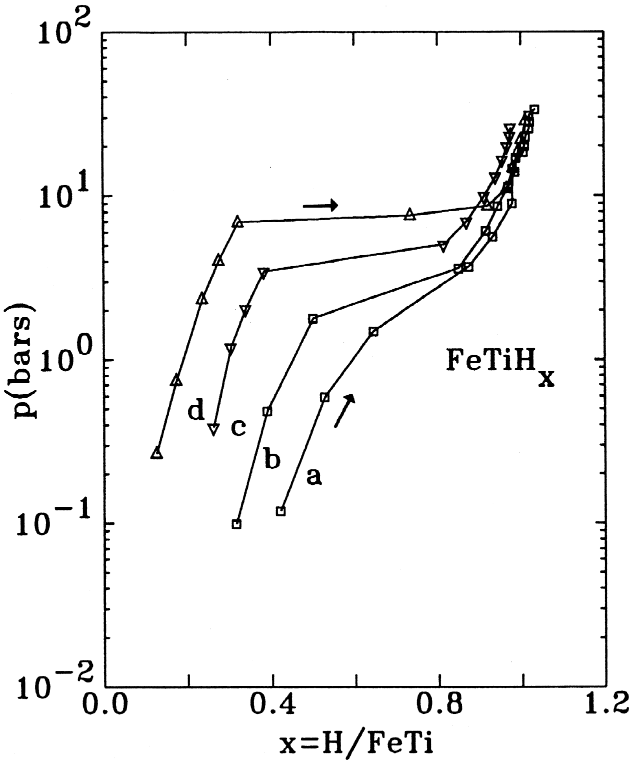

Fig. 7. Pressure–composition isotherms at room temperature for nanocrystalline FeTi in the as-ball-milled state (a) and after annealing at 300 °C for 0.5 h (b), at 400 °C for 0.5 h (c) and after prolonged annealing at 400 °C (d) [29].

The above result clearly shows that the unrelaxed material is in fact much easier to hydrogenate than the relaxed one. Much lower hydrogen pressures are required to obtain the same hydrogen content. However, it is not clear yet, how stable the unrelaxed structure is against prolonged absorption/desorption cycling, since hydrogenation may induce some local structural changes.

2.5. Multi-phase materials

Multi-phase nanocrystalline materials consist of two or more phases having different hydrogenation characteristics. The phases may belong to one system, but have different composition (e.g. Mg_2Ni+Mg in the Mg–Ni system), or come from completely different systems (e.g. Mg_2Ni+FeTi). Ball milling is of great use in the fabrication of such materials. Precise ball-milling conditions may result in the production of a special type of new composite, where two (or more) phases are finely distributed, both consisting of grains of the size of tens of nanometers. P–c isotherms of such composites consist of two plateau pressures, each of them corresponding to the different phase. Fig. 8 shows an example of a two-phase material consisting of Mg and Mg_2Ni. The lower plateau corre-

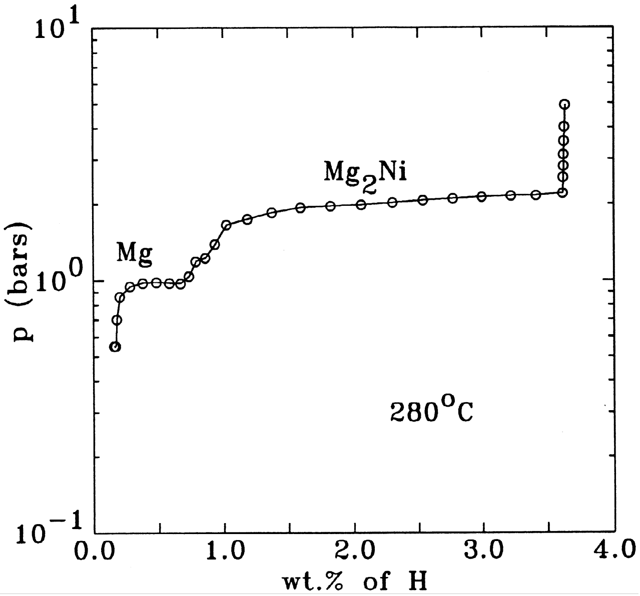

Fig. 8. Pressure–composition isotherm for nanocrystalline Mg_2Ni+Mg measured for desorption at 280 °C.

sponds to the hydrogenation of nanocrystalline magnesium and the higher may be attributed to Mg_2Ni.

3. Kinetic properties

For most metal hydrides the kinetics of hydrogenation are not determined by the bulk equilibrium thermodynamic parameters. For example, the driving force for hydrogenation of Mg is very high, even at room temperature. However, the absorption occurs only after elaborate activation and even then only at high temperature.

Instead, the rate of absorption is controlled by the following factors:

- the rate of hydrogen dissociation at the surface
- the capability of hydrogen to penetrate the surface, which is typically covered by an oxide layer
- the rate of hydrogen diffusion into the bulk metal and through the hydride already formed.

Development of new materials with fast absorption requires solutions for all the above problems. A favorable combination of these factors provides an outstanding improvement of absorption characteristics of the material, as is shown for nanocrystalline hydrides.

We begin with the problem of hydrogen diffusion in the material. To enhance the hydrogen diffusion, a special microstructure of the material should be developed. In the case of nanocrystalline materials, very small grain size gives an enormously increased amount of grain boundaries in the material. Although grain boundaries may act as hydrogen traps for very small hydrogen amounts, for higher hydrogen contents it was shown that diffusion coefficient of hydrogen in nanocrystalline Pd is higher than that for single-crystalline palladium [15]. Hydrogenation begins with filling of the easily accessible sites at the disordered (or amorphized) grain boundaries [20]. This leads to the easier access of hydrogen atoms to the nanograins, by avoiding long-range diffusion of hydrogen through the already formed hydride phase, which is one of the most difficult stages of absorption. The second factor, which may significantly improve hydrogen absorption, is the surface-to-volume ratio. The large surface-to-volume ratio in powders obtained by ball-milling enhance the accessibility of the material for hydrogen penetration. Additionally, ball-milling presumably creates a specific state of the surface, possibly with special surface defects and imperfections. All this promotes hydrogen absorption, which is consistently reported in various papers [30–32]. Accordingly, ball-milled, nanocrystalline materials appear to have an ideal microstructure for hydrogen absorption. Microstructure of the ball-milled powder of Mg_2Ni is shown in Fig. 9. The powder (of the size of 20–50 μm)

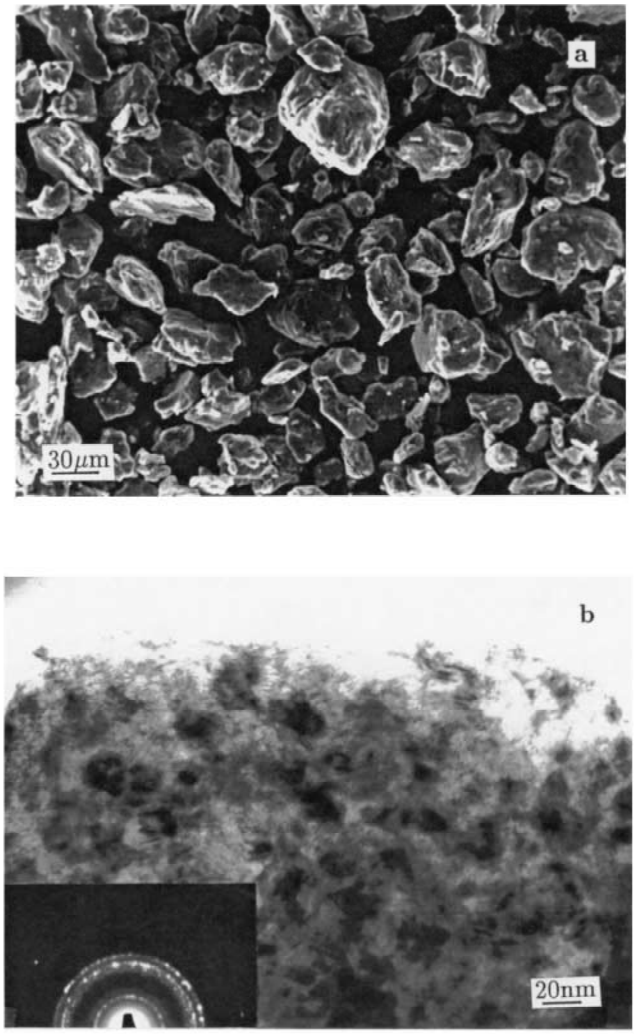

Fig. 9. SEM and TEM micrographs of the microstructure of nanocrystalline Mg_2Ni.

consist of very small grains (20–30 nm), which are randomly oriented in the powder particles [23]. As expected, hydrogen absorption of the nanocrystalline material significantly exceeds absorption rates for the conventional alloy. Fig. 10 shows that polycrystalline Mg_2Ni exhibits almost no absorption at 200 °C, but nanocrystalline material absorbs hydrogen with good kinetics.

The rate of absorption may be improved even more radically, when the other kinetic limitations are also reduced. Hydrogen dissociation is one of the critical factors in the hydrogen absorption [33]. For example, pure surfaces of Mg do not have sufficient ability to adsorb and dissociate hydrogen molecules to enable atomic diffusion inside the metal [34]. Magnesium oxides may actually help dissociation of hydrogen molecules, but on the other hand the oxide layer significantly slows down the overall absorption rate. On the other hand, for FeTi the sticking coefficient of hydrogen on the clean surface is much higher, but the oxide layer reduces dissociative chemisorption of hydrogen almost completely. Therefore the probable mechanism of activation is that the oxide layers are broken up to expose clean metal surfaces so that the overall rate of absorption is enhanced [35,36]. Hydrogen dissociation can be changed dramatically by using catalysts [37]. The proper catalyst enables fast and effective dissociation of hydrogen molecules. The efficiency of the catalyst is determined by its ability to ‘‘flood’’ the metal surface with hydrogen atoms to such an extent that the kinetic barrier of the oxide layer is diminished. Therefore, both the efficiency in dissociation and also the proper distribution of the catalyst on the metal surface are of the equal importance. It was reported that a metal surface (e.g. of magnesium) fully covered by a layer of the catalyst may be much more active for hydrogen absorption [37,38]. However, the enhancement of absorption rate is reduced again when the interface layer of magnesium hydride is formed, because of the very slow hydrogen diffusion in the hydride layer [39,40].

Our results with Pd as a catalyst have proved the efficiency of hydrogen dissociation [41]. The amount of Pd is very small (less than 1 wt.%) and the catalyst is in the form of very small particles (of the size of 50 nm), attached to the surface of the powders. Fig. 11 shows SEM and TEM micrographs of Pd particles on Mg_2Ni [23]. Fig. 10 shows absorption rate at 200 °C for Mg_2Ni (curve c) with the catalyst. Hydrogen absorption is in this case very fast, even for the first hydrogenation cycle (after exposure to air and without subsequent activation) [23]. Mg_2Ni absorbs hydrogen even at room temperature, with good kinetics (Fig. 12). Although the efficiency of our method of catalysis is indeed outstanding, the actual micro-mechanism of the action of palladium clusters still needs more

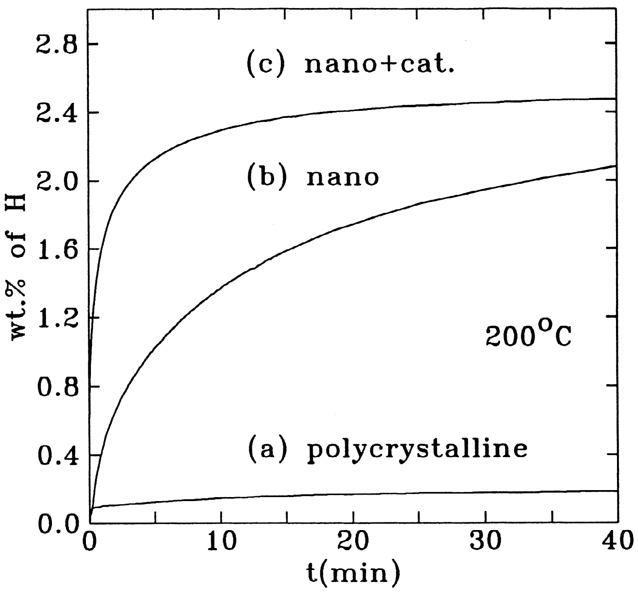

Fig. 10. Rate of hydrogen absorption by Mg_2Ni: polycrystalline (a), nanocrystalline (b) and nanocrystalline with catalyst (c); first cycle, no activation, temperature 200 °C, pressure 15 bar.

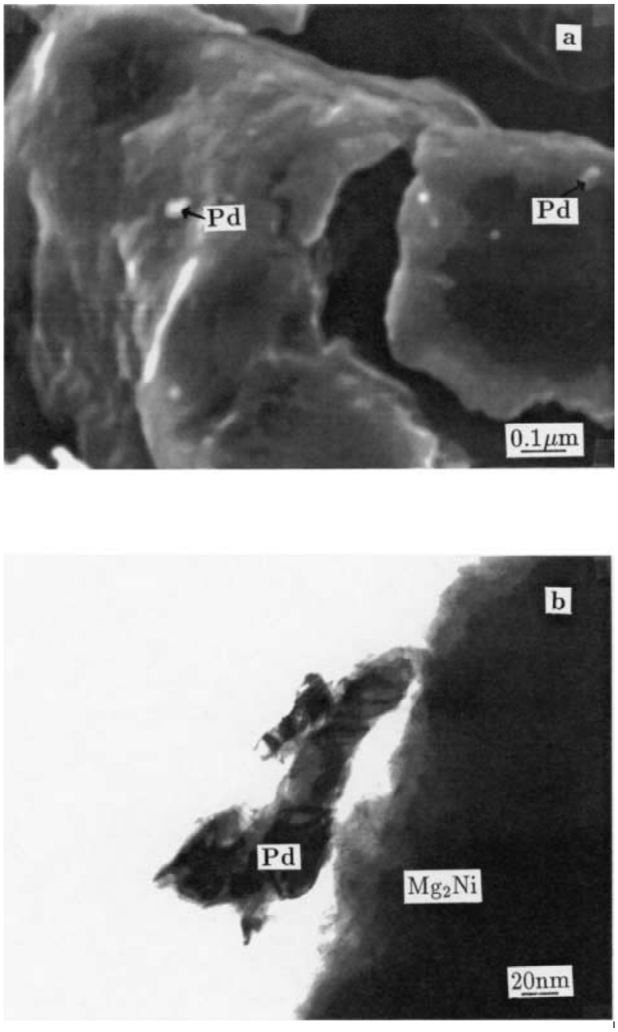

Fig. 11. (a)—SEM micrograph of Mg-based alloy with attached small particle of catalyst. (b)—TEM micrograph of the catalyst particle on Mg_2Ni [23].

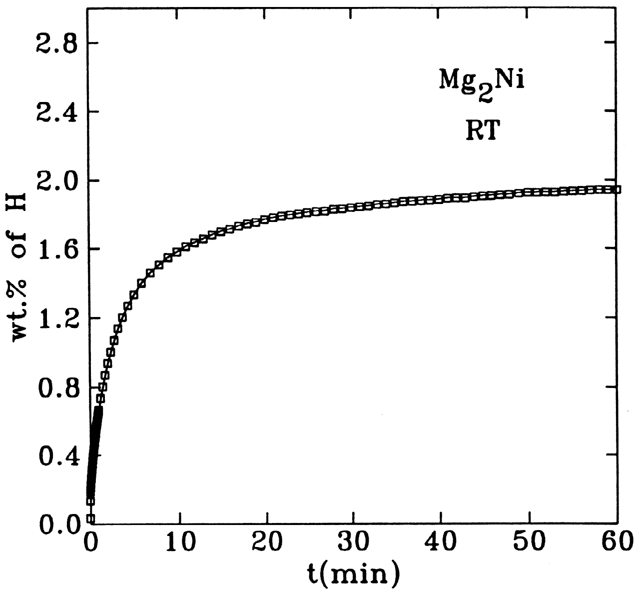

Fig. 12. Room temperature absorption for nanocrystalline Mg_2Ni; no activation.

detailed studies. At present, the “spill-over” process seems to be the most probable mechanism of the catalysis [42].

The practical consequence of catalysis is that the hydrogenation process becomes insensitive to surface oxidation so that the problem of poisoning of the metal surface by exposure to air is circumvented. As a consequence, activation becomes unnecessary and the powders readily absorb hydrogen in the as-prepared state, even after exposure to air. The powders are also not pyrophoric, even when very fine.

The kinetic factors for the desorption of hydrogen are analogous to absorption, and require similar considerations. The desorption rate may be limited by hydrogen diffusion in the material, and by recombination into hydrogen molecules on the surface. Therefore, the enhancement of desorption may be obtained by the similar methods as those applied for absorption.

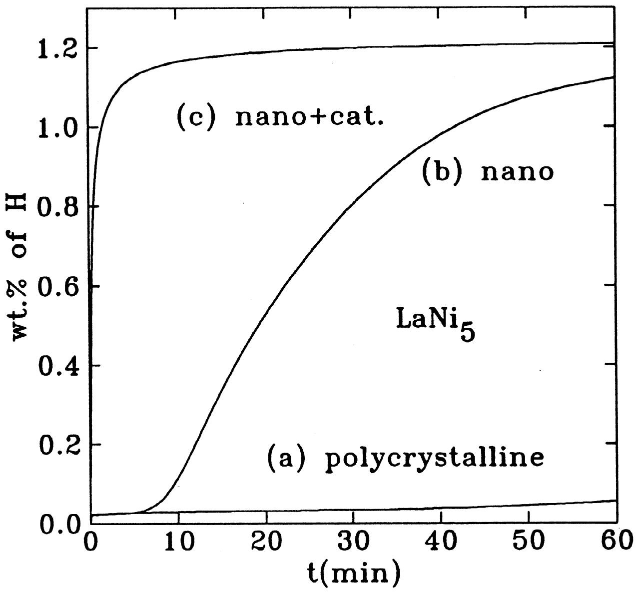

Fig. 13. Rate of hydrogen absorption by $LaNi_5$: polycrystalline (a), nanocrystalline (b) and nanocrystalline with catalyst (c); no activation, temperature 40 °C, pressure 15 bar [41].

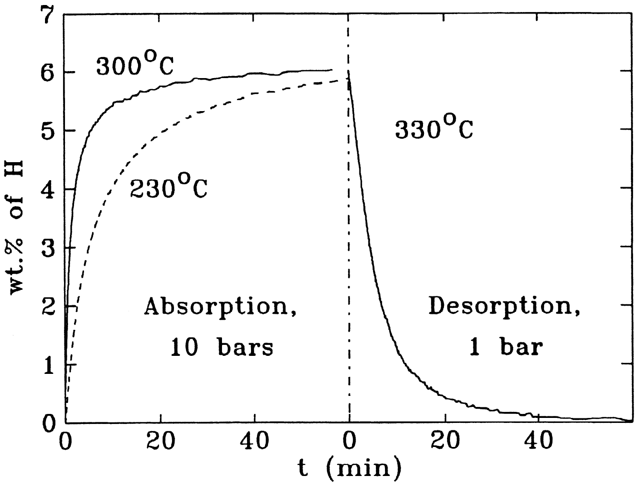

Fig. 14. Absorption and desorption for a nanocrystalline Mg-based alloy.

The above procedures may be successfully applied to different hydrides, providing in each case exceptional improvement in hydrogen sorption as shown for example for $LaNi_5$ in Fig. 13 [41]. The same may be applied to the light alloys containing magnesium, which combine two important advantages: high hydrogen capacity and low cost. Examples of the performance of light nanocrystalline alloys are presented in Fig. 14 [43] and Fig. 15. Fig. 16 shows absorption at low temperature of a light alloy. In all cases the nanocrystalline powders were exposed to air between the fabrication and hydrogenation, and exhibited no pyrophoric tendency. After the exposure to air (in some cases of the order of weeks) the kinetic hydrogenation

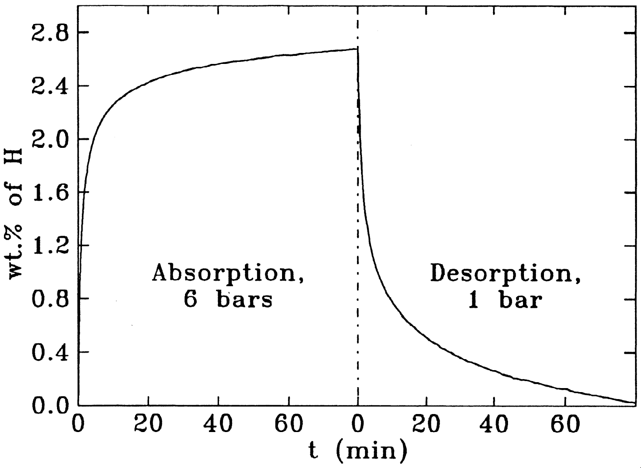

Fig. 15. Absorption and desorption for a nanocrystalline light alloy at 235 °C.

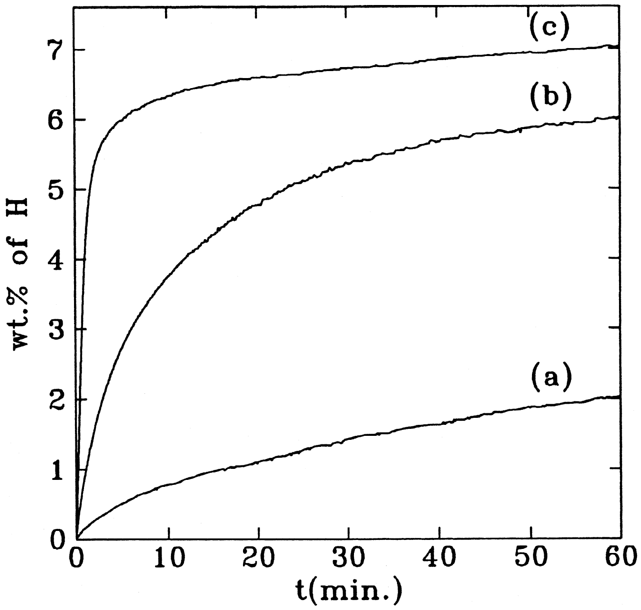

Fig. 16. Low-temperature absorption of a light nanocrystalline alloy: 110 °C (a), 170 °C (b), 190 °C, (c) (20 bars).

curves were measured, without prior activation or hydrogen treatment, and found to be unaltered. Finally, the nanocrystalline powders do not decrepitate upon absorption/desorption cycling.

4. Conclusions

The development of new materials for hydrogen storage requires overcoming many thermodynamic and kinetic limitations. In the new generation of advanced materials, proper engineering of the alloy composition, surface properties, microstructure, grain size etc., allows us to design and control properties of the material, according to the requirement of the particular application. A variety of metastable phases and microstructures offers enormous possibilities of modifying the p–c–T characteristics in favour of better performance.

This paper presents a new class of material for hydrogen storage: nanocrystalline hydrides. These materials show substantially enhanced absorption and desorption kinetics, even at relatively low temperatures. Moreover, powders with catalyst do not require activation. Recent results on nanocrystalline hydrides have proved that by adopting a special microstructure and appropriate catalyst the use of light metals for hydrogen storage is now viable. Nanocrystalline hydrides allow us to create a storage device with a high hydrogen capacity (of the order of 5–6 wt.%) combined with excellent kinetics at temperatures much lower than traditional hydrides, over a pressure range of 1–10 bars.

Acknowledgments

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References

[1] S. Suda and G. Sandrock Zeit, *Phys. Chem.*, *183* (1994) 149.
[2] B. Bogdanović and B. Spliethoff, *Int. J. Hydrogen Energy*, *12* (1987) 863.
[3] F.J. Liu and S. Suda, *J. Alloys Comp.*, *232* (1996) 212.
[4] H. Imamura, N. Sakasai and Y. Kajii, *J. Alloys Comp.*, *232* (1996) 218.
[5] B. Huang, K. Yvon and P. Fischer, *J. Alloys Comp.*, *227* (1995) 121.
[6] W. Bronger, *J. Alloys Comp.*, *229* (1995) 1.
[7] S. Orimo, H. Fujii and M. Tabata, *J. Alloys Comp.*, *210* (1994) 37.
[8] H. Iba and E. Akiba, *J. Alloys Comp.*, *231* (1995) 508.
[9] R. Griessen, *Phys. Rev. B*, *30* (1983) 7575.
[10] E. Batalla, J.O. Ström-Olsen, Z. Altounian, D. Boothroyd and R. Harris, *J. Mater. Res.*, *1* (1986) 765.
[11] J.R.C. Bowman, *Mater. Sci. Forum*, *31* (1988) 197.
[12] L. Zaluski, S. Hosatte, P. Tessier, D.H. Ryan, J.O. Ström-Olsen, M.L. Trudeau and R. Schulz in *Metal–Hydrogen Systems* (M.R. Oldenbourg Verlag, ed.), Uppsala, 1992, p. 1067.
[13] L. Zaluski, P. Tessier, D.H. Ryan, C.B. Doner, A. Zaluska, J.O. Ström-Olsen, M.L. Trudeau and R. Schulz, *J. Mater. Res.*, *8* (1993) 3059.
[14] H.-J. Fecht, *Mater. Sci. Forum*, *126* (1993).
[15] R. Kirchheim, T. Mütschele, W. Kieninger, H. Gleiter, R. Birringer and T.D. Koble, *Mater. Sci. Eng.*, *99* (1988) 457.
[16] J.A. Eastman, L.J. Thompson and B.J. Kestel, *Phys. Rev.*, *B48* (1993) 84.
[17] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, *J. Mater. Sci.*, *31* (1996) 695.
[18] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, *Mater. Sci. Forum*, *225–227* (1996) 875.
[19] P. Tessier, Ph.D. Thesis, McGill University, 1995.
[20] U. Stuhr, H. Wipf, T.J. Udovic, J. Weissmüller and H. Gleiter, *J. Phys.: Condens. Matter*, *7* (1995) 219.
[21] P. Tessier, L. Zaluski, A. Zaluska, J.O. Ström-Olsen and R. Schulz, *Mater. Sci. Forum*, *225–227* (1996) 869.
[22] J.J. Reilly and J.R.H. Wiswall, *Inorg. Chem.*, *13* (1974) 218.
[23] L. Zaluski, A. Zaluska and J.O. Ström-Olsen, *J. Alloys Comp.*, *217* (1995) 245.
[24] D.H. Everett and A.P. Sermon, *Z. Phys. Chem. Neue Folge*, *114* (1979) 109.
[25] L. Zaluski, A. Zaluska and J.O. Ström-Olsen unpublished results.
[26] V.G. Gryaznov, I.A. Polonsky, A.E. Romanov and L.I. Trusov, *Phys. Rev. B*, *44* (1991) 42.
[27] T.B. Flanagan, *Metal Hydrides*, chap. on Thermodynamics of metal–hydrogen systems. NATO Advanced Study Institutes Series, Series B: Physics, 1981.
[28] K. Nomura, H. Hayakawa, E. Akiba, S. Shin and S. Ono, *Proc. MRS Int. Meeting on Advanced Materials*, 1989 p. 45.
[29] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, *J. Alloys Comp.*, *227* (1995) 53.
[30] A. Stepanov, E. Ivanov, I. Konstanchuk and V. Boldyrev, *J. Less-Common Met.*, *131* (1987) 89.
[31] H. Aoyagi, K. Aoki and T. Masumoto, *J. Alloys Comp.*, *231* (1995) 804.
[32] M.-Q. Lü, H.-F. Zhang, Y.-L. Wang and W.-D. Wei, *J. Alloys Comp.*, *191* (1993) 319.

[33] L. Schlapbach, *Hydrogen in Intermetallic Compounds II*, chap. on Surface properties and activation, Topics in Applied Physics, 1992.

[34] J.K. Nörskov, A. Houmüller, P. Johasson and A.S. Pedersen, *J. Less Common Met.*, *46* (1981) 257.

[35] F.D. Manchester and D. Khatamian, *Mater. Sci. Forum*, *31* (1988) 261.

[36] C.P. Chen, B.H. Liu, Z.P. Li, J. Wu and Q.D. Wang, *Z. Phys. Chem.*, *181* (1993) 259.

[37] H.H. Uchida, H.-G. Wulz and E. Fromm, *J. Less Common Met.*, *172–174* (1991) 1076.

[38] F. Stillesjö, S. Ólafsson, B. Hjörvasson and E. Karlsson, *Zeit. Phys. Chem.*, *181* (1993) 353.

[39] B. Vigeholm, J. Kjoller, B. Larsen and A.S. Pedersren, *J. Less-Common Met.*, *89* (1983) 135.

[40] J. Rýden, B. Hjörvarsson, T. Ericsson, E. Karlsson, A. Krozer and B. Kasemo, *Z. Phys. Chem. Neue Folge*, *164* (1989) 1259.

[41] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, *J. Alloys Comp.*, *217* (1995) 295.

[42] T. Fleisch and R. Abermann, *J. Catalysis*, *50* (1977) 268.

[43] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, *Mater. Sci. Forum*, *225–227* (1996) 853.