

Chapter 2

Experimental Methods

2.1 Film Preparation

Mg-based thin films used in this study were prepared by a custom-designed direct current (DC) magnetron sputtering system with a background pressure of around 2×10^{-4} Pa. Glass sheets and silicon wafers were chosen as the substrates. The films prepared on glass substrates were used for the electric, optical, and electrochemical measurements, and the films prepared on silicon substrates were used for the structural characterizations, such as XRD and SEM. Before sputtering, the glass and silicon substrates were cleaned with deionized water, acetone, and absolute ethyl alcohol for 15 min, respectively. The magnetron discharges were generated under an argon pressure of 0.6 Pa with the argon flow rate of 76 sccm. The purity of argon pressure is 99.99 %. The overall purity of Mg, Ti, Al, and Pd is 99.99 %. After Mg film deposition, 10 nm Pd cap layer was deposited on the top, which is necessary to protect Mg against oxidation and to promote hydrogen dissociation.

After deposition, the samples were transferred into a steel chamber which was evacuated to 10^{-3} Pa later. Then, it was loaded with certain amount of hydrogen (99.99 %). Thereafter, the hydrogen absorption and desorption measurements were conducted under different temperatures. The dehydrogenation process was performed in dry air at different temperatures for tracing the desorption mechanism. The hydrogen absorption and desorption testing apparatus of thin films is shown in Fig. 2.1. Before hydrogenation, no activation treatments were adopted.

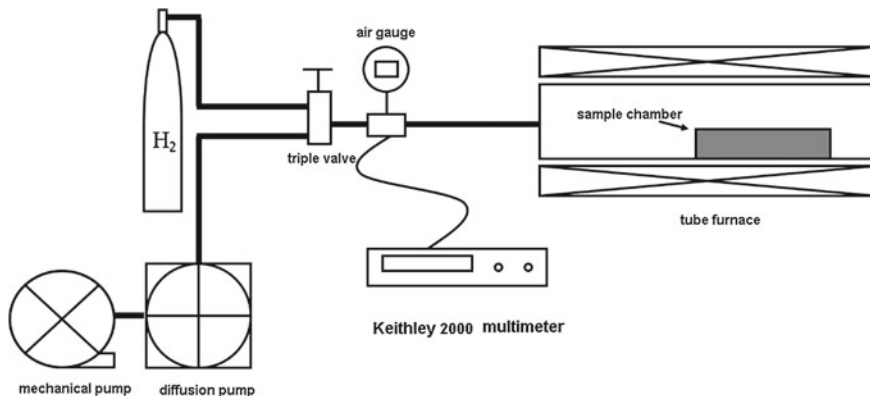


Fig. 2.1 The diagrammatic sketch of the hydrogen absorption and desorption apparatus

2.2 Thin Film Characterization

2.2.1 X-Ray Diffraction

XRD measurements of all the thin films in this study were performed in the D/MAX 2400 X-ray diffractometer produced by Rigaku Corporation (Japan). The parameters of this instrument were as follows: the sweep range: 3–140 °C; degree of stability ≤ 0.05 %; degree of accuracy: 0.006°; reproducibility $\leq \pm 0.002^\circ$.

The operation of X-ray diffractometer is quite simple: the thin film samples can be stuck on the sample groove with plasticine, and the measurements can be conducted after setting up the sweep range, sweep rate, and slit width.

2.2.2 Scanning Electron Microscope/Energy Dispersive Spectrum Analysis (SEM/EDS)

The SEM images were acquired by Hitachi S-4800 produced by Hitachi (Japan). Meanwhile, EDS spot scanning and lateral scanning were used to analyze the different elements distributions of the materials. The parameters were as follows: acceleration voltage: 0.5–30 kV; secondary electron image resolution (high acceleration voltage = 15 kV): 1 nm; secondary electron image resolution (low acceleration voltage): 2 nm; magnification times (LOW MAG): 30x–2000x; magnification times (HIGH MAG): 100x–800000x.

2.2.3 Transmission Electron Microscopy (TEM)

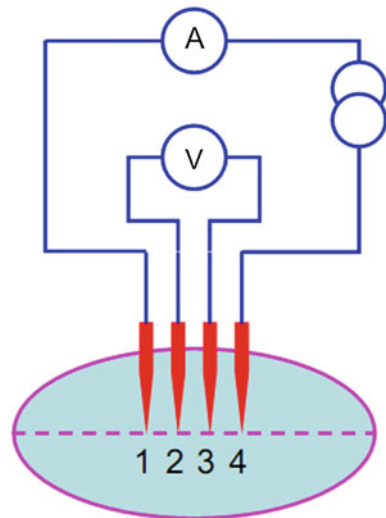
The TEM images were acquired by JEM-2100F transmission electron microscope produced by JEOL (Japan). The main parameters of this instrument were as follows: dot resolution: 0.19 nm; linear resolution: 0.1 nm; resolution of STEM: 0.2 nm; energy resolution of energy spectrum: 130.8 eV; magnification times: 50–1500000; the elemental range of EDS analysis: 5B–92U.

2.3 Property Measurements of Thin Films

2.3.1 Electrical Resistance Measurements [1–3]

The in situ electrical resistance measurements of thin films during hydrogen absorption and desorption process were performed in a temperature-controlled chamber equipped with a four-point electrical resistance measuring system. Before the measurement, the chamber was evacuated to 10^{-2} Pa, and maintained at the required temperature. Afterwards, 99.99 % H_2 was introduced to the chamber. The electrical resistance changes were measured by Keithley 2000 digital multimeter, and the results were recorded with a computer software, as shown in Figs. 2.2 and 2.3.

Fig. 2.2 The diagrammatic sketch of four-point electrical resistance measuring system



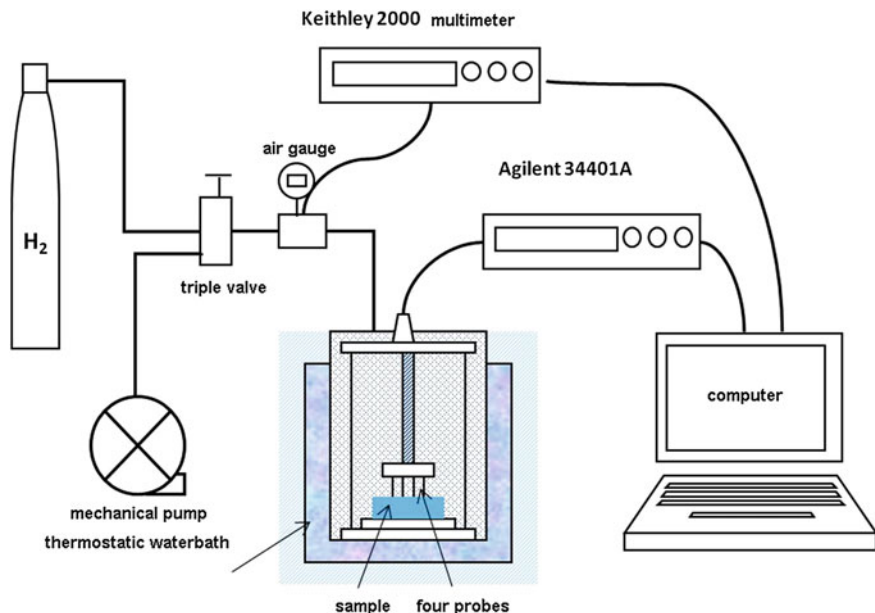


Fig. 2.3 The diagrammatic sketch of in situ electrical resistance measuring apparatus

2.3.2 Optical Transmittance Measurements [1–3]

The optical transmission measurements at 298 K were performed using a UV–Vis recording spectrophotometer (Shimadzu UV-2401PC) with a dual beam measurement system. The UV–Vis transmission spectra at higher temperatures were measured with a Shimadzu UV-3100 spectrometer. The measurement wavelength range was 400–800 nm.

According to Lambert–Beer’s law, $\ln(T/T_0)$, the logarithm of the optical transmittance is expected to vary linearly with the hydrogen concentration in the film. Assuming that it was totally dehydrogenated when the transmittance kept constant as a function of time, it was then possible to determine the initial desorption rates from the slopes of the curves. Therefore, the amount of Mg hydride transforming to Mg metal (reacted fraction γ) in desorption process could be calculated.

The desorption data of different films can also be analyzed using the Johnson–Mehl–Avrami theory [4]. Upon a first-order phase transition, the reacted fraction is given as a function of time, by $\gamma = 1 - \exp[-(kt)^n]$, where γ is the reacted fraction, t is the desorption time, $k = k(T)$ is the temperature-dependent kinetic constant, and n is the reaction order. A linear interpolation of the plots, $\ln(-\ln(1 - \gamma))$ versus $\ln(t)$, could yield the value of n and k . Unlike bulk materials, the reacted fractions of thin films were difficult to be calculated using the conventional gravimetric and volumetric method. Thus, γ values were obtained

according to the transmittance data. The value of the exponent was $n = 1$ for the desorption process. The temperature-dependent desorption rates generally followed the Arrhenius type law. According to the Arrhenius formula, the activation energies of different Mg-based films during the hydrogen desorption process in air can be calculated.

2.3.3 Electrochemical Property Measurements [5, 6]

All the electrochemical experiments were carried out at room temperature in KOH solution with a three-electrode cell. Platinum foil and Hg/HgO were used as the counter and reference electrode, respectively.

Prior to the cyclic voltammetry measurements, the films were subjected to an activation procedure between -450 and $+450$ mV as a scan rate of 50 mV s^{-1} . This potential range corresponded to the $\text{Pd}(\text{OH})_2$ formation/removal on the Pd cap layer. The sweep potential range was -1.2 – 0.45 V, and the scan rate was 50 mV s^{-1} .

Hydrogen diffusion coefficient was an important kinetic parameter for hydrogen storage materials. Hagi's model was applied to analyze the current with respect to the discharge time to calculate the hydrogen diffusion coefficient [7, 8]. When the discharging time t is long enough ($>3L^2/\pi^2 D_H$), the relationship between the anodic current I_d and hydrogen diffusion coefficient D_H can be described as: $\ln(I_d) = -\pi^2 D_H / 4d^2 t + \text{Constant}$, where I_d is the current density, t is the discharge time, D_H is the diffusion coefficient, and d is the thickness of the film. The hydrogen diffusion coefficients of different samples can be obtained from the slopes of the curves of $\ln(I_d)$ as a function of t .

The diffusion coefficients of the Mg-based films were determined by the electrochemical multipotential steps method in KOH solution. The fast scan (100 mV s^{-1}) cyclic voltammetry was applied to clean the surface prior to measurement. The Mg-based film electrodes were first held at a cathodically polarized potential (-1.10 V vs. Hg/HgO) for 1.5 h and subsequently switched to an anodically polarized potential (-0.5 V vs. Hg/HgO) for another 1.5 h. The hydrogen diffusion coefficients can be calculated according to the relationship between the anode current and the discharge time.

The charge–discharge cycles of thin films were obtained by galvanostatic methods. During the charge and discharge measurements, the electrodes were first fully charged at a certain current value followed by 10 min relaxation, and then discharged at a certain current value. The cut-off voltage was set as -0.6 V versus the Hg/HgO reference electrode. The capacity retention rate (S_n) can be calculated as: $S_n(\%) = C_n / C_{\max} \times 100 \%$. Where C_n is the discharge capacity of the electrode at the n th cycle and C_{\max} is the maximum discharge capacity.

References

1. Xin GB, Yang JZ, Wang CY et al (2012) Superior (de)hydrogenation properties of Mg-Ti-Pd trilayer films at room temperature. *Dalton Trans* 41:6783–6790
2. Xin GB, Yang JZ, Zhang GQ et al (2012) Promising hydrogen storage properties and potential applications of Mg-Al-Pd trilayer films under mild conditions. *Dalton Trans* 41:11555–11558
3. Xin GB, Yang JZ, Fu H et al (2013) Excellent hydrogen sorption kinetics of thick Mg-Pd films under mild conditions by tailoring their structures. *RSC Adv* 3:4167–41704
4. Avrami M (1941) Granulation phase change, and microstructure-kinetics of phase change III. *J Chem Phys* 9(2):177–184
5. Xin GB, Yang JZ, Fu H et al (2013) Pd capped $\text{Mg}_x\text{Ti}_{1-x}$ films: promising anode materials for alkaline secondary batteries with superior discharge capacities and cyclic stabilities. *Int J Hydrogen Energy* 38:10625–10629
6. Xin GB, Wang YY, Fu H et al (2014) Promising electrochemical hydrogen storage properties of thick Mg-Pd films obtained by insertion of thin Ti interlayers. *Phys Chem Chem Phys* 16:3001–3006
7. Hagi H (1990) Diffusion-coefficient of hydrogen in palladium films prepared by Rf-sputtering. *Mater Trans JIM* 31(11):954–958
8. Yang L, Yang-Tse C (1996) Hydrogen diffusion and solubility in palladium thin films. *Int J Hydrogen Energy* 21(4):281–291

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