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HYDROGEN STORAGE DEVELOPMENT

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Abstract

A summary of the hydride development efforts for the current program year (FY98) are presented here. The Mg-Al-Zn alloy system was studied at low Zn levels (2 – 4 wt%) and midrange Al contents (40 – 60 wt%). Higher plateau pressures were found with Al and Zn alloying in Mg and, furthermore, it was found that the hydrogen desorption kinetics were significantly improved with small additions of Zn. Results are also shown here for a detailed study of the low temperature properties of Mg_2NiH_4, and a comparison made between conventional melt cast alloy and our vapor process material.

Background and Approach

The purpose of the work described in this report is to demonstrate improved hydrogen storage materials and systems. The project uses an integrated approach which includes materials development for improved performance as well as engineering efforts to optimize storage systems. Our lightweight hydride alloy development has been focused on Mg alloys [1-3]; however, recent promising results on a catalyzed allanate material [4] have prompted us to study this system as well, and it is anticipated that we will pursue these types of materials as part of our hydride development activities in the future. Engineering efforts this year have been limited by operating budget to cost, size and weight analyses applicable to a specific fixed site application [5].

Our approach in the Mg-based hydrides is to study bulk alloy additions which increase equilibrium overpressure, in combination with stable surface alloy modifications and particle size control to improve kinetic properties. These efforts attempt to build on the considerable previous work in this area, but examines specific alloy systems in greater detail and with attention to known phase properties and structures. Hydride pressure-composition-temperature measurements are correlated with detailed microstructural analyses in these studies. Different material synthesis methods are used, including melt-cast, rapid solidification and mechanical alloying. We have also compared performance in a Mg-Ni alloy prepared by our vapor process [1] to material prepared by these conventional techniques.

In our hydride bed engineering studies, we consider heat and fluid flow within beds as well as considering system integration. The work attempts to improve performance and reduce fabrication costs through modeling and experimental measurements, using our extensive knowledge of material behavior in hydrogen environments.

There are three main objectives to this work:

1. Develop improved light weight, low cost hydrides for energy applications.
2. Develop improved and innovative hydride bed designs.
3. Demonstrate and evaluate hydrogen storage systems.

The project is broadly organized into two tasks - hydride development and storage system engineering. Additional projects this year include a Phase 1 study with International Fuel Cells, Inc. on a PEM fuel cell-hydride application, IEA experimental collaborations on hydride development, a comprehensive hydride data base and a safety analysis of hydrogen use in underground mines (this study is scheduled to begin July 1, 1998). This report will describe recent work on hydride material development.

Past Results

Earlier pressure-composition-temperature (PCT) measurements were performed on a series of Mg-Al-Zn alloys. This work was motivated by our observations that adding Zn to Mg and Mg alloys resulted in improved kinetic and equilibrium properties . A systematic survey was implemented to more fully explore the effects of added Zn in Mg-Al alloys. Two sets of melt-cast alloys were prepared and initial measurements were performed. These measurements have been essentially completed this year and will be described in the next section.

Addressing manufacturing issues, a process for bed immobilization was tested. This process consists of the injection of inert microporous carbon material into the void space of packed hydride material to prevent mass transport as the particles fracture and during hydrogen cycling. Microscopic examination and experimental measurements demonstrated successful immobilization with less than 1 % added to the bed weight. This is far less than the normal filtering and internal packaging weight and greatly reduces the assembly complexity of typcial bed designs. Limited cycle tests did not show any evidence for a loss in capacity from hydrocarbon production.

A novel vapor process was previously reported for the fabrication of Mg_2Ni with improved properties. To better understand these improvements, a study was initiated as part of the IEA Hydrogen Agreement to provide more analytical capability through task sharing and collaboration. In this program we provided detailed PCT and kinetic measurements on vapor process Mg_2Ni and commerical melt cast Mg_2Ni. Experiments were also performed to compare the low and high temperature hydride phases. This work has been completed this year and is described below.

Mg-Al-Zn Alloy Development

PCT measurements and electron microscopy characterizations were made on various compositions of Mg-Al-Zn to survey the low Zn (2-4 at %), mid range Al and Mg (40-60 at%) region of the phase diagram. Most of the alloys under study were from melt-cast ingots; however, it was found that Zn could easily be added to existing Mg-Al alloys by mechanical mixing. The high vapor pressure of Zn resulted in uniform doping of the material at 300° C.

Zinc is believed to occupy substitutional sites on the Al sublattice in these alloys, that is:

$$Mg_xAl_y > Mg_x(Al,Zn)_y$$

Referring to Figure 1, essentially two levels of equilibrium plateau pressures at 300°C may be followed across the Al+Zn axis. The lower level of plateau pressures are those of Mg-Al alloys without Zn. These generally required a temperature of 300° C or higher to allow completion of the measurements because of relatively slow desorption kinetics. By comparing these values to the Mg point on the ordinate, the addition of Al can be seen generally to increase the plateau pressure. The higher level of plateau pressures are those with Zn added to the Mg and Al. Although not shown, the Zn-containing materials had superior kinetic properties and could be characterized down to 200°C. As indicated by the symbols for the equilibrium phases in this alloy system (at the higher Al + Zn contents), each point can be correlated to distinct phases of both the binary Mg-Al and the ternary phase diagrams. Thus, the points suggest improvements in known, stable phases. However, the most promising results occur in the region associated with the R phase. In this region, Al+Zn compositional swings of only a few percent result in differently coordinated phases. This region has been difficult to survey using conventional fabrication methods due to the propensity of the melt to precipitate the ordered γ and β phases during cooling. This leads to the correct average concentration, but imbalances the local concentration away from the the R phase region. This behavior is seen in figure 2 where the results of microscopic analysis are compared to the average concentration on the phase diagram for a representative sample following PCT measurements at 300° C.

We have found that a more effective approach is to start with Mg-Al alloys and introduce the Zn by a vapor process similar to that used in the formation of Mg_2Ni. This can be observed in figure 3 where gas atomized single phase powders of a Mg-Al alloy has been heated under hydrogen in the presence of Zn particles. Note the lack of microstructural variation. Condensation of the Zn on the Mg-Al particles and subsequent solid state diffusion results in complete homogenization of the alloy. This was also found to occur for other Mg-Al compositions. We believe we now have sufficient knowledge to fabricate a single phase alloy at the highest plateau pressure in this series. Currently, we are determining the optimum Zn concentration for best performance and lowest weight.

Low Temperature Studies of Mg2Ni

It is generally accepted that an ordered phase transformation from a cubic to a monoclinic structure occurs at 210-230° C in Mg_2Ni. We have found that this transformation is coincident with greatly diminished hydrogen kinetics. In TEM studies by Noreus [6] and verified by us (N. Yang), it was also observed that the occurrence of a microtwin deformation microstructure correlated with whether the hydride phase was formed above or below the transition temperature. The microtwins were present in hydrides formed above the transition temperature and were stable under observation.

In collaboration with D. Noreus, Univ. of Stockholm, as part of our IEA activities, we have compared PCT measurements at low temperatures of these two structures using two different starting materials – traditional melt-cast samples of Mg_2Ni and those formed by our vapor process. In figures 4 and 5, two sets of isotherms are shown with PCT measurements at 200°C (473K) and 180°C (453K). Within each plot frame can be recognized two sets of data for the vapor process (VP) material and the melt-cast (M) material. In addition, the hydride phase for each of these starting materials were formed - either at 300°C (HT) or at 180°C (LT). As mentioned earlier, microtwins were present in the HT hydride, but not in the LT hydride. At 200° C, we can see that no differences in the plateau pressures can be attributed to the hydride formation temperature, but that there are differences due to the fabrication processes. At 180°C, we see measurable differences in plateau pressures that can be attributed to the hydride formation temperature in both alloy lots. The lower plateau pressure in the microtwinned hydride is consistent with the more stable structure produced when the material relaxes by forming the defects. The opposite is true in the unstable hydride without microtwins. Interestingly, the change in plateau pressure does not correlate directly with the cubic-monoclinic transition temperature, but rather occurs at a lower temperature. The difference in free energy between the two microstructures can be estimated from the plateau pressures to be 0.85 kJ/mole and appear to nucleate in the region 180-200°C.

Note in all cases that the vapor process material, which does not have a Mg impurity phase, has a higher equilibrium pressure than the commercial alloy. Our analyses have shown the vapor process alloy to be single phase, and hydrogen capacity measurements indicates that full capacity varies only ~5% in a temperature range from 180-300°C. We attribute the lower plateau pressures in the conventional alloy (M) to the presence of the Mg impurity phase. Differences in the plateau pressures are shown in the van't Hoff plots of Figures 6 and 7. In Figure 6, the data from the melt-cast alloys can be seen to be consistently below the solid line at temperatures lower than 300°C. The solid line represents an extrapolation of earlier Reilly-Wiswall data and its slope reflects an activation energy of 65KJ/mole. The melt-cast data indicates a slightly more stable hydride (68.6 KJ/mole) at lower tempratures. Little variations were found about the transition temperature. In the plot shown in Figure 7, the vapor process data can be seen to agree with the Reilly-Wiswall data down to temperatures as low as 150°C. Deviations in the plateau pressures do occur in this material above the transition temperature, indicating another effect. However, the microtwinning effect (HT-LT) in both materials can be seen to be much less than differences between the two starting alloys.

The detailed understanding we have achieved of the behavior of Mg_2NiH_4 at low temperatures (180-250°C) may help in identifying the role that relaxation microstructures have hydride stability and hydrogen kinetics of other magnesium alloy hydrides.

References

1. S.E. Guthrie, G.J. Thomas, D. Noreus and E. Ronnebro
   Properties of Mg2NiH4 at 450-570 K
   Conference Proceedings Materials Research Society (MRS) 1998 Spring Meeting, San Francisco, CA April 1998

2. S.E. Guthrie and G.J.Thomas
   A Novel Process for Fabricating Mg_2Ni
   presented at the Society for Advanced Material Processing and Engineering (SAMPE), Anaheim, CA, June 1998
   accepted for publication in the meeting proceedings

3. S.E. Guthrie and G.J. Thomas
   The Properties of Mg_2Ni Formed by a Vapor Phase Process
   IEA Task 12 Annual Report

4. B. Bogdanovic and M. Schwickardi
   Ti-doped alkali metal aluminum hydrides as potential novel reversible hydrogen storage materials.
   J. Alloys and Compounds, V. 253 (1997) p.1

5. G. J. Thomas
   Hydride Bed Design Considerations for a Fuel Cell Application
   Phase 1 Study Report

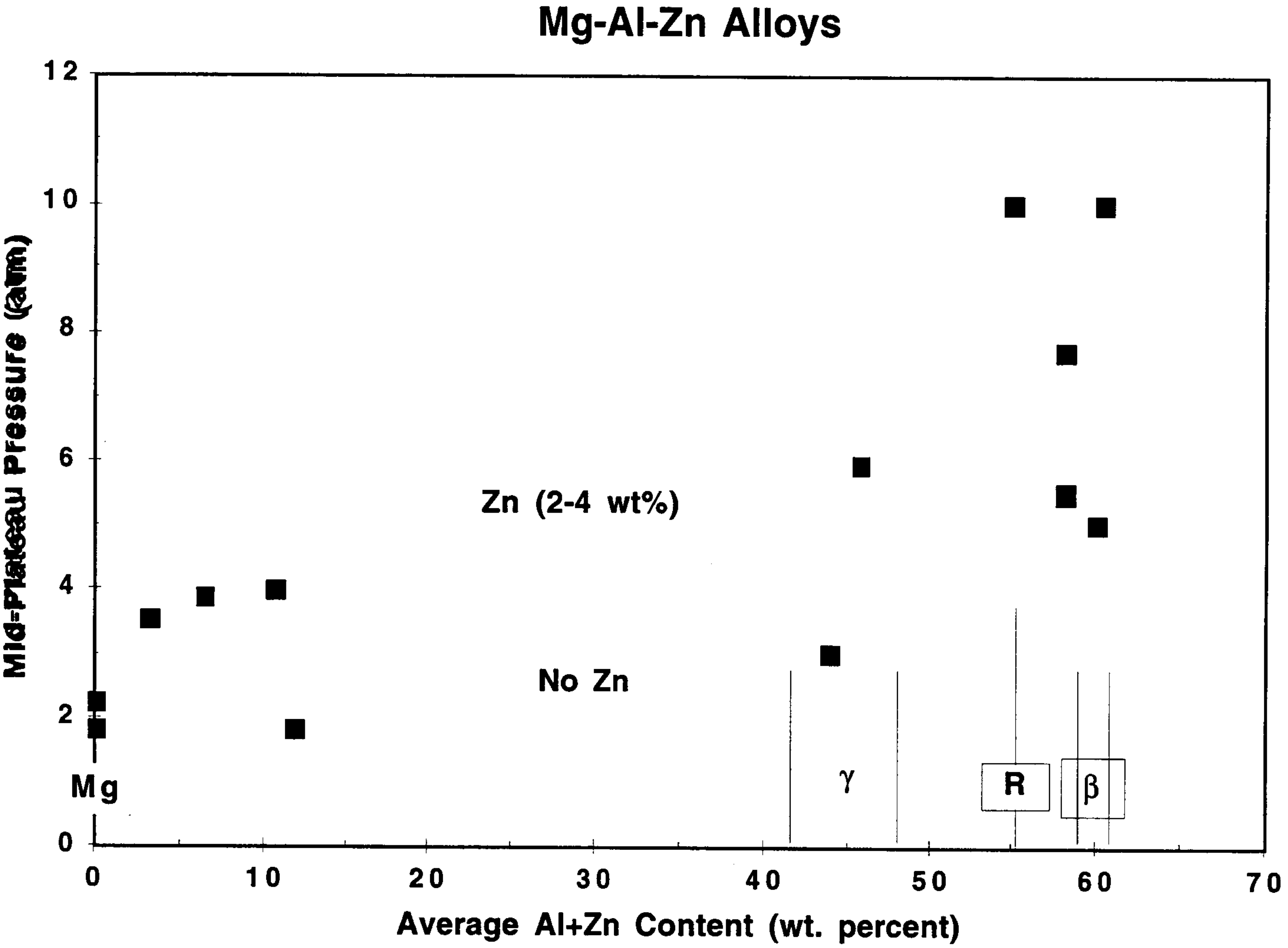

Figure 1. The equilibrium hydrogen pressure measured at the midpoint of the plateau are shown for the different Mg-Al-Zn alloy compositions. As stated in the text, Zn is believed to substitutionally occupy Al sites. All of the lower pressure data were found in alloys without Zn. Only 2 to 4 wt% Zn increased plateau pressures significantly and also increased hydrogen desorption kinetics.

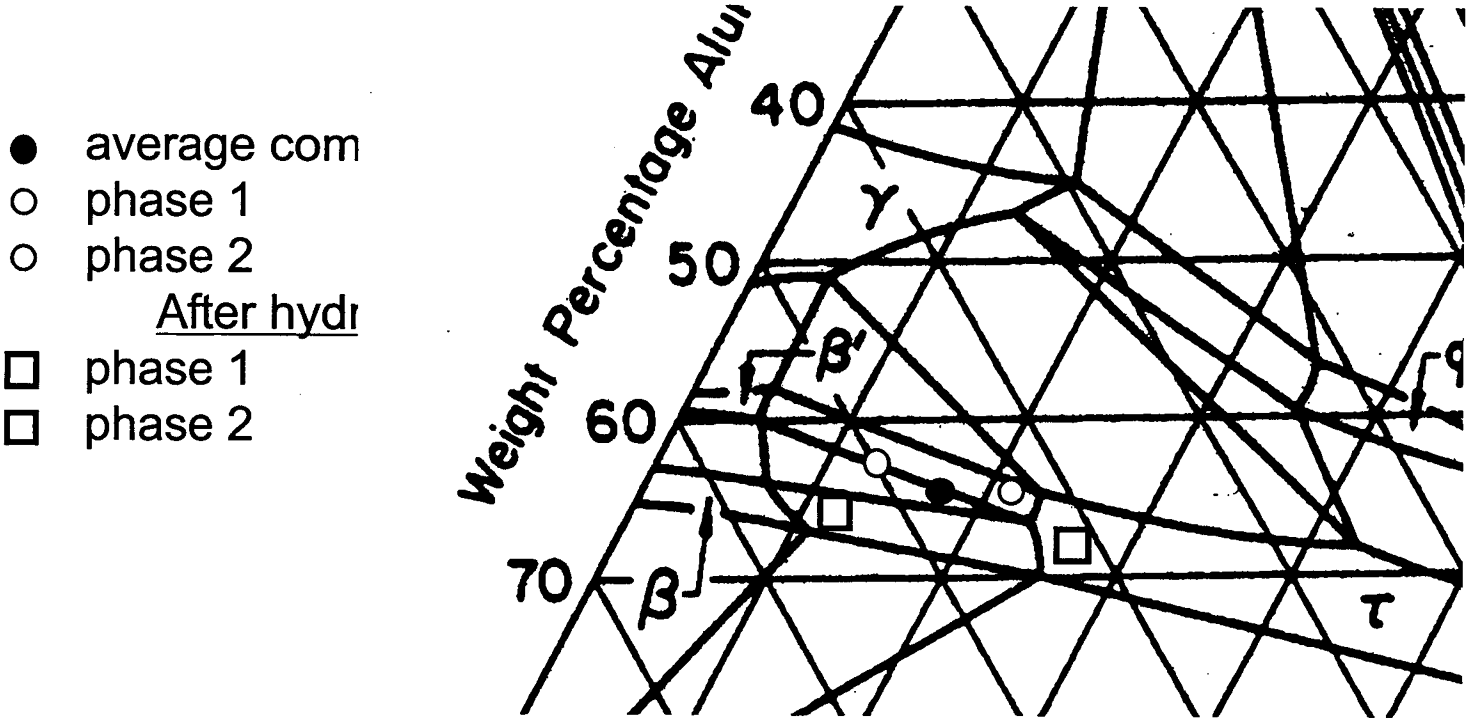

Figure 2. A section of the Mg-Al-Zn phase diagram is shown. The horizontal lines correspond to Mg weight percentage, while the diagonal lines parallel to the Al axis correspond to Zn weight percentage. The black circle indicates the average concentration of the starting material. Compositional analysis shows two phases present, with concentrations indicated by the open circles. After hydride measurements were completed, the compositions of the two phases had changed to the values indicated by the open squares.

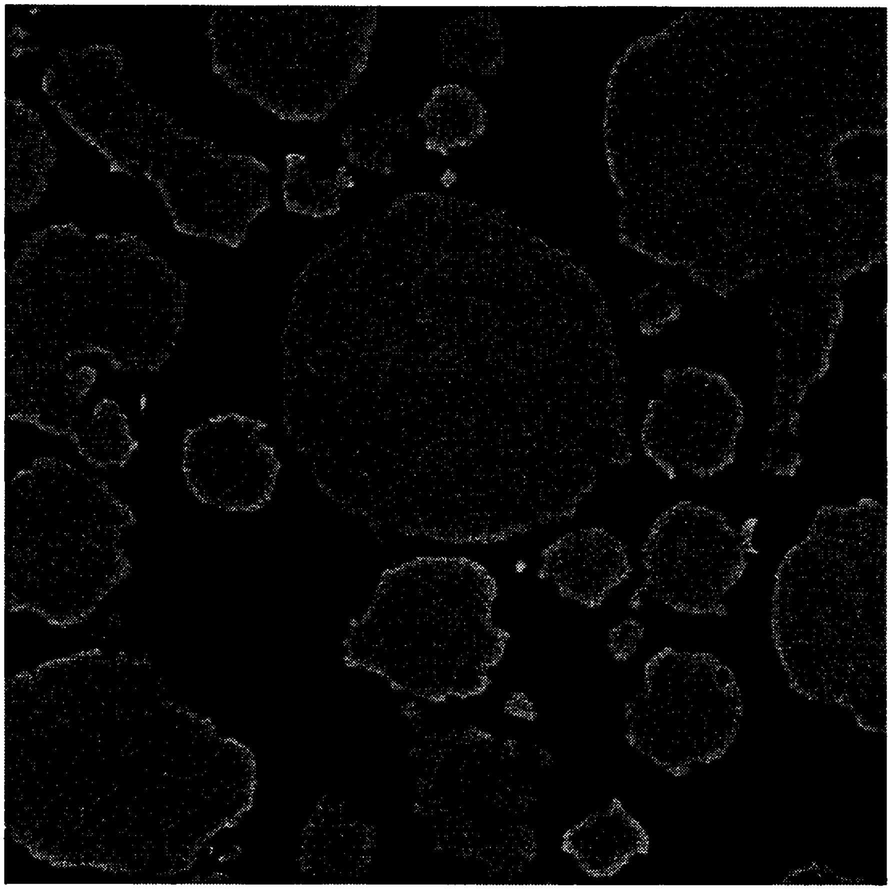

Figure 3. Backscattered electron image of a polished cross-section of a Mg-Al-Zn alloy following hydride measurements. The starting material was a gas atomized powder of Mg-Al which was mechanically mixed with Zn particles. No excess Zn is evident and quantitative analysis of the elemental compositions within the powder particles are consistent with the initial quantity of added Zn. The lack of contrast variations within the particles indicates that the composition is very uniform and that no other phases are present.

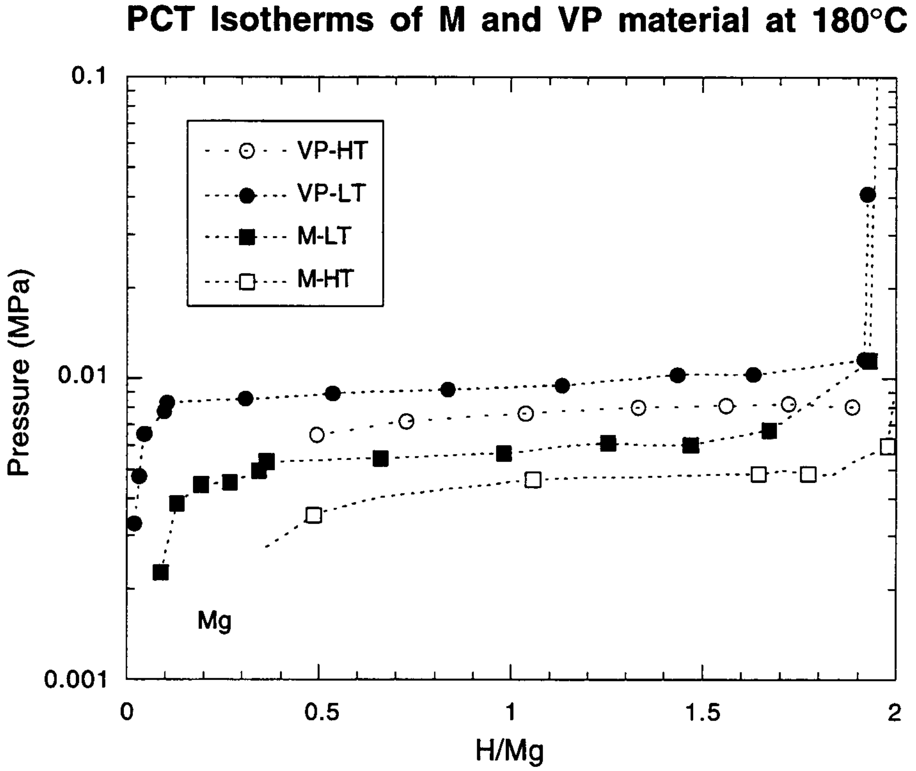

Figure 4. Isotherms at 180°C reveal plateau differences between the LT and HT conditions. In both materials (melt and VP), the lower hydride formation temperature lead to a higher plateau.

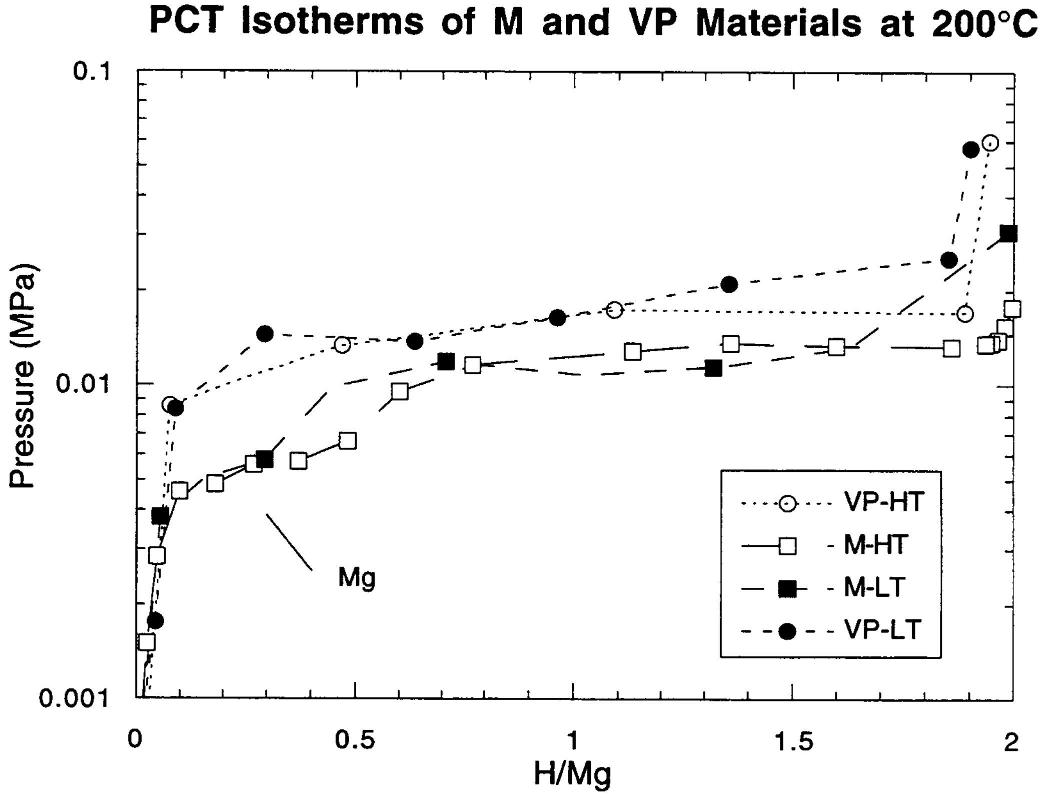

Figure 5. Isotherms at 200°C relect little differences between hydride plateau values suggesting that the microtwin effect vanishes by 200°C for both materials.

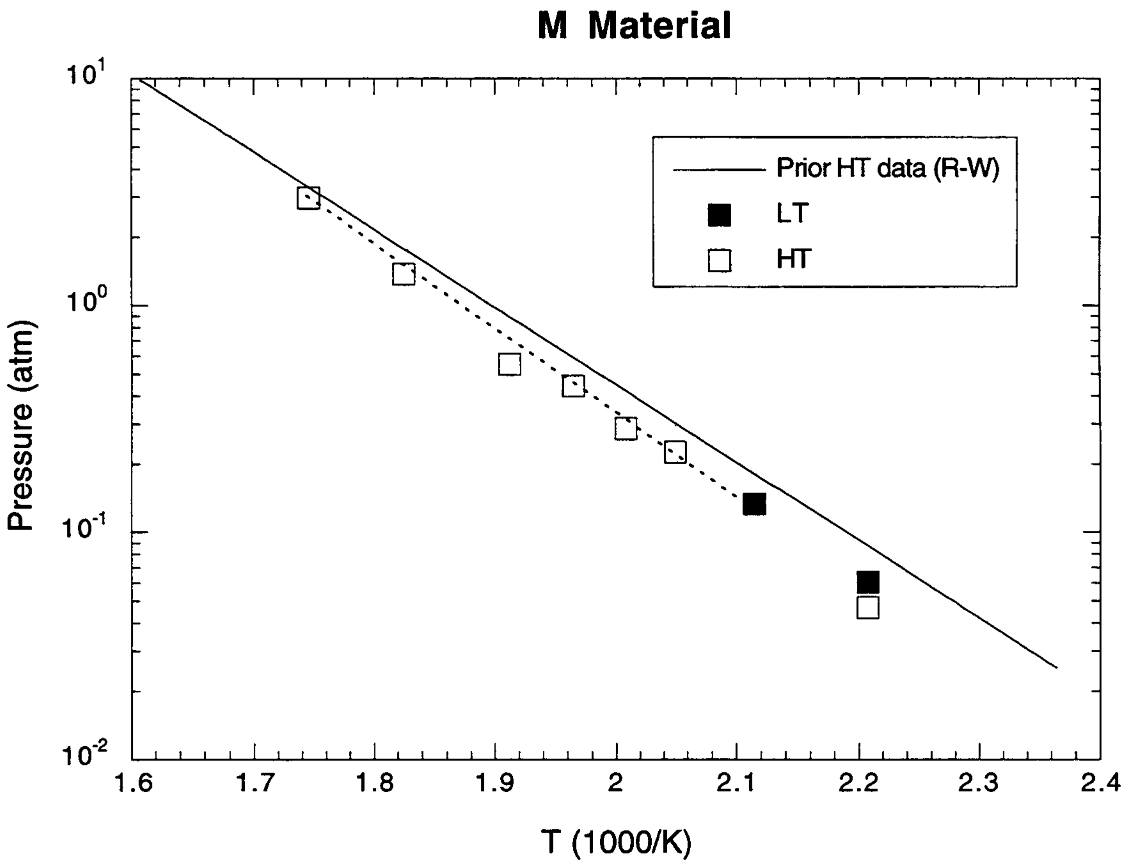

Figure 6. Vant Hoff plot of melt alloy deviatied from a composite data set of HT and VP results. LT measurements were only made at 180°C and 200°C.

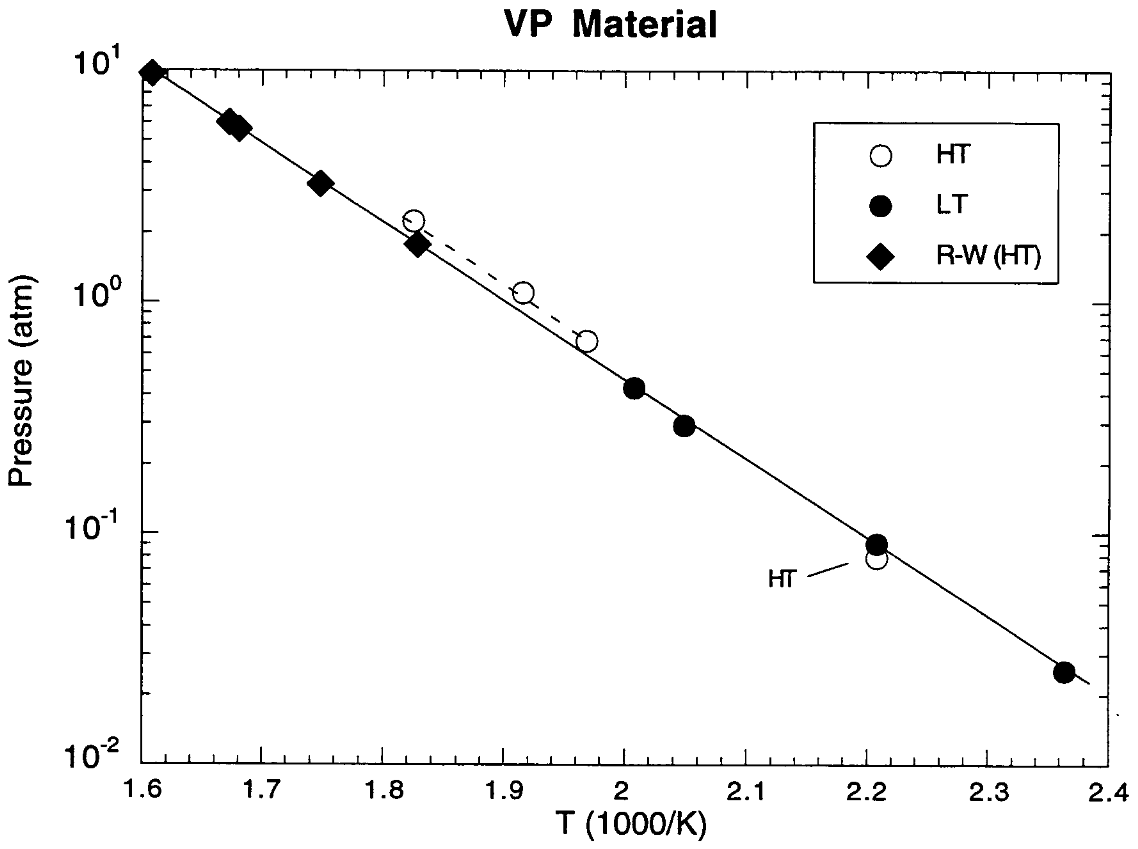

Figure 7. Vant hoff plot of VP alloys suggests that the LT sample preparation leads to a relationship consistent with high temperature Reilly-Wiswall (HT) results. HT conditions may imply (dashed line) a cross-over at or about 200°C given the consistently higher values of the VP-HT at higher temperatures.