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Thermodynamics of Hydrogen in Thin Films and Mathematical Calculations

Munkhsaikhan G.[1]**, Nyamsuren Do.**[2]**, Dorjkhand S.**[1]

[1]*- Material Science and Nanotechnology Division, IPT, MAS, Mongolia*
[2]*-School of Mathematics, MUST, Mongolia*

Abstract: The behavior of Mg/Pd and Mg/Cr thin films, exposed to a hydrogen pressure, was investigated. Two experimental methods for determining the thermodynamics of hydrogen in thin films have been presented in this paper. The first method based on the dependency of the resistance variation rate of the sample on hydrogen pressure and used for determining plateau pressure. The second approach is relying on the on hydrogen uptake during the hydrogen loading process. The bulk data for comparison have been calculated using mathematical calculations.

Keywords: hydrogen uptake, bulk MgH_2, metal hydrides, thin films, mathematical calculations.

INTRODUCTION

Hydrogen is an appealing energy carrier, in particular for mobile. But, storage remains a critical problem. While high pressure tanks are being used in several prototype cars today, the capacity is small and the volume large and it is likely that safety concerns will also call for alternative solutions. Light metal hydrides are a possible solution to this problem [1]. These Metals can absorb hydrogen in atomic form and thereby act as hydrogen "Sponges". Many scientific and engineering studies have been carried out of the absorption/ desorption of hydrogen in light metals and development of such storage devices.

One example metal hydrides is magnesium hydride, MgH_2, which contains 7.6% hydrogen by weight. Unfortunately, there are two serious problems though: (1) the diffusion of hydrogen through the hydride is so slow that loading and unloading of hydrogen takes very long time and (2) the hydrogen binds so strongly in magnesium hydride that temperature in excess of 700 K is needed to release the hydrogen, while a release temperature around 400 K would be preferable [2].

The first problem, the dissociation of hydrogen molecules on the surface, can be solved by adding a small amount of a catalytically active metal like Pd on the surface of the magnesium.

The second problem with pure Mg as a hydrogen storage device is the most serious one, namely the high enthalpy of formation of the hydride. Some improvement has been shown to occur by adding Ni or Cu to Mg [3]. The desorption temperature of the Mg_2Ni alloy is about 50 degrees lower than for pure Mg, but this is still far from low enough. The addition of the heavy transition metal greatly reduces the storage capacity, down to 3.6% from 7.6% in pure Mg. A better solution would be to add a light metal that has low affinity to H. This strategy has apparently been tried and will be pursued in this paper.

MATHEMATICAL CALCULATION OF THE BULK MAGNESIUM HYDRIDES

The theoretical data for bulk magnesium hydride have been used from the experimental calculations of Bogdanovic and etc [4]. The plateau pressure of hydrogenation of bulk MgH_2 is shown in Fig. 1 as a function of temperature.

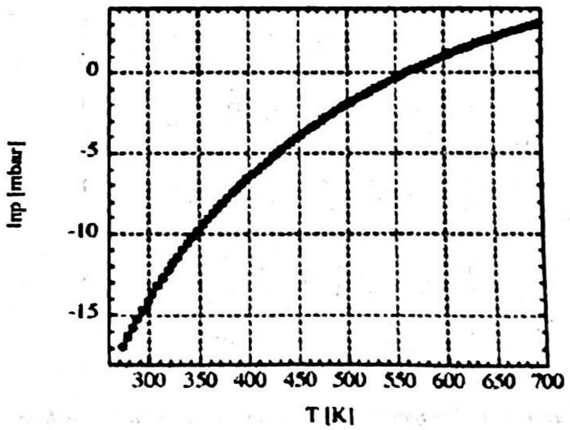

Figure 1. lnp versus temperature plot for bulk MgH_2.

A LabView Programme is used for improving of the mathematical calculations in comparison of theoretical data with experimental data, which is obtained in text format. The plateau pressure, enthalpy and entropy values have determined plot, which shown in Fig.2.

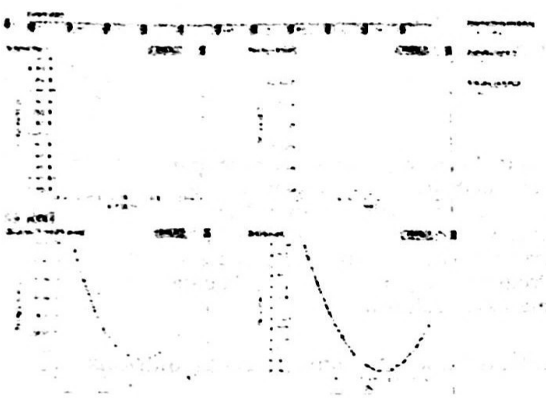

Figure 2. An application of the LabView Programme in mathematical calculations.

SAMPLE PREPARATION AND EXPERMENTAL PROCEDURES

Mg/Pd and Mg/Cr thin films were grown on a polished MgO (001) substrate with DC-magnetron sputtering at an Argon gas pressure of $3.6*10^{-8}$ mbar, which is shown in Fig. 3. All samples were grown at room temperature with a total thickness of 100 nm. The deposition rate during growth was 0.1nm/s. Finally, the sample was covered with a 10 nm thick Pd layer, which acts as a catalyst. The sample was finally cleaved to the dimensions 10x5 mm for the resistance measurement.

Figure 3. DC magnetron sputtering chamber for growth of the thin film

The resistance of the sample was measured with a resistance meter, which applies a 1-2 mA AC current and measures the voltage drop with a four-point probe technique. The sample temperature is controlled by an Eurotherm 94C-heating unit driven by a feedback loop through a PID amplifier. A high vacuum pump lowers the pressure over the sample down to 10^{-6} mbar before hydrogen is introduced into the chamber. The pressure gauge, which ranging from 0 to 100 mbar (precision up to 10^{-2} mbar) is used to monitor H_2 pressure. H_2 pressure was raised by small steps and this induced changes in the sample's resistance. All physical quantities, i.e. time, resistance, pressure and temperature, were monitored and recorded by a LabView program, the latter three through a GPIB interface system.

The thin film sample was inspected in an optical microscope, where no visible cracks or pealing of film was observed after dehydrogenation.

The quality of the sample structures was investigated using low- and high-angle X-Ray Diffraction (XRD). The measurement showed that the sample was polycrystalline.

RESULTS AND DISCUSSION

Mg/Pd Thin Films-Hydrogen Uptake Method

When hydrogen molecules are adsorbed on thin film surface they can dissociate into two hydrogen atoms that diffuse into the thin film. At low hydrogen concentration when the hydrogen atom diffuses into magnesium the reaction between hydrogen and magnesium is endothermic [3] and the hydrogen randomly occupies the available sites. As the hydrogen concentration increases the lattice expands and the reaction becomes exothermic as the phase transition to MgH_2 and Mg-Pd-H occurs. This causes lattice expansion, up to 13.1% and continuous deformation of the metal lattice [5].

An example of the typical change in resistance for hydrogen loading for $Mg_{0.95}Pd_{0.05}$ thin film at temperatures 80, 90, 100°C and in the pressure range 0-1 mbar is shown in Fig. 4. The hydrogen gas pressure was increased in six discrete steps from zero to a maximum pressure of 1 mbar for each temperature. The interval between the pressure steps was kept constant at 3 minutes. Each resistance step is related to a new pressure step in the resistance plot.

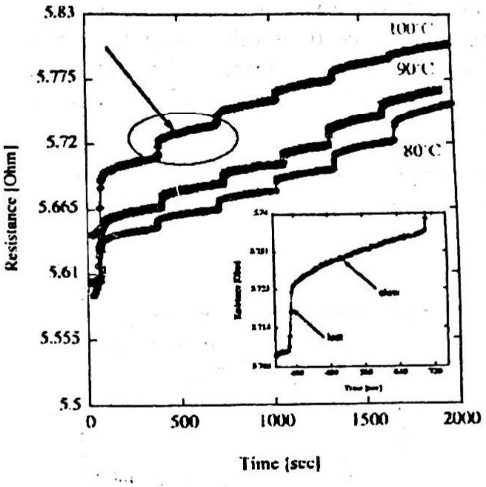

Figure 4. The absolute resistance as a function of time at 80, 90, 100°C. The hydrogen pressure was increased in discrete steps from 0-1mbar H_2 pressure. The resistance change is shown also as a function of a time at temperature 100°C, which consists from fast and slow part.

A large change in resistance is seen at the first pressure step, while for next steps the change becomes smaller. This shows that hydrogen atoms are entering into the thin film. The resistance change is smaller when the thin film is saturated by hydrogen.

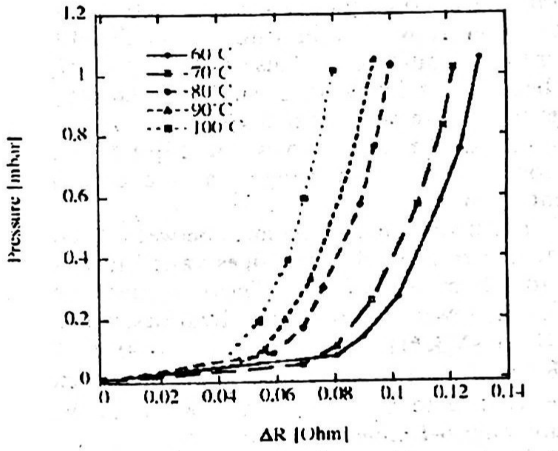

Figure 5. Pressure versus fast resistance change in hydrogen pressure range of 0-1 mbar for different temperatures.

The behavior of resistance change in the plot shows initially a fast resistance change and then a slow resistance change. To examine this further the hydrogenation pressure is plotted as a function of the fast resistance change of the sample (Fig. 5). The plot shows a typical isotherm behavior. All isotherms are placed in right temperature order and show the similar behavior. The same behavior was seen in the measurements performed in the pressure range of 0-10 mbar that is not presented here.

The slow resistance change of the films shown an opposite behavior, where all curves show the same resistance change independent on the temperature, except for the 60°. The measurements in the pressure range 0-10 mbar also show similar behavior as 0-1 mbar. The conclusion, that can be drawn, from this is that the fast change in resistance is likely to represent the hydrogen uptake, while the slow change is showing a slow structural time dependent relaxation of the thin film.

To further confirm that, the data from fast part of both pressure ranges were analyzed to determine the enthalpy and entropy changes of the hydrogen gas.

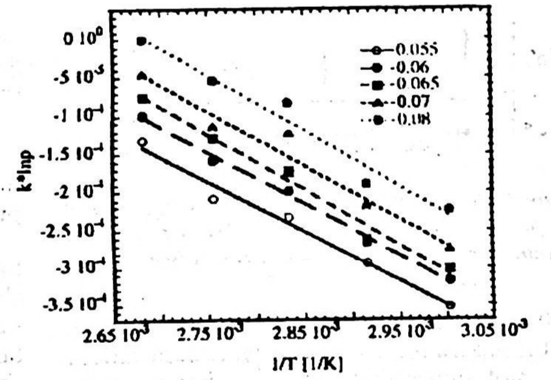

Figure 6. A selection of the Van't Hoff plot for Mg_xPd_{1-x} thin film for the fast part of the resistance change in hydrogen pressure range of 0-1 mbar. The plot shows the logarithm of the H_2 pressure versus reciprocal temperature. The enthalpy and entropy changes of hydrogen gas for $Mg_{0.95}Pd_{0.05}$ thin film were deduced from the solubility isotherms P-ΔR-T using the Van't Hoff relation [6].

The enthalpy and entropy changes of hydrogen gas for Mg_xPd_{1-x} thin film were deduced from the solubility isotherms P-ΔR-T using the Van't Hoff relation [7]

$$\ln p^{\frac{1}{2}} = \frac{\Delta H}{k_B T} - \frac{\Delta S}{k_B} \qquad (1)$$

Here, p is the pressure of the hydrogen gas, T the hydrogenation temperature, ΔH and ΔS are the enthalpy and entropy change, k_B is the Boltzmann constant. The results of analysis for 0-1 mbar pressure range were presented in Fig. 6, where *lnp* was plotted against *1/T* for different resistance change values. The solid lines in the plot are linear fits of Eq. 1 to the data. From the slope and intersection of the lines, the enthalpy and entropy changes were calculated. The arrhenius plot for pressure range of 0-10 mbar shows similar behavior, which is not presented here.

The enthalpy changes for both pressure range are plotted with resistance change in Fig. 7, where the bulk magnesium and palladium hydride enthalpy lines are also shown for comparison [8, 3].

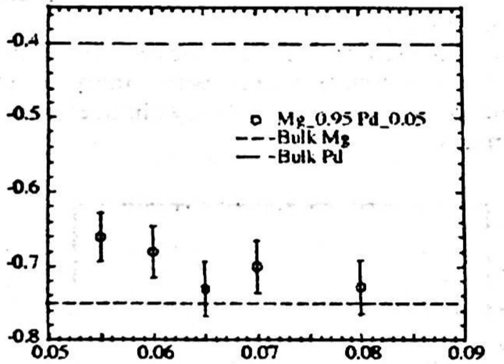

Figure 7. The total enthalpy change for Mg_xPd_{1-x} thin film as a function of the resistance change. The bulk values for the entropy change are also shown for comparison.

The pressure range 0-1 mbar in the plot is related for low hydrogen concentration. The plot shows that enthalpy change values are close to the bulk H and a bulk like MgH_2 behavior is likely seen in the pressure range 0-1 mbar. As a concentration of hydrogen in the pressure range 0-10 mbar becomes higher the thin film is followed to the Pd-H behavior.

The enthalpy change values in the pressure range 0-1 mbar varied from -0.65 to -0.73 eV/H_2. These values are significantly smaller than the bulk value of the Pd-H, which is -0.4 eV/H_2 and closer to the bulk value of the MgH_2, -0.75±0.07 eV/H_2. The enthalpy change in the pressure range 0-1 mbar determined to be -0.69±0.03 eV/H_2 [8].

These values also varied from -0.45 to -0.38 eV/H_2 in the pressure range 0-10 mbar, which have a slight difference between the values obtained for bulk Pd-H, -0.4 eV/H_2 but can be considered to be the same within the accuracy of the measurements. A significant shift is observed between the enthalpy change values of measurements and the bulk value of the MgH_2, which is -0.75±0.07 eV/H_2. The enthalpy changes in the pressure range 0-10 mbar found to be -0.41±0.03 eV/ H_2, which is closer to the bulk value of the Pd-H and much higher than bulk value of the MgH_2.

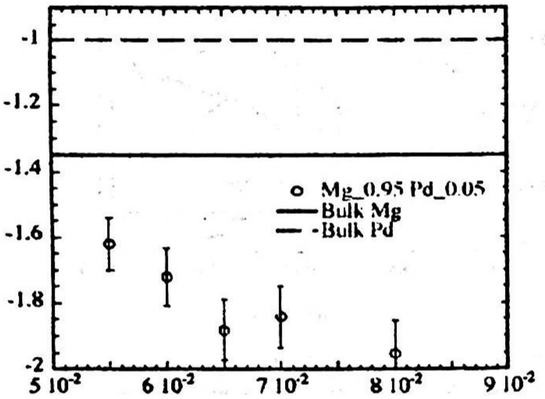

Figure 8. The total enthalpy change for Mg_xPd_{1-x} thin film as a function of the resistance change. The bulk values for the entropy change are also shown for comparison.

The entropy change is presented in Fig. 8 together with bulk data. The values of the bulk magnesium and palladium hydride are also presented [3].

The measurement results in the plot show that initially at low hydrogen concentration the change in entropy in thin film is significantly smaller than in bulk Pd-H. This shows that MgH_2 bulk behavior is likely seen, since the entropy change values are somewhat lower than in bulk MgH_2. Then the film shows an Mg-Pd like behavior with increasing a hydrogen concentration.

For hydrogen gas pressures between 0 and 1 mbar, the entropy change values varied from -1.61 to -1.95 meV/K*H_2. These values are significantly lower than both bulk hydrides, which are -1 meV/K*H_2 (Pd-H) and -1.35±0.05 meV/K*H_2. The entropy change of the hydrogen gas determined to be -1.8±0.2 meV/K*H_2 in the pressure range 0-1 mbar.

The entropy change in the pressure range 0-10 mbar have values from -1.22 to -1.21 meV/K*H_2. The plot shows that, the entropy values have almost same values and placed between the corresponding values for both bulk hydrides values. The average value of the entropy change is found to be -1.21±0.07 meV/K*H_2 which is somewhat lower than the bulk value of the Pd-H and higher than bulk value of the MgH_2. The inserted error bars for both plots are the uncertainties from the measurements.

Mg/Cr thin films-Resistance Rate Method

For the Mg-Cr thin films, hydrogenation procedure was same as for Mg/Pd films. Kinetics of hydrogen uptake in this films was extremely slow, thus **Resistance Rate Method** have been taken for determining the plateau pressure, which is shown below.

According to the previous measurements on Mg/Pd, resistance of thin film should increase with hydrogen gas pressure. Thus, by using increase of resistance variation speed, i.e. dR/dt, it is possible to measure this derivative for each pressure value, by letting resistance rise. Each part of the curve R (t) linearly fitted and these yields are dR/dt. The plot log dR/dt versus pressure should exhibit a well-defined kink corresponding to the plateau pressure, as resistance rises much faster when pressure is greater than the plateau pressure. The plateau pressure is given by the cross point of the fit of the two parts of the curve (Fig.9). Plot shows that the plateau pressure for temperature 333K is 1.11±0.2 mbar.

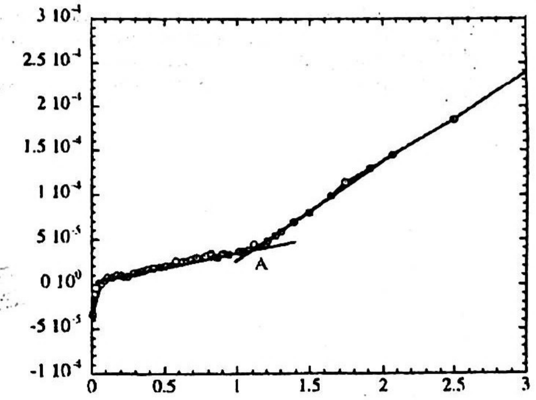

Figure 9. $\log\frac{dR}{dt}$ *versus pressure for Mg/Cr thin film at the temperature 333K with fits. The two crossing lines determine the plateau pressure, which is equal to 1.11±0.2mbar.*

This method has proven to be much faster and precise than other methods as considerations regarding resistance stabilization become irrelevant. Five isotherms were taken, at 60-100 and 120°C. Data from the plot was used to build an Arrhenius plot $k_B ln\ p(T)$ (Fig.10), from which entropy and enthalpy change were extracted. From the Arrhenius plot the enthalpy change value for Mg/Cr sample was determined to be 0.50±0.03 eV/H_2, which is somewhat lower than the bulk hydride and entropy value was found to be -1.35±0.05 meV/ k*H_2 which is quite close to bulk value.

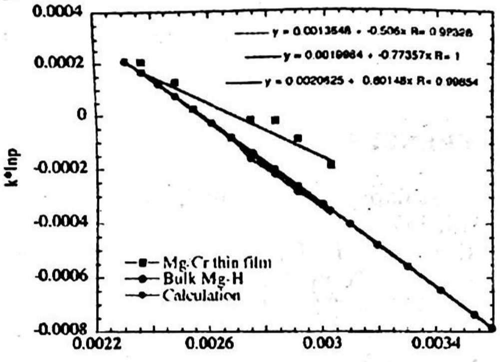

Figure 10. *Arhhenius plot for Mg/Cr thin film. The bulk hydride values are shown for comparison.*

SUMMARY AND CONCLUSION

We have investigated the thermodynamics of hydrogen in Mg/Pd and Mg/Cr thin films in the different temperature range with resistance measurements.

The enthalpy and the entropy changes of hydrogen gas were deduced from the P-ΔR-T isotherms, in two different pressure ranges 0-1 and 1-10 mbar for Mg/Pd thin films using hydrogen uptake. This shows that in Mg/Pd thin film a bulk like MgH_2 behavior is seen in the pressure range of 0-1 mbar, while likely bulk Mg-Pd behavior is seen in the higher pressure range.

The enthalpy and entropy changes for Mg/Cr sample were found to be 0.50±0.03 eV/H_2 and -1.35±0.05 meV/ k*H_2 respectively, where the entropy change value has a value which is very to the bulk value.

This is the first aim on this type of thin film and no previous measurements have taken. Therefore, it is too early to establish some conclusion about the enthalpy and entropy changes of hydrogen gas in this type thin film. A more thorough investigation, followed by a comparison with the theoretical data, is needed to build up some empirical model.

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Товч агуулга

Mg/Cr ба Mg/Pd нимгэн хальсан дахь устөрөгчийн термодинамик шинж чанарыг туршлагын үндсэн 2 аргад тулгуурлан тодорхойлов. Эхний арга нь нимгэн хальсанд устөрөгч нэвтрэх үед түүний эсэргүүцлийн өөрчлөлтийн хурд болон даралтын хамаарлыг ашиглан ханасан даралтын утгыг олоход үндэслэнэ. Дараачийн арга нь устөрөгчийн нимгэн хальс дахь нэвтрэлтэд үндэслэсэн болно. Туршлагын үр дүнг уг магнийн гидридийн хувьд гарган авсан математикийн тооцооны дүнтэй харьцуулалт хийсэн болно.