Proceedings of the 1998 U.S. DOE Hydrogen Program Review

NREL/CP-570-25315

IMPROVED MG-BASED ALLOYS FOR HYDROGEN STORAGE

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Abstract

The overall objective of this on-going work is to develop low temperature alloys capable of reversibly storing at least 3 wt.% hydrogen since, allowing greater than for 2 wt.% at the system level which is required by most applications. Surface modification of Mg can be used to improve its H-sorption kinetics We show here that the same Mg-transition metal-based multi-component alloy when prepared by melt-spinning results in a more homogeneous materials with a higher plateau pressure as compared to preparing the material by mechanical grinding. We have also shown that mechanically alloyed $Mg_{50}Al_{45}Zn_5$ results in a sample having a higher plateau pressure. This work was done under a cost-shared USDOE contract #DE-FC36-96GO10145.

Introduction

Because metal hydrides offer many advantages such as safety, long life, and high volumetric energy density, they are a very attractive means for hydrogen storage for PEM fuel cells and for other applications such as internal combustion engines. This is especially true for small vehicles and for portable power. H-Storage of >2 weight percent at the system level is required to meet both gravimetric energy density and system cost targets. Therefore, the development and commercialization of high capacity, low cost Metal Hydride Storage Systems (MHSS's) will enable the broad-based commercialization of metal hydride technology.

Technical Discussions

Technical Goals

Our goal is to develop commercially viable metal hydrides capable of storing greater than 3 wt.% hydrogen, that will result in a system storage capacity of >2wt.%. For this, we need to develop an alloy having greater than 3 wt.% H-Storage capacity, capable of delivering H_2 at the requirements for the PEM fuel cell, namely

- greater than 1 atm. Pressure
- desorption below 150°C

Additional requirements:

- Cost and availability of raw materials
- Ease of large scale manufacturing
- Long cycle life
- Resistance to poisoning of impurities in hydrogen gas

Technical Challenge

The greatest challenge in developing Mg-based, high capacity, low temperature alloys is to affect the thermodynamic properties of Mg. A key reason for this challenge is the limited number of elements with which Mg forms solid solutions and its low miscibility with most transition metal elements.

Past Results

We have previously shown [1,2,3] that in the process of making multi-component Mg-transition metal-based alloys for the storage of hydrogen using a high energy mechanical alloying process:

- Addition of graphitic C and heptane improves alloy yield and H-sorption kinetics.

- Increase in grinding speed significantly improves the diffusion of transition metal (TM) elements into Mg particles, produces smaller particles, and results in improved kinetics.

- For a fixed alloy composition, processing parameters affect alloy properties.

- Addition of several TM elements improve kinetics without appreciable change in H-storage capacity. There is also a small decrease in the value of ΔH.

Current Year Accomplishments

Surface Modification

A series of experiments were done to study the effect of surface modifiers on the kinetics of clean, mechanically ground Mg. Alloying was done for 6 hours at 930 rpm. For the surface modification experiments, catalytic materials were added during the last 30 minutes of grinding (except in the case of Ni, where three different grinding duration's were tried). The modifiers included elements such as Fe, Co, Ni, Mn, Cu, Mo and Pd, and pre-alloyed fine powders such as Mg_2Ni, Ni-Mo. **Figure 1** shows the effect of surface modification of some of these modifiers on the desorption kinetics of Mg. We see that while Mg_2Ni had the most significant affect on the kinetics of the alloy, 30 minutes of grinding with NiMo has the same effect as 90 minutes of Ni grinding. **Figure 2** shows the difference in SEM's between 30 min. Ni modification and 30 min. Mg_2Ni modification. Mg_2Ni modification results in homogeneous incorporation of catalyst throughout the sample.

Bulk Modification and Effect of Process

Modification with Transition Metal Elements

Bulk modification affects both kinetics and thermodynamic properties. We have shown that the modification of Mg-Ni-Mo-C by the incorporation of additional elements (Cu, Si, Fe, Mn) results in improved kinetics and a slight improvement in the PCT plateau pressure. The same multi-component material was prepared by melt spinning (MS). The ribbons as shown in **figure 3b** from the melt-spinning are very brittle. In contrast to the sample prepared by mechanical alloying (MA), the melt spun sample (MS) was very homogeneous. From **figure 4** we see that while the dehydriding kinetics of the as-prepared sample was not as good as the MA prepared sample, by using the results from surface modification, this problem was overcome. Curves 2 and 2a in **figure 4** are for MA sample and curve 1 is for the MS sample. Curve 3 represents the kinetics of the MS sample having a surface coating of Mg_2Ni.

Figure 5 shows the 300°C desorption isotherms of several Mg-transition metal-based alloys, including the material made by melt spinning (with and without a surface modifier coating). It can be seen that the MS sample results in a higher plateau pressure, indicating additional alloying or interactions between Mg and the modifier elements.

Modification with Low-Weight Elements (Al, Zn, C)

Several samples of Mg-Al-Zn were prepared by MA process. **Figures 6, 7** and **8** show the dehydriding kinetics, XRD's and P-C isotherms respectively, for this alloy. The slower desorption kinetics as compared to the Mg-Ni-Cu-Mn-Fe-Si-C sample (also shown here for comparison) is probably due to the absence of a transition metal element catalyst. The XRD pattern indicates the formation of certain Mg-Al(Zn) compounds during the alloying process. The PCT data shows that the plateau pressure of the Mg-Al-Zn alloy is significantly higher than for Mg-TM alloy (also included in this figure for comparison). The important point to note is the absence of a MgH_2 region. This Mg-Al-Zn system is presently not optimized.

Cycling Study

Some samples were subjected to cycling between vacuum and 200psia at 300°C. The hydrogen gas used is 99.9995% pure. **Figures 9** and **10** show that after 500 absorption/desorption cycles while there is some degradation in kinetics, there is not much loss in H-storage capacity. Tests are ongoing.

Acknowledgements

We thank the U. S. Department of Energy for providing partial funding under contract #DE-FC36-96GO10145.

References

1. K. Sapru, L. Ming, J. Evans and N. Stetson, 1997. "Develop Improved Metal Hydride Technology for the Storage of Hydrogen" in Proceedings of the 1997 U.S. DOE Hydrogen Program Review, Herndon, Virginia, pp255-276.

2. K. Sapru, L. Ming, J. Evans and N. Stetson, 1998. "Disordered Mg-Based Alloys for Hydrogen Storage" in Proceedings of the 1998 U.S. NHA Annual Meeting, Herndon, Virginia, in print.

3. K. Sapru, L. Ming, J. Evans and N. Stetson, 1998, "Effect of Processing Parameters on Mg-Based Hydrogen Storage Materials Prepared by Mechanical Alloying", 12th World Hydrogen Energy Meeting, Argentina, to be published.

Figures

Figure 6 Desorption Kinetics at 300°C
Figure 7 XRD of Mg-Al-Zn/C Prepared by MA
Figure 8 Desorption P-C-T Curves for Mg-Al-Zn/C by MA
Figure 9 Desorption Kinetics at 300°C
Figure 10 Desorption Kinetics at 300°C

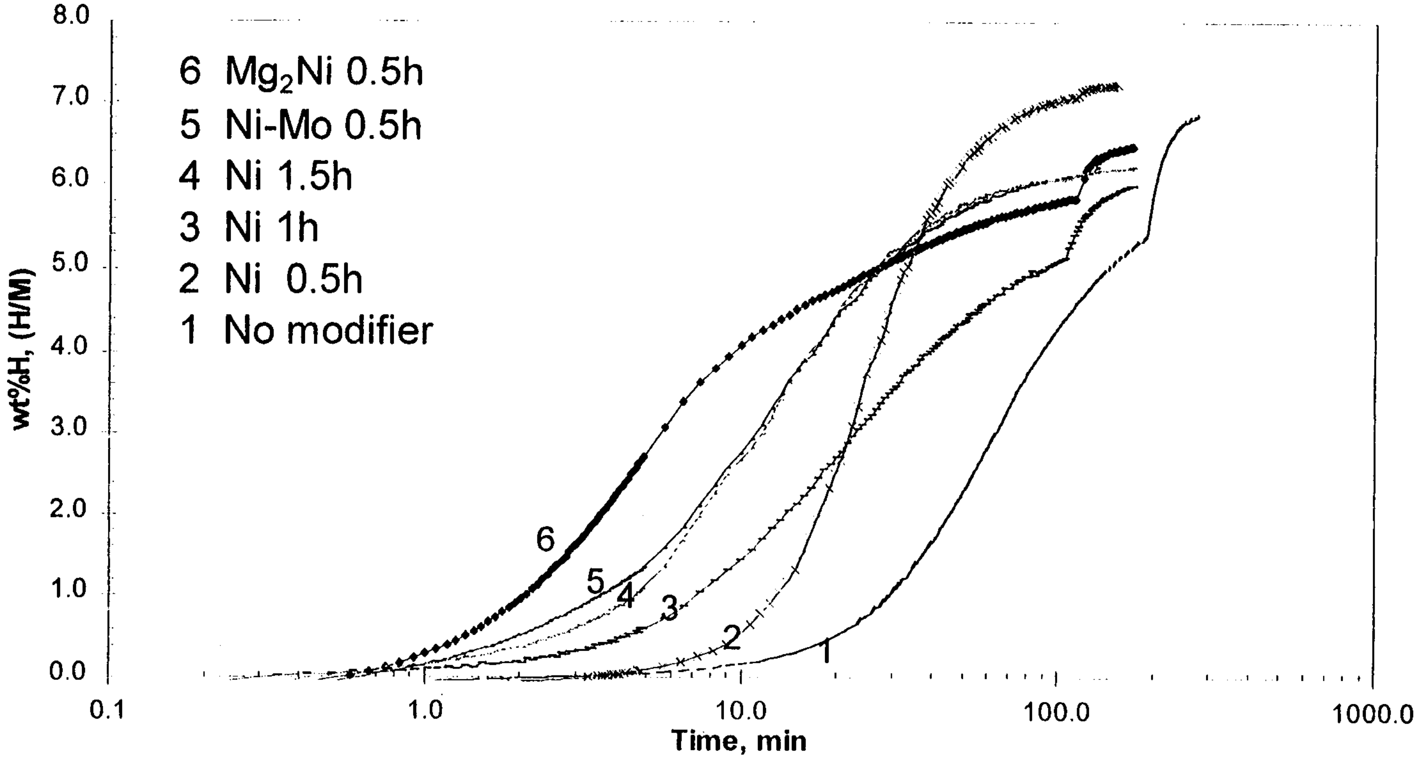
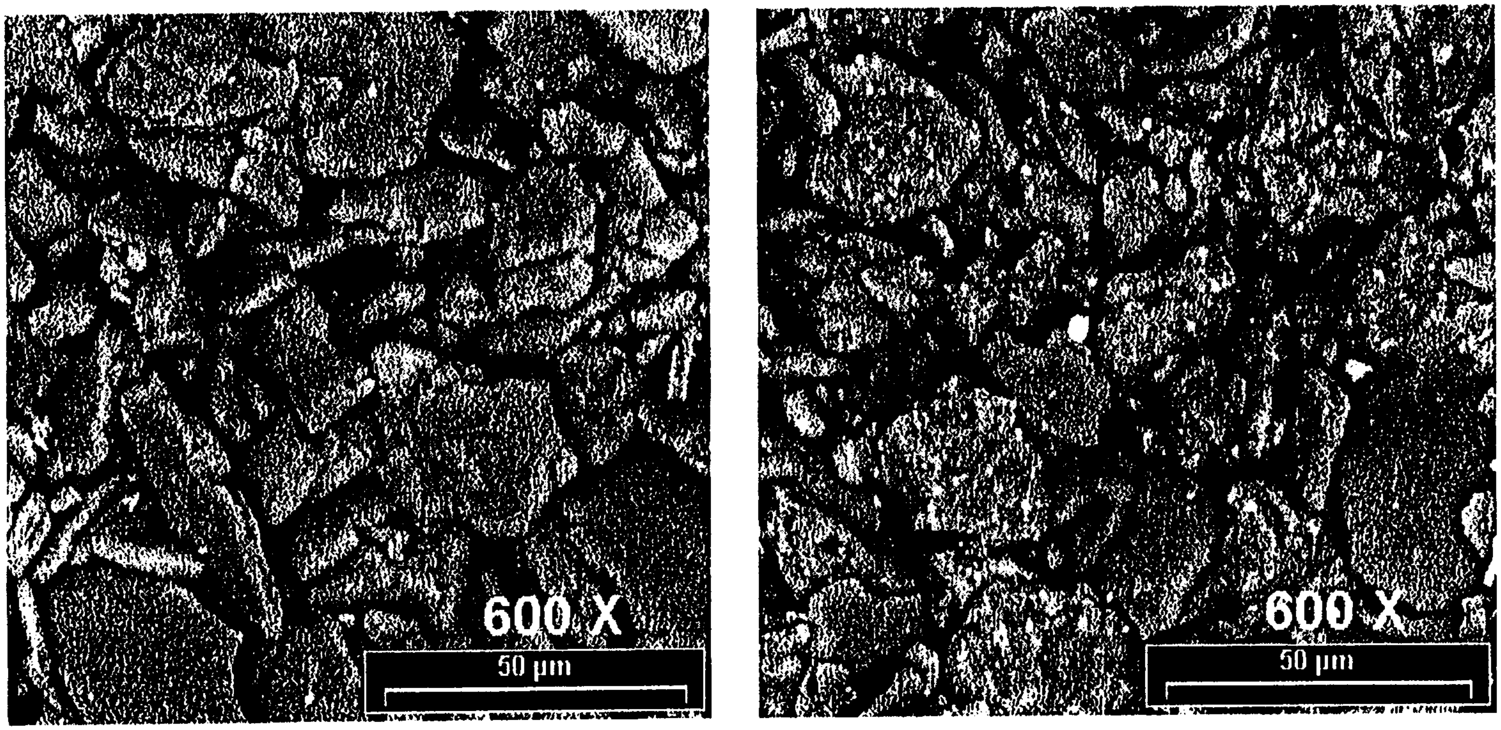


Figure 1 Desorption Kinetics at 300°C



a)

b)

Figure 2 SEMs of Mg with Surface Modification: a) Ni; b) Mg_2Ni

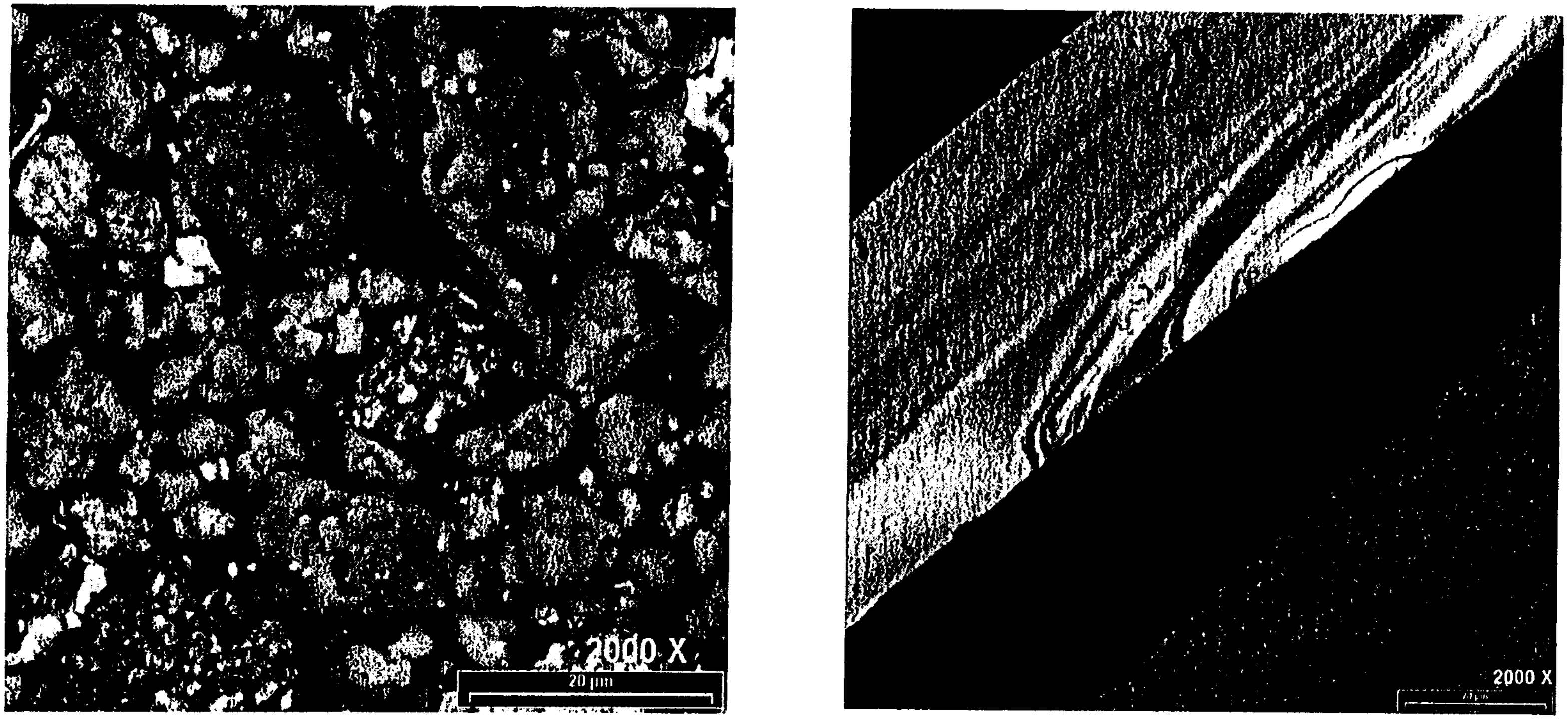


Figure 3 a) SEM of MA Material

b) SEM of MS Ribbons

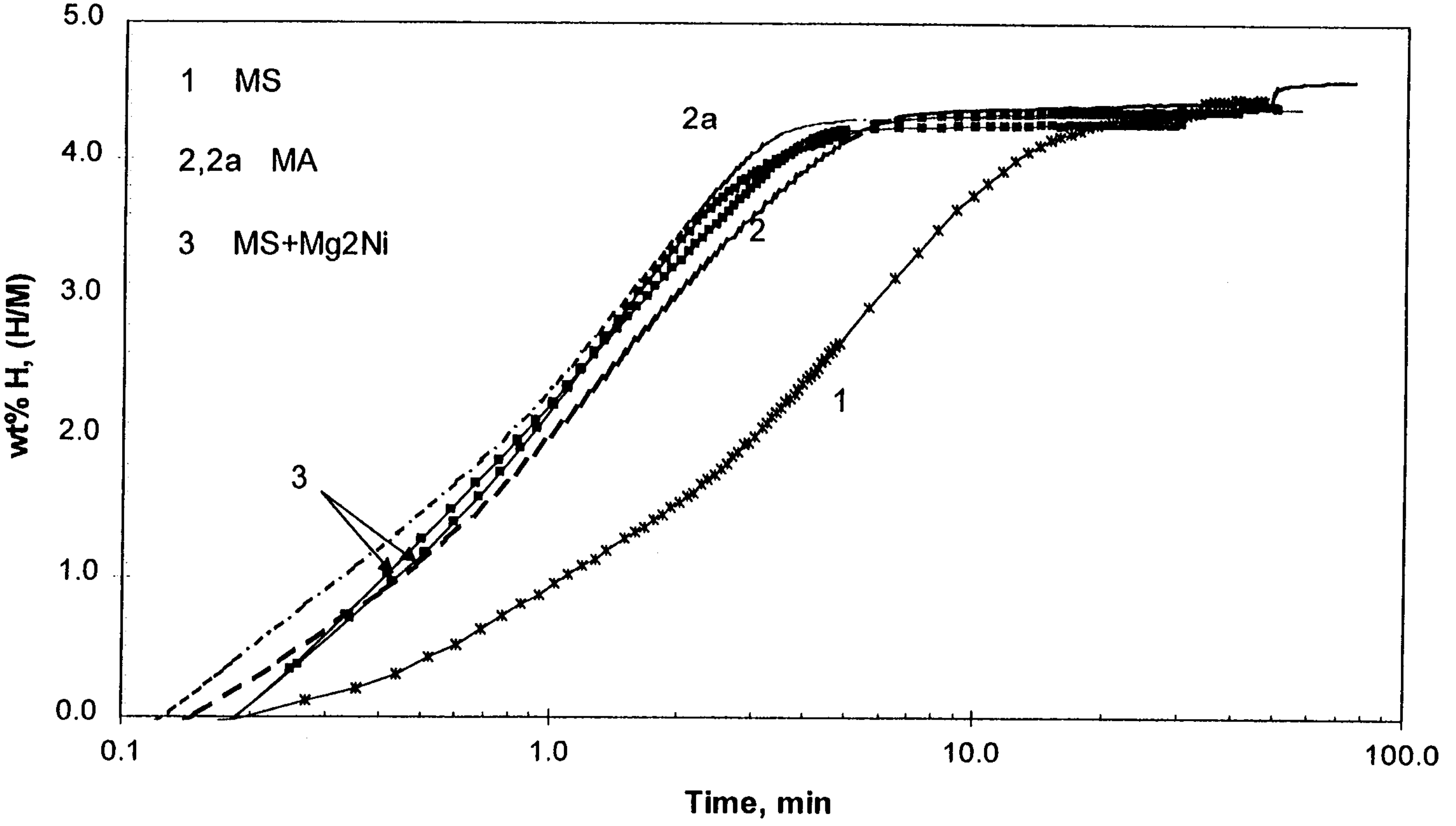


Figure 4 Desorption Kinetics at 300°C

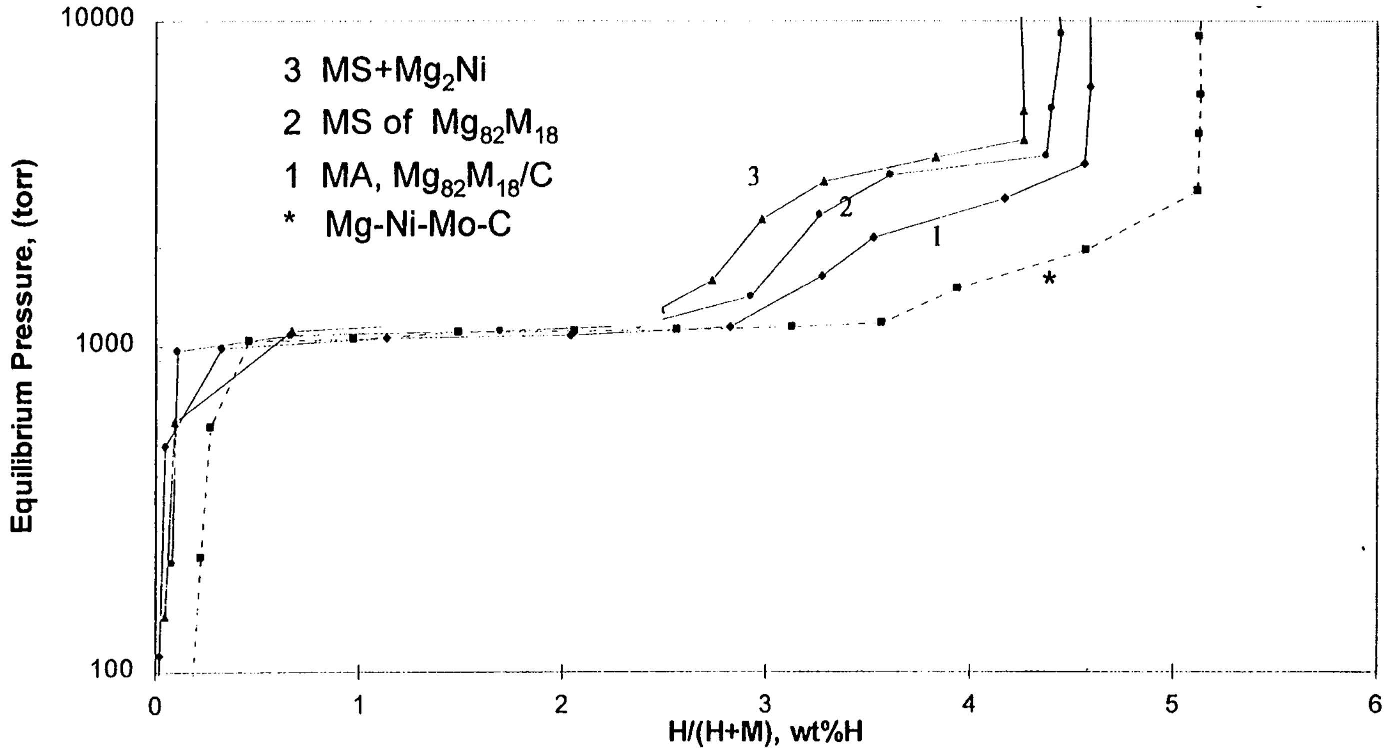


Figure 5 Desorption P-C Isotherms at 300°C

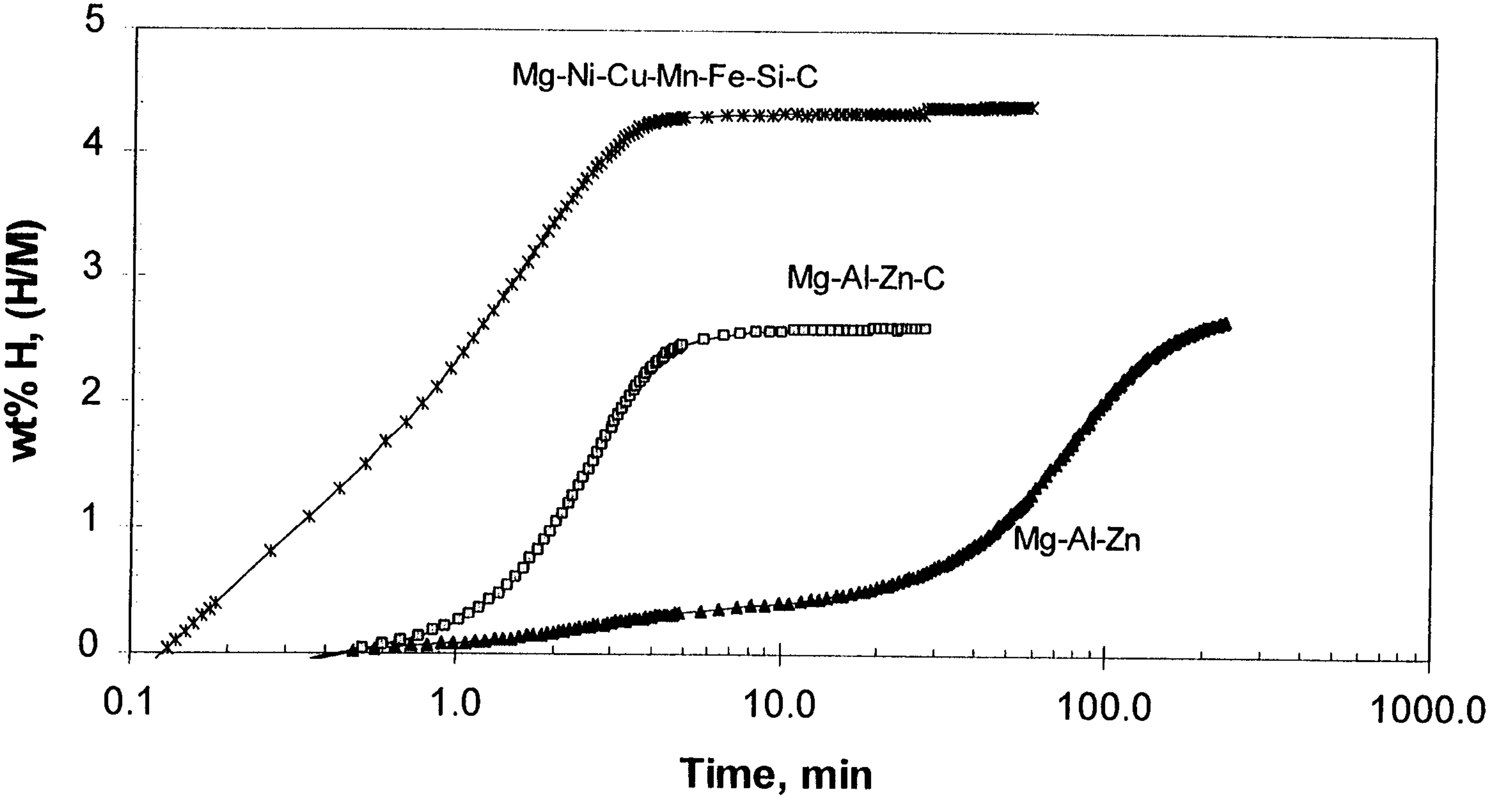


Figure 6 Desorption Kinetics at 300°C

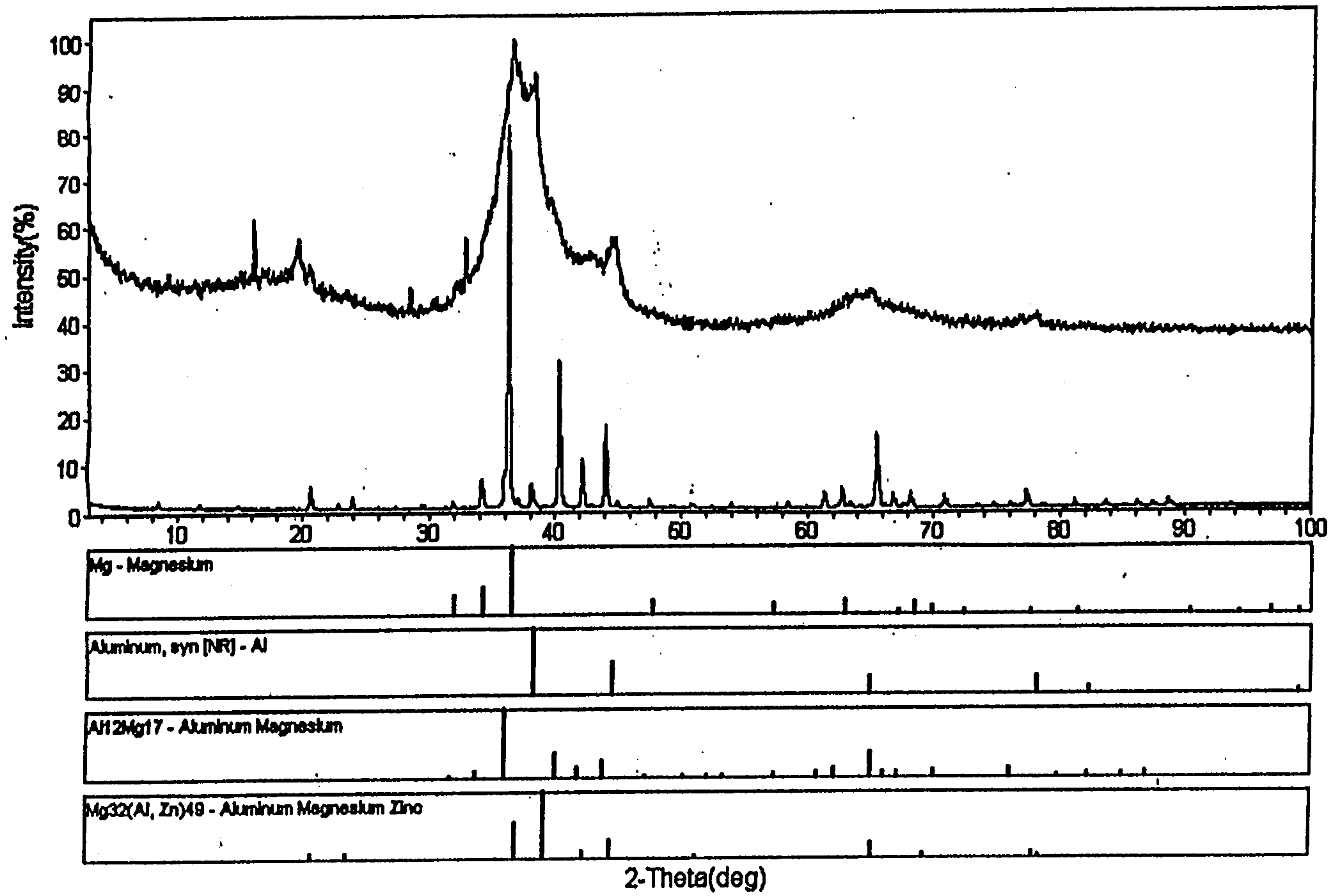


Figure 7 XRD of Mg-Al-Zn/C Prepared by MA

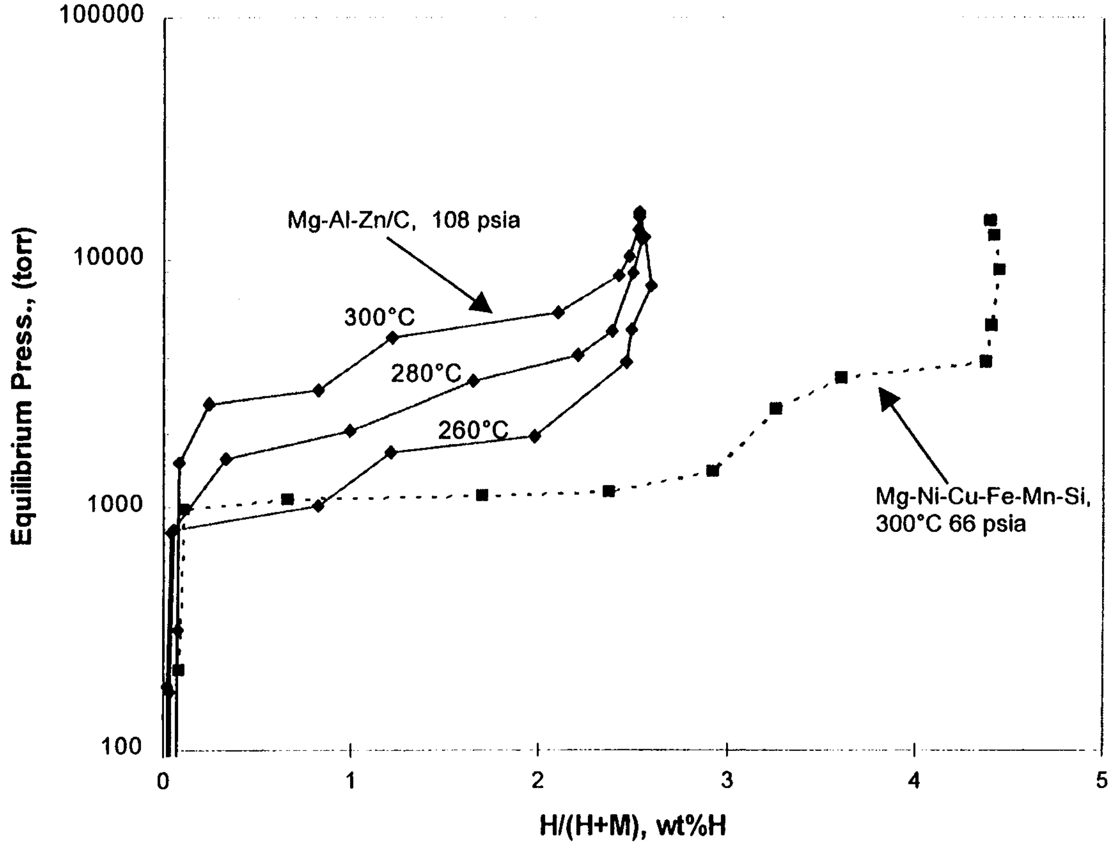


Figure 8 Desorption P-C-T Curves for Mg-Al-Zn/C by MA

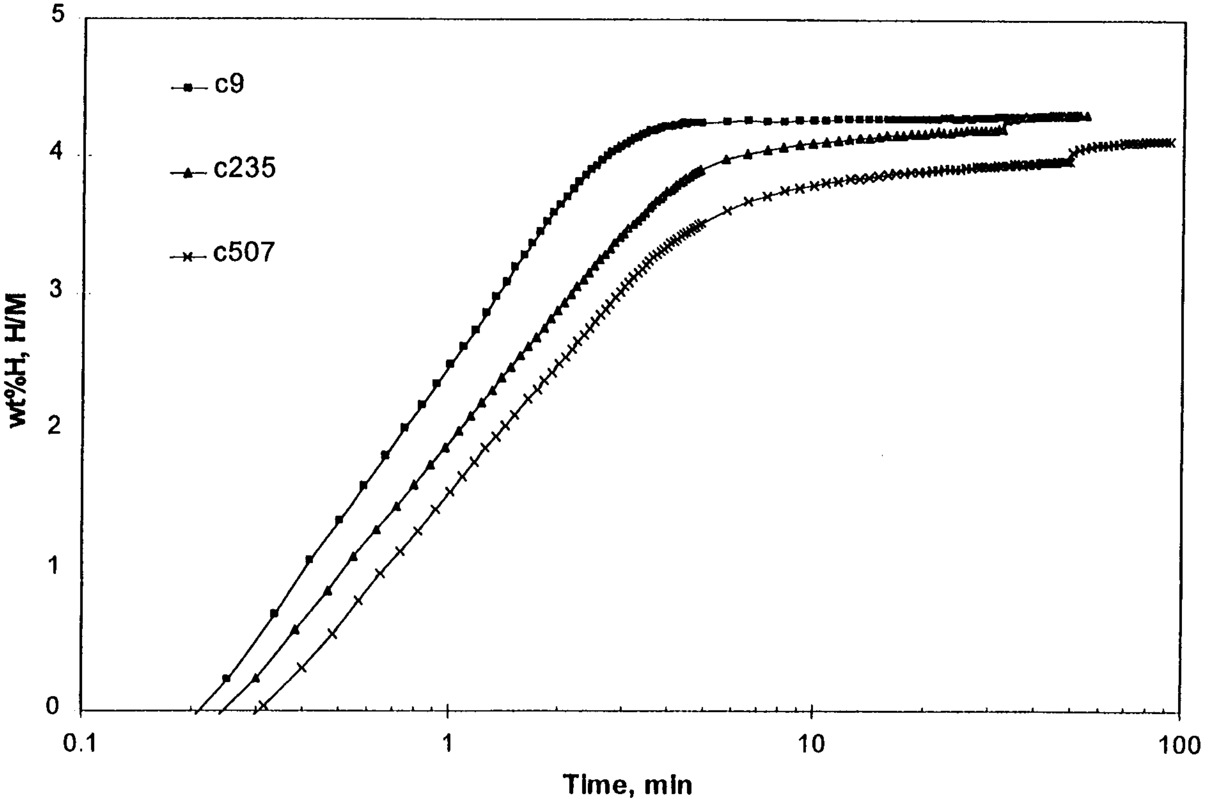


Figure 9 Desorption Kinetics at 300°C

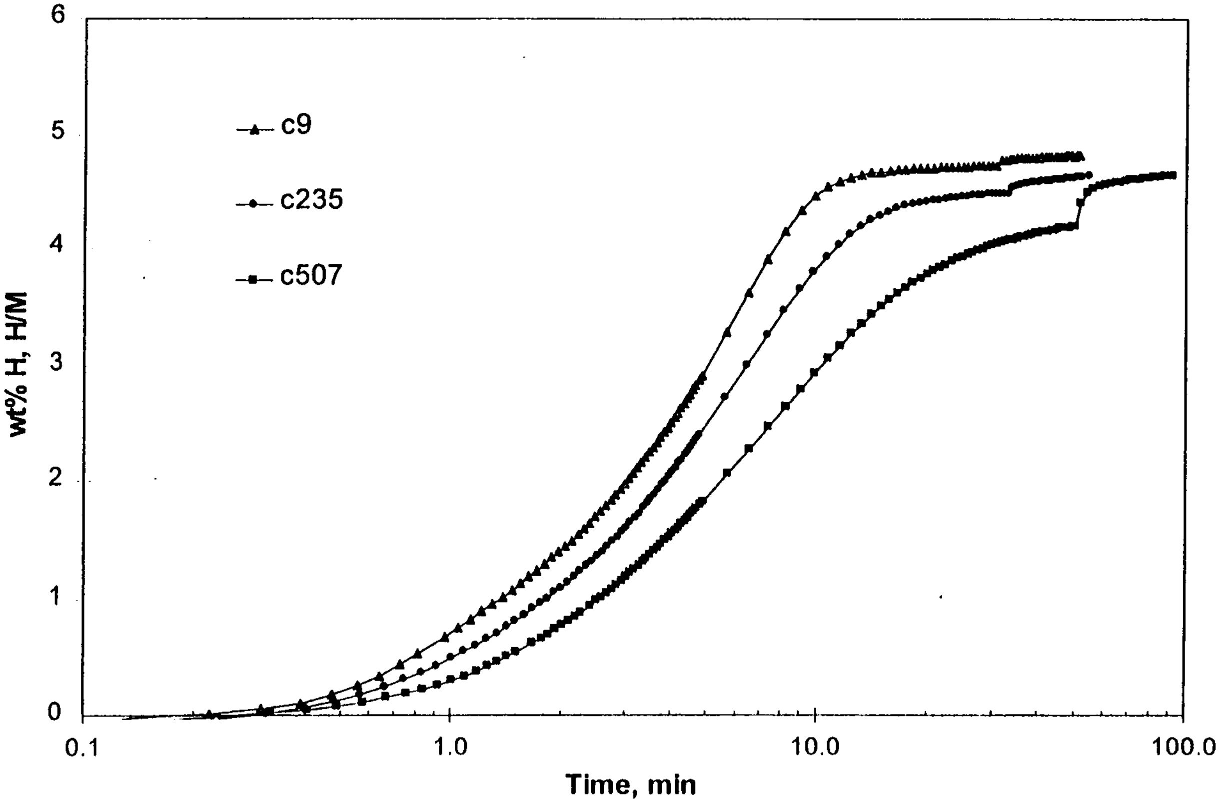


Figure 10 Desorption Kinetics at 300°C