

A Screening Method for Hydrogen Storage Alloys

Hasan AKYILDIZ, Gülhan ÇAKMAK, Serdar TAN and Tayfur ÖZTÜRK
*Middle East Technical University, Department of Metallurgical and Materials Engineering,
06531, Ankara-TURKEY*
e-mail: ozturk@metu.edu.tr

Received 16.03.2007

Abstract

A screening method is described that can be used for rapid evaluation of metallic systems for their hydrogen storage potentials. The method makes use of a single sample of compacted elemental powders that are sintered to yield nearly all phases and compounds of the respective phase diagram. The sample is then evaluated in a Sievert's type apparatus by charging with hydrogen of initially known pressure and recording the pressure change as a function of temperature. Deviation from linearity in the pressure-temperature relationship is a sign of hydrogen sorption in that particular system. As to which phase (or phases) absorbs hydrogen is determined with the detailed comparison of X-ray analysis of the sample before and after hydrogenation. The method is applied to Mg-Al binary with success. In Mg-Ni-Al ternary, the method is partially successful due to the limited number of phases that could be formed. This could be remedied either by mechanical milling of powders before compaction or, preferably, by splitting the ternary system into regions of similar solidus temperatures.

Key words: Combinatorial method, hydrogen storage, internal reaction, Mg-Al, Mg-Ni-Al, Mg₁₇Al₁₂.

Introduction

A large number of studies (e.g., Zaluska et al., 1999; Bobet et al., 2001; Güvendiren et al., 2004) were carried out, especially in the last decade, and hydrogen storage characteristics of various metallic compositions were characterized. Typically such studies require a lengthy preparation of a specific composition, its processing, and a characterization procedure to establish its sorption properties. Not all studies are, however, successful for end purposes. Thus, before efforts are concentrated on a particular composition, a rapid method to establish hydrogen storage potential of various phases and compounds in a binary or multi-component system would be beneficial.

The search for rapid methods for the discovery of new materials is not new. The first application of such methods dates back to the 1950s and refers to the field of phase diagram determination itself. Thus, in order to construct phase diagrams, Boettcher et al. (1955) deposited thin films

with composition gradients and used electron diffraction to identify the phases. Hanak, in the early 1970s, took this approach one step forward and, following co-sputtering to obtain compositional variation, screened various properties, e.g., superconductivity, from the thin film compositions. He proposed that this multiple-sample concept was far more efficient than studying the one-composition-at-a-time approach. The application of this concept was not necessarily limited to thin film work. Just as the phase diagrams may be constructed from diffusion couples or diffusion-multiples (e.g. Jin, 1981), they could also be used for screening purposes. Thus Zhao (2001) used bulk samples made up of phases formed through inter-diffusion of several materials in intimate contact with one another and mapped them using localized micro-scale property measurements.

First applications of the rapid search for hydrogen storage alloys were reported in the 9th International Symposium on Metal-Hydrogen Systems in 2004. There were 2 methods reported, one by the

present authors based on powder metallurgical processes (Akyıldız et al., 2004) and the other by Zhao et al. (2004). The latter, as above, made use of diffusion multiples from bulk constituents and used time-of-flight secondary ion mass spectroscopy as the screening method. Recently a thin film method was developed by Dam et al. (2007). The method makes use of an optical screening technique and can be used for binary or ternary systems provided that the phases involved change their optical state upon hydriding.

The current paper follows an earlier report (Akyıldız et al., 2004) and gives a detailed account of the screening method, together with its applications to alloy systems Mg-Al and Mg-Ni-Al. The method makes use of metallic powders as diffusion-multiples and uses commonly available X-ray diffraction techniques as the screening tool.

Materials and Methods

A schematic representation of the steps involved in the screening method is shown in Figure 1. The method involves mixing and hot compaction/sintering of elemental powders. As such, the method relies on the internal reaction of elemental powders to yield all phases and compounds in a single sample. In mixing, elemental powders, preferably similar particle size, are blended in equal volumetric proportions. This is for the purpose of maximizing particle-particle contact among different elemental powders. Hot compaction and sintering are carried out in the solid state at the highest possible temperature. Liquefaction is avoided as it would lead to the formation of single or fewer phases in the system. This treatment leads to the formation of a series of phases across the respective phase diagram (Zhang et al., 2001).

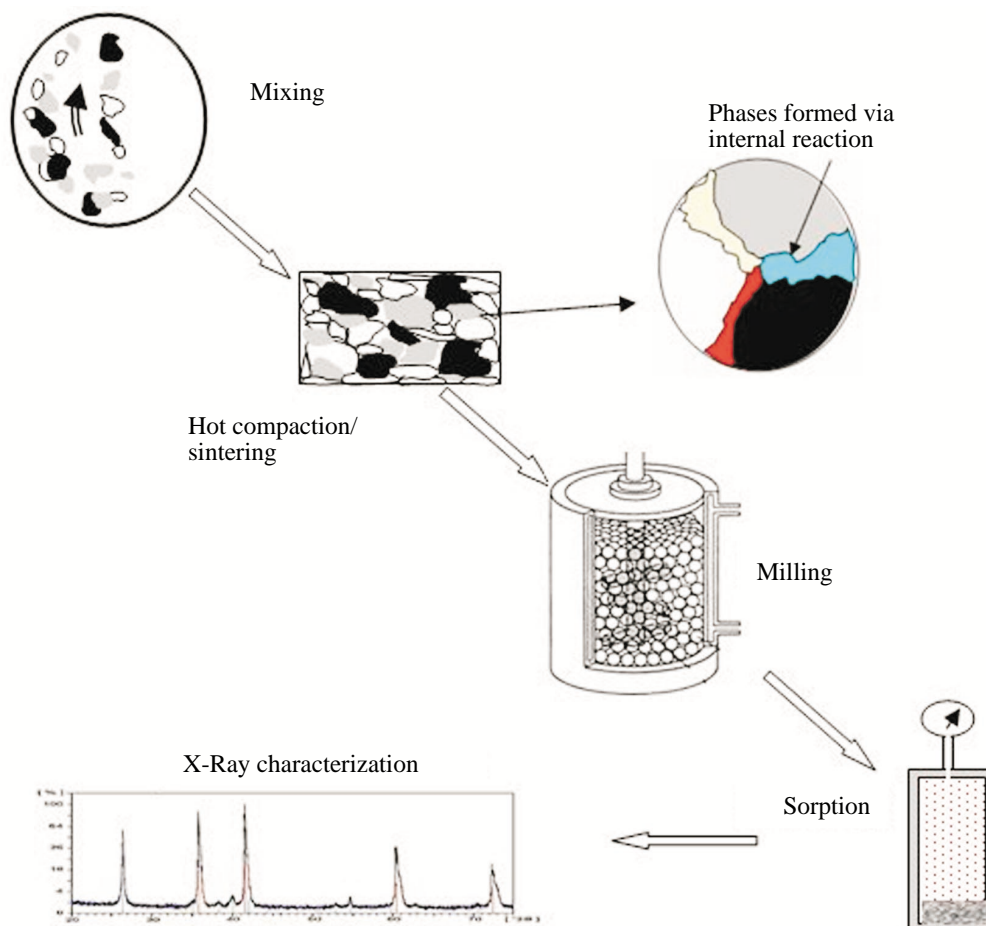


Figure 1. A schematic representation of the steps involved in the screening method.

The sample is then milled and subjected to hydrogenation experiments in a Sievert's type apparatus. The experiment simply involves heating and cooling of samples with a slow rate under a certain hydrogen pressure. Absorption or desorption is noted by monitoring the pressure change as a function of temperature. The samples are then examined in hydrided and dehydrided conditions with X-ray diffraction so as to identify the phase(s) involved in sorption.

The method was applied to Mg-Al binary and Mg-Ni-Al ternary systems. Powder samples were mixed with equal volumetric proportions with the addition of 1 wt% TiH₂. Particle sizes of the powders were approximately 40 μm for Mg and Ni, and 30 μm for Al. The powder mixtures were then hot pressed at 400 °C for 3 h. Following this solid-state sintering, the samples were ground by hand into coarse powders, and then attritor-milled with 5 wt% graphite addition. Milling was carried out with a ball-to-powder ratio of 10 in a glow box under argon atmosphere. The samples for hydrogenation experiments were typically 0.5 g. The hydrogenation experiments were carried out at a pressure (room temperature) of 1 MPa. The samples were heated up to 400 °C in increments of 5 °C/min. The samples were cycled (hydrided and dehydrided) once and cooled to room temperature before measurement. Thus the data reported in this work refer to the second cycle.

Results and Discussion

Mg-Al Binary System: Sintering of Mg-Al powders was successful in that all phases relevant to Mg-Al system were obtained in a single sample. Figure 2 shows the microstructure of the sintered sample. As verified with EDAX analysis, the sample contains Mg₂Al₃ and Mg₁₇Al₁₂ intermetallics together with Mg and Al phases. As checked with X-ray diffraction, the amount of Mg₂Al₃ is much less than that of Mg₁₇Al₁₂.

The pressure-temperature diagram of the sintered and milled Mg-Al powders is given in Figure 3. With no reaction, the pressure is expected to change linearly with temperature. This is the case up to about 250 °C. Above this temperature, the rise in pressure is less than expected, implying that the powder absorbed hydrogen. In fact, at higher temperatures, the rise in pressure is more than compensated for by the absorption. Thus, there is a net drop in pressure. The drop in pressure starts around

300 °C, and continues up to 340 °C. Above approximately 375 °C, the trend is reversed. The pressure beyond this temperature rises more quickly than expected. Thus, the hydrogen that was absorbed at a lower temperature is now desorbed. The experiment was terminated at 400 °C. It appears, judged from the initial slope, that desorption at 400 °C is only partially complete.

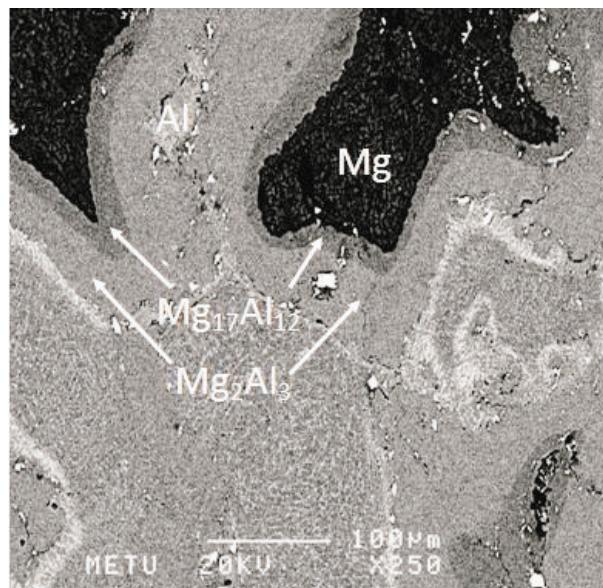


Figure 2. Microstructure (back scattered image) of Mg-Al elemental powders sintered at 400 °C. Mg and Al phases are evident in the structure together with intermetallics Mg₁₇Al₁₂ and Mg₂Al₃ formed as a result of internal reaction.

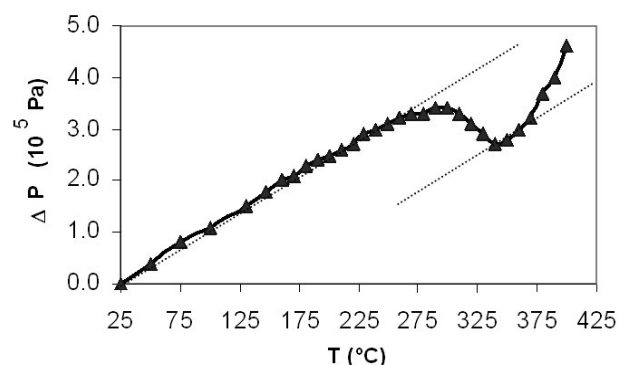


Figure 3. Variation of hydrogen pressure with temperature in a constant volume experiment for a multi-phase sample based on Mg-Al binary. Pressure drop close to 275 °C is due to hydrogen absorption, see text for details.

To identify the phases involved in the reaction, 2 samples (hydrided and dehydrided) were prepared. For the former, the sample was heated up to 400 °C and cooled slowly to room temperature under hydrogen. For the latter, the sample was subjected to the same treatment with the exception that, upon reaching 400 °C, the hydrogen was discharged and the system was taken under vacuum and kept so while the chamber was cooled to room temperature.

The X-ray diffractograms of the hydrided and dehydrided samples are given in Figure 4. In the hydrided sample, MgH_2 is the dominant phase. Thus hydrogen is absorbed in the sample in the form of MgH_2 . Additional phases present in this sample are $\text{Mg}_{17}\text{Al}_{12}$, Mg_2Al_3 , Al, and Mg. In the dehydrided sample, there is no hydride phase. The sample is dominated by $\text{Mg}_{17}\text{Al}_{12}$, whose intensity is now much stronger. The amount of Mg_2Al_3 is reduced drastically. Al, if present, occurs only in a trace amount.

The observations made in this study are consistent with those reported by Bouricha et al. (2000), and imply that, upon hydriding, $\text{Mg}_{17}\text{Al}_{12}$ absorbs hydrogen by a disproportionation reaction. As a result, $\text{Mg}_{17}\text{Al}_{12}$ is split into MgH_2 , Mg_2Al_3 , and Al. The reaction appears to be reversible in the sense that, upon dehydriding, the phases combine, forming the parent $\text{Mg}_{17}\text{Al}_{12}$ phase.

Thus, of the variety of phases present in the sample, it is only the $\text{Mg}_{17}\text{Al}_{12}$ phase that has a potential as a hydrogen storage material. This is, of course, true for the current experimental conditions,

i.e. no special activation treatment, pressure level up to 1 MPa, temperatures up to 400 °C. With the application of higher pressure or temperature, the other phases may also absorb hydrogen. For the current experimental condition, Mg does not appear to be active; the amount that is present in the milled sample appears to be unaffected both in the hydrided and dehydrided sample. The same is true for Mg_2Al_3 , which is known (Mintz et al., 1980) to absorb hydrogen via a disproportionation reaction similar to $\text{Mg}_{17}\text{Al}_{12}$ but with much slower kinetics and under higher hydrogen pressures (Bouricha et al., 2000) (see below).

Mg-Ni-Al Ternary System: The microstructure of sintered Mg-Ni-Al compact is given in Figure 5. Sintering was not altogether successful in that Ni particles remain unreacted in the structure. In addition to Ni, the other phases present are Mg_2Al_3 , $\text{Mg}_{17}\text{Al}_{12}$, and Mg, i.e. the same phases as in Mg-Al. A distinct Al phase could not be observed in the structure, indicating that it had been consumed totally in the internal reaction.

The pressure-temperature diagram of the milled Mg-Ni-Al is given in Figure 6. The diagram indicates a pressure drop, i.e. absorption at temperature around 225 °C. From the reduced level, the pressure increases linearly up to 350 °C. At this temperature, the pressure starts rising with a faster rate, indicating desorption. Beyond 375 °C, the slope is nearly the same as the initial one before absorption. Thus hydride formed remains stable over a temperature interval of 150 °C.

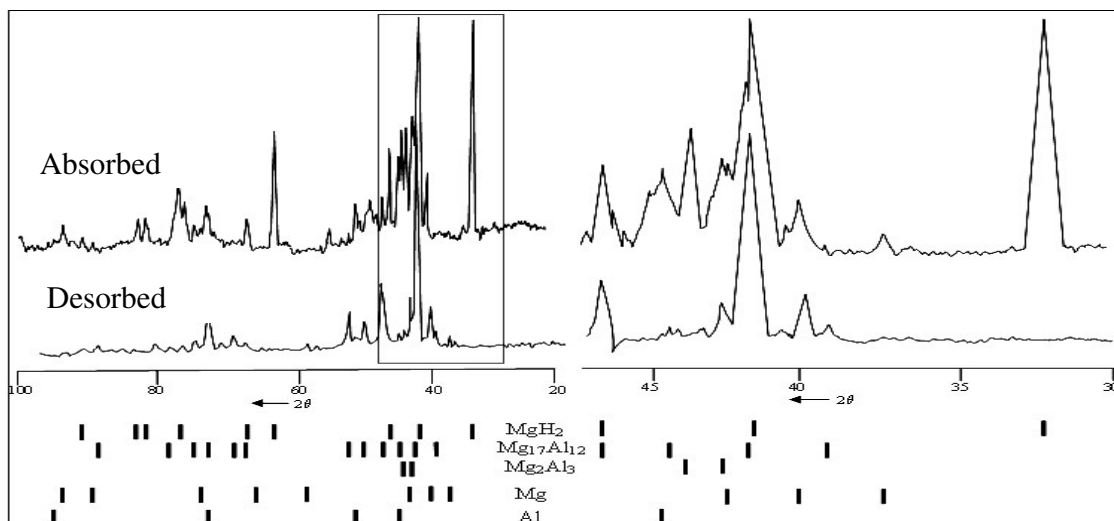


Figure 4. X-ray diffractogram ($\text{CoK}\alpha$) of hydrided (above) and dehydrided (below) multi-phase sample based on Mg-Al. Note that, in the hydrided sample, MgH_2 is formed together with Al and Mg_2Al_3 .

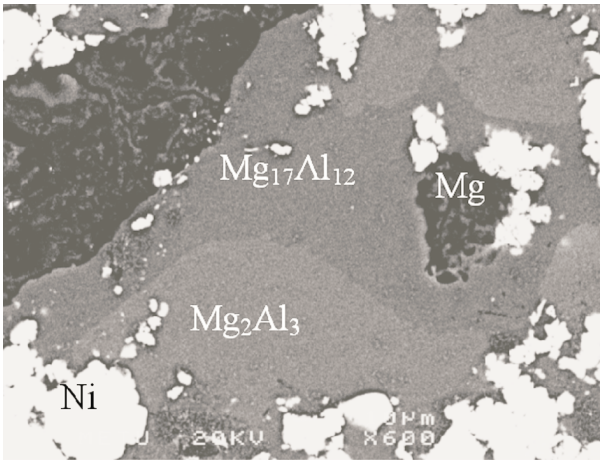


Figure 5. Microstructure of Mg-Ni-Al elemental powders sintered at 400 °C. Ni particles remain largely unreacted, Mg phase is Al rich. Intermetallics $Mg_{17}Al_{12}$ and Mg_2Al_3 are the main products of internal reaction.

To identify the phases involved in the reaction, 2 samples are prepared as before. The X-ray diffractograms of the hydrided and dehydrided samples

are given in Figure 7. In the dehydrided sample, the phases largely confirm what was reported above. The diffractogram is dominated by Ni peaks, and the other phases present are $Mg_{17}Al_{12}$ and a small amount of Mg_2Al_3 . The phases included Mg, which could barely be identified, and an additional weak phase identified as Al_3Ni .

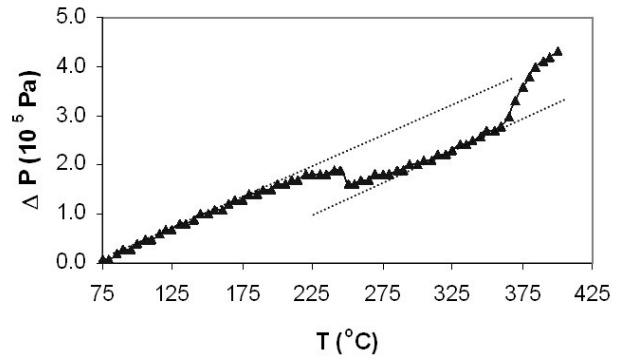


Figure 6. Variation of hydrogen pressure with temperature in a constant volume experiment for a multi-phase sample based on Mg-Ni-Al ternary. Note pressure drop at temperatures close to 225 °C.

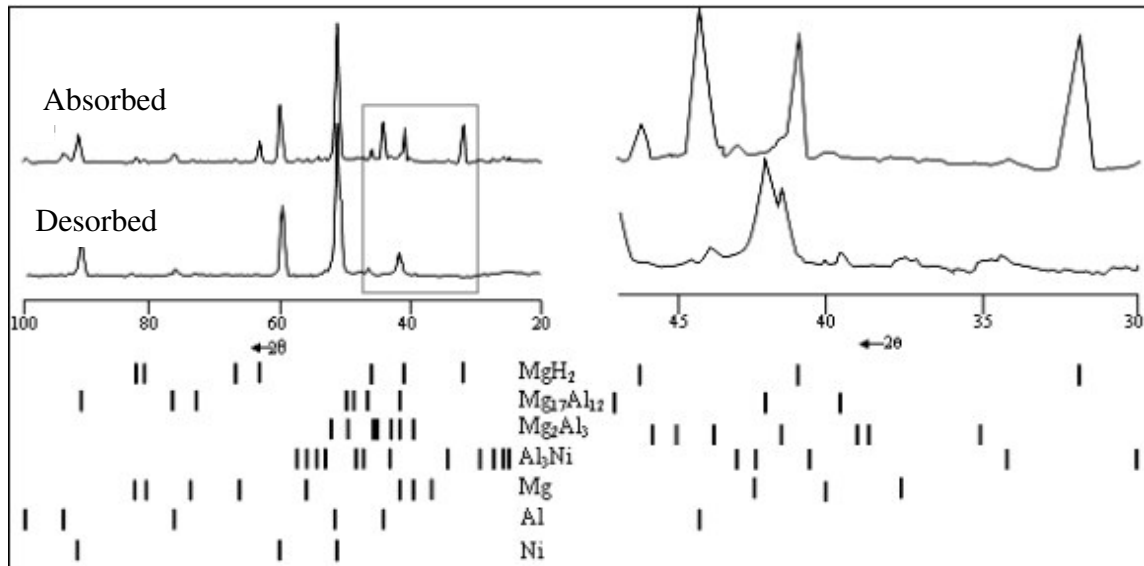


Figure 7. X-ray diffractogram (CoK_{α}) of hydrided (above) and dehydrided (below) multi-phase sample based on Mg-Ni-Al. Note that, in the hydrided sample, MgH_2 is formed together with Al.

In the hydrided sample, the diffractogram is similar to that of Mg-Al except for the presence of Ni peaks. Here again, the main phases formed are MgH₂ and Al. The amount of Mg₁₇Al₁₂ is reduced drastically, implying that it is the absorbing phase. Interestingly Mg₂Al₃, which was a product of the disproportionation reaction in Mg-Al, does not seem to be present in the current sample in comparable amounts. It is probable that (with the presence of Ni) Mg₂Al₃ also absorbed hydrogen, and, as a result, disproportionated into MgH₂ and Al. This implies a 2-step reaction. In the pressure-temperature curve, however, there is no clear sign of such a 2-step reaction. To be conclusive on this point, a repeat experiment would be required with improved sensitivity in pressure measurement and preferably with a much slower heating rate.

In this study, it appears that the mixing and sintering of elemental powders to form all phases in a single sample works well for Mg-Al. Obviously, the method can be used for other, similar, binary systems. Mg-Al system has the characteristics that the melting or solidus temperature of all phases and compounds are similar. The method, on the other hand, did not work well for Mg-Ni-Al. The phases formed in this system consisted of Mg₁₇Al₁₂, Mg₂Al₃, and Al₃Ni. Other binary intermetallics Mg₂Ni, MgNi₂, AlNi, AlNi₃, and Al₃Ni₂ did not form during sintering, nor did the ternaries such as Mg₃AlNi₂ (Guan-glie et al., 2001).

To improve the current method, a milling stage could be introduced before compaction so that, in a subsequent sintering, more phases could be obtained (Zhang et al., 2001). This would be particularly relevant for Mg-Ni-Al, or other similar binary or multi-component systems, i.e. the systems that involve phases or compounds of widely different melting or solidus temperature. In fact, milling of elemental powders to synthesize intermetallics is a well established method (e.g., Liang et al., 1998; Gasiorowski et al., 2004) and can be applied to binary as well as multi-component systems. Although the introduction of milling would help to improve the reactivity of the powders and be useful in that respect, it would, at the same time, result in the structural refinement of the powder mixture. Too much reduction would be detrimental, as it would eliminate the compositional variation in the sample and would have the same effect as the liquefaction, i.e. formation of fewer (or a single) phases.

Another approach would be to split the systems

into parts so that the differences in the melting points of phases would be much less. Splitting is quite straightforward in the case of binary systems. Al-Ni binary system, for instance, can be split into 2 parts; Al-Al₃Ni₂ and Al₃Ni₂-Ni. The former may be sintered at 600 °C, whereas in the latter the use of much higher sintering temperature, e.g., 1000 °C, would be possible. For the current elemental mixture of Mg-Ni-Al, as judged from the relevant binaries, the whole field may be examined in terms of 3 triangular divisions. These divisions are Al-Mg-MgNi₂, Al-MgNi₂-Al₃Ni₂, and Al₃Ni₂-MgNi₂-Ni. The sintering temperature for the first and second could be 450 °C and 600 °C, respectively, and for the third it could be as high as 1000 °C.

Conclusion

In this study, a method was described for rapid evaluation of metallic systems for their hydrogen storage potentials. The method comprises the following steps:

- i) *The production of a sample by sintering of compacted elemental powders that would yield the complete range of phases in the relevant phase diagram.*
- ii) *The hydrogenation of the sample by charging it in a Sievert's type apparatus with hydrogen of initially known pressure and recording the pressure as a function of temperature.*

When the pressure-temperature relationship is linear, the system may be abandoned without any further effort. If it is non-linear, the evaluation will proceed further, since it implies that a phase (or phases) exists in the sample that reacts with hydrogen. Then, the final step would be:

- iii) *Identification of hydrogen sorbing phase(s) by measuring X-ray diffractogram of the sample before and after hydrogenation and making a detailed comparison between the two.*

The method was applied to Mg-Al binary with success; all phases and compounds in the Mg-Al phase diagram could be formed in a single sample and, of these phases, Mg₁₇Al₁₂ could be singled out as a candidate for hydrogen storage material. In Mg-Ni-Al ternary, the method was less successful due to the limited number of phases formed. This could be remedied either by mechanical milling of powders before compaction or, preferably, by splitting the

ternary system into regions of similar solidus temperature.

Acknowledgment

This work was supported by TÜBİTAK (MISAG 213), which the authors gratefully acknowledge.

References

- Akyıldız, H., Çakmak, G., Tan, S., and Öztürk, T., "A Rapid Method to Assess Hydrogen Storage Potentials in Binary and Multi-component System" The 9th International Symposium on Metal-Hydrogen Systems; Fundamentals and Applications, Book of Abstracts, Figiel et al., (ed.), p. 49, Cracow, Sept. 2004.
- Bobet, J.L., Akiba, E. and Darriet, B., "Study of Mg-M (M=Co, Ni and Fe) Mixture Elaborated by Reactive Mechanical Alloying: Hydrogen Sorption Properties", International Journal of Hydrogen Energy, 26, 493-501, 2001.
- Boettcher, A., Haase, G. and Thun, R., "Strukturuntersuchung von Mehrstoffsystemen Durch Kinetische Elektronenbeugung", Zeitschrift für Metallkunde, 46, 386-400, 1955.
- Bouaricha, S., Dodelet, J.P., Guay, D., Huot, J., Boily, S. and Schulz, R., "Hydriding Behavior of Mg-Al and Leached Mg-Al Compounds Prepared by High-energy Ball-milling", Journal of Alloys and Compounds, 297, 282-293, 2000.
- Dam, B., Gremaud, R., Broedersz C. and Griessen, R., "Combinatorial Thin Film Methods for the Search of New Lightweight Metal Hydrides", Scripta Materialia, 56, 853-858, 2007.
- Gasiorowski, A., Iwasieczko, W., Skoryna, D., Drulis, H. and Jurczyk, M., "Hydriding Properties of Nanocrystalline Mg_{2-x}M_xNi Alloys Synthesized by Mechanical Alloying (M=Mn, Al)", Journal of Alloys and Compounds, 364, 283-288, 2004.
- Guanglie, L., Linshen, C., Lianbang, W. and Huan-tang, Y., "Study on the Phase Composition of Mg_{2-x}M_xNi (M=Al, Ti) Alloys", Journal of Alloys and Compounds, 321, L1-L14, 2001.
- Güvendirren, M., Baybörü, E. and Öztürk, T., "Effects of Additives on Mechanical Milling and Hydrogenation of Magnesium Powders", International Journal of Hydrogen Energy, 29, 491-496, 2004.
- Hanak, J.J., "Multiple-Sample-Concept in Materials Research-Synthesis-Compositional Analysis and Testing of Entire Multi-component Systems", Journal of Materials Science, 5, 964, 1970.
- Jin, Z., "A Study of the Range of Stability of Phase in Some Ternary Systems", Scandinavian Journal of Metallurgy, 10, 279-287, 1981.
- Liang, G., Boily, S., Huot, J., Van Neste, A. and Schulz, R., "Mechanical Alloying and Hydrogen Absorption Properties of the Mg-Ni System", Journal of Alloys and Compounds, 267, 302-306, 1998.
- Mintz, M.H., Gavra, Z., Kimmel, G. and Hadari, Z., "The Reaction of Hydrogen with Magnesium Alloys and Magnesium Intermetallic Compounds", Journal of the Less Common Metals, 74, 263-270, 1980.
- Zaluska, A., Zaluski, L. and Ström-Olsen, J.O., "Synergy of Hydrogen Sorption in Ball-milled Hydrides of Mg and Mg₂Ni" Journal of Alloys and Compounds, 289, 197-206, 1999.
- Zhang, D.L. and Ying D.Y., "Solid State Reactions in Nanometer Scaled Diffusion Couples Prepared Using High Energy Ball Milling", Materials Science and Engineering A, 301, 90-96, 2001.
- Zhao, J.C., "A Combinatorial Approach for Structural Materials", Advanced Engineering Materials, 3, 143-147, 2001.
- Zhao, J.C., Lemmon, J.P. and Smentkowski, V.S., "Combinatorial Discovery of Hydrogen Storage Materials", The 9th International Symposium on Metal-Hydrogen Systems; Fundamentals and Applications, Book of Abstracts, Figiel et al., (ed.), p. 167, Cracow, Sept. 2004.