

Combinatorial study of thin film metal hydride by prompt gamma activation analysis

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Abstract Cold neutron prompt gamma activation analysis (PGAA) was used to determine the mass of hydrogen in Mg hydride thin films with varying hydrogenation times. The results suggest that hydrogenation of the Mg thin films remains unsaturated even after 48 h of treatment, contrary to the indications of inferential hydrogen measurement

methods. To demonstrate PGAA as an effective combinatorial methodology for hydride thin films, a continuously varying composition gradient of thin $Mg_yTi_{(1-y)}$ hydride film with y ranging from 0.65 to 0.94 was prepared and analyzed by both PGAA and instrumental neutron activation analysis (INAA). The variation in the molar ratio of Mg, Ti, and H was obtained for nine 5 mm wide segments of the film.

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Introduction

Hydrogen storage materials are under intense study worldwide as a practical means for on-board storage of alternative, non-fossil fuel for mobile applications [1]. Sophisticated analytical techniques, combining high accuracy, reliability, and rapid throughput, are essential for identifying promising materials. Thin film combinatorial methodologies provide a high-throughput screening method for discovery of potential candidate materials [2]. However, while hydrogen sorption in bulk is frequently measured with a Sievert's apparatus [3], it is difficult to measure thin-film samples in this way. The reason is that the differential pressure from hydrogen sorption in thin films is orders of magnitude less than in bulk hydride material. One technique used for measurement of thin film combinatorial samples during hydrogenation (i.e., in situ) is to monitor the change in the infrared (IR) emissivity [4] of a sample during hydrogen exposure. This assumes the emission of infrared radiation of a material changes with its hydrogen contents or the amount of a hydride phase. However, other factors

such as surface roughness, local temperature, and the distribution of phases also affect the IR emission.

Prompt gamma activation analysis (PGAA) uses a high-resolution germanium detector to count characteristic prompt gamma rays emitted by an excited compound nucleus returning to the ground state after neutron absorption. In addition to being a direct and nondestructive method, PGAA is unique in its ability to measure hydrogen due to its appreciable neutron absorption cross section and the simplicity of the resulting gamma spectrum [5, 6].

The cold neutron beam used for PGAA at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) enables high sensitivity for hydrogen analysis, partially due to the high neutron absorption cross section for cold neutrons, which is 0.74 barns compared to 0.33 barns for thermal neutrons [7]. Moreover, the single gamma line at 2,223 keV produced following a neutron capture by H has no interference peak with the materials commonly used as thin-film substrates, e.g., sapphire (Al_2O_3) or fused silica (SiO_2).

The goal of this research is to establish PGAA as an effective method for the measurement of kinetics and thermodynamics of hydrogenation in combinatorial thin-film H storage materials. Several projects are underway to broaden the instrumental capacity to meet the requirements set by this goal. The first step is to use PGAA to establish the relationship between hydrogenation times of hydride thin films with the absolute content of hydrogen absorbed. A second step is to spatially resolve the molar ratios of Mg, Ti, and H in a roughly 2 cm \times 5 cm thin Mg–Ti hydride film with continuous gradient composition by using a collimated neutron beam. While the H mass content is exclusively determined by PGAA, the Mg and Ti are measured by both PGAA and INAA.

Experimental

Background at current facility

The cold neutron PGAA facility at NCNR has been in operation since early 1990 and is extensively used for various research projects [8]. The cold neutrons are delivered to the PGAA station 41 m away from the cold neutron source through multiple reflections off the inner surface of a ^{58}Ni coated neutron guide. At about 1 m before reaching the sample position, the neutron guide splits into two sections. The lower section ends with a Mg window from which neutrons exit and propagate through the air to reach the sample. The upper section of the guide continues, delivering the neutrons to downstream instruments [9]. This guide configuration elevates the overall gamma background level in the vicinity of the sample even with the lower neutron

guide (for PGAA) closed and also limits the size of the sample chamber. Experiments to optimize the background and to provide a versatile sample environment are ongoing. In this work, special attention was paid to reducing the background in order to differentiate several-micrograms quantities of H and Mg, typical in thin films prepared by physical vapor deposition. To this end, a cubic tent with 12 cm edges was constructed from 70- μm Teflon¹ FEP film wrapped around an Al frame, replacing an evacuated Mg sample chamber that was previously used. The tent was flushed with He gas at a low flow rate during sample irradiation, improving the detection limits for both H and Mg.

Sample preparation

A c-plane sapphire substrate approximately 4.5 cm \times 2 cm was mounted on the heating stage of an electron-beam evaporation chamber. Ti was evaporated as an oxygen getter while the substrate was covered to provide a chamber base pressure of 2.67×10^{-5} Pa. The Mg was deposited at a rate of 0.125 nm/s to a maximum thickness of 1.2 μm , measured using a deposition controller. Afterwards a Pd capping layer of 7 nm was deposited on top of the Mg to prevent oxidation and to act as a catalyst for the breaking of H–H bonds in H_2 gas. After deposition, the wafer was cut into six pieces of approximately 10 mm \times 10 mm for hydrogenation. Hydrogenation times of 0.75, 1.5, 6, 12, 24, and 48 h were chosen to maximize the amount of data taken for low H contents and to ensure eventual saturation of the entire film with H. Each sample was hydrogenated separately at 250 °C in 5.07×10^5 Pa of H to ensure the transformation of Mg to MgH_2 .

In addition, a 1 μm thick Mg–Ti composition gradient film was deposited by sputtering elemental Mg and Ti targets onto a c-plane sapphire substrate. The magnetron sputtering chamber has a base pressure of 6.65×10^{-6} Pa with three 5.08 cm guns located on a center cluster. Each gun can be individually rotated and tilted to deposit either uniform or thickness-graded films. The guns for Mg and Ti were tilted toward one another to form a natural composition spread across a 5 cm long wafer. A separate gun with an elemental Pd target was used to deposit a uniform capping layer after the deposition of the Mg–Ti gradient was completed. The sample was subsequently hydrogenated at 250 °C in 1.01×10^6 Pa of H for 24 h. After hydrogenation strong reflections from the MgH_2 and Mg phases were observed by X-ray diffraction, indicating successful hydrogenation for making the thin Mg–Ti hydride film sample.

¹ Certain trade names and company products are identified in order to adequately describe the experimental procedure. In no case does such identification imply, recommendation, or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best for the purpose.

Determination of H in MgH_x thin films at increasing hydrogenation times by PGAA

After having the varied length of hydrogenation times for each of the six samples, they were individually irradiated with cold neutrons at a thermal equivalent neutron flux of $8.8 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ while counting by Compton suppression gamma spectrometry. The sample was inserted into a heat-sealed Teflon bag, which was attached to a monofilament Teflon string suspended on an aluminum U-shaped frame. The detector's field-of-view is perpendicular to the neutron beam. The sample holder is placed at a 45° angle to both the detector and beam. The evacuated Mg sample chamber was used for this measurement, partially because the Mg content was not the targeted analyte, and partially because the Teflon tent was not yet fabricated.

Each sample was counted in the beam between 12 and 24 h to ensure adequate counting statistics. The determined H concentration in each sample was normalized by the Al gamma-ray count rate to account for the slight difference in sample geometry, assuming the sapphire substrate has uniform thickness and therefore, the area of the substrate is proportional to the activated gamma-ray intensity from Al.

A portion of the same sapphire substrate was used as a blank sample for background subtraction. It was counted in the neutron beam for 1 day with the same conditions as the samples.

The mass of H in the sample was determined based on comparison of PGAA count rate with thin-film type standards such as a polypropylene film with thickness of $6.3 \mu\text{m}$ and a Mylar film with thickness of $1.5 \mu\text{m}$. They were laid separately on the surface of the same blank sapphire to mimic the real neutron environment for sample. A urea-titanium-graphite standard was also irradiated and the ratio method was used for H quantification [10].

Determination of H, Ti, and Mg in sequential regions of a thin Mg–Ti hydride film by PGAA

The aforementioned Teflon tent was substituted for the Mg chamber and continuously flushed with He gas to reduce Mg background for PGAA measurement. INAA was also used for Mg determination following PGAA irradiation due to its higher sensitivity for Mg and the low mass of Mg deposited in the sample. The thin Mg–Ti hydride film was cut into nine pieces, roughly 1 cm^2 each, after hydrogenation to ensure the following PGAA and INAA measurement would measure the same region.

Each sample was counted by PGAA in the He environment for 20–24 h using the urea-titanium-graphite as the H standard. A Ti pure metal foil and MgO pellet were used for Ti and Mg standards.

Again, the Al concentration was assumed proportional to the amount of substrate, and this was used to correct for

slight variations in sample size. The measured Mg, Ti, and H masses were all normalized to match the area of one of the sample, roughly 1 cm^2 .

Determination of Ti and Mg in sequential regions of the same thin $\text{Mg}_y\text{Ti}_{(1-y)}$ hydride film by INAA

Each of nine thin film samples was irradiated along with high-purity Ti and Mg foil standards in the RT-2 pneumatic irradiation channel of the NIST reactor at $3.4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ neutron flux for 60 s. Immediately after irradiation, the samples and standards were counted at 4 cm from an intrinsic Ge gamma-ray detector equipped with loss-free counting electronics [11]. The Mg and Ti content of each sample was determined via the decay of ^{27}Mg and ^{51}Ti using the comparator method with appropriate self-absorption corrections for the differences in thickness of the samples and foil standards.

Results and discussion

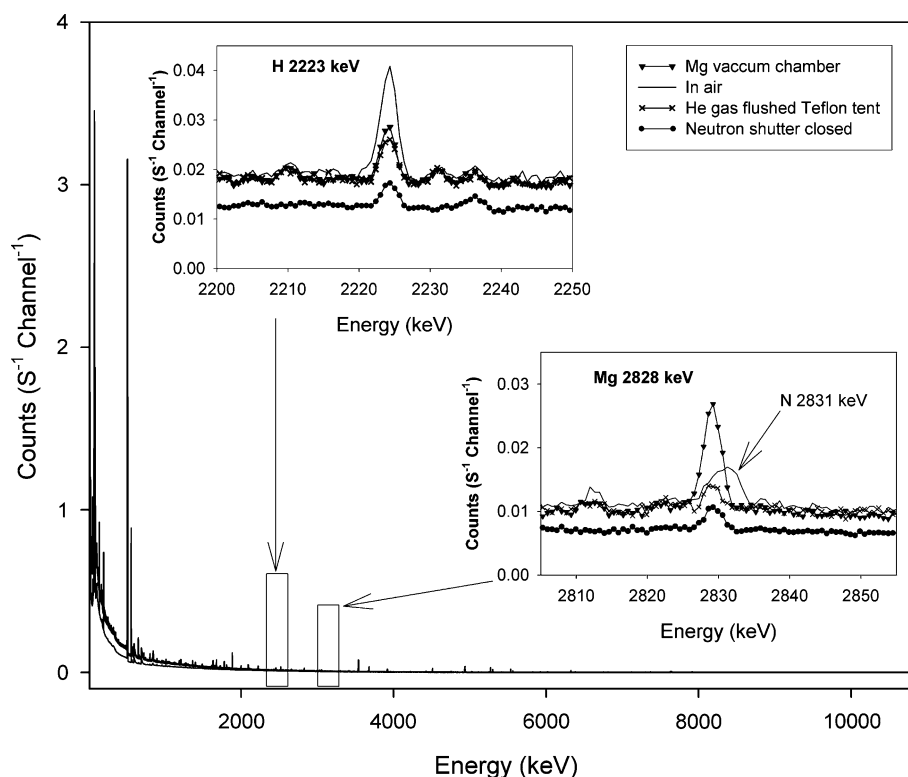
PGAA background under different sample environments

Four sample environmental backgrounds were evaluated, i.e., the background with (1) Mg vacuum chamber; (2) He gas flushed Teflon tent; (3) in air; and (4) with the PGAA neutron shutter closed. The four spectra are displayed in Fig. 1 with the regions containing the single H peak (2,223 keV) and one of the Mg peaks (2,828 keV) displayed as insets. The corresponding count rates of those peaks are listed in Table 1. The He gas environment reduces the H count rate by 25% compared to the Mg chamber. Both chambers effectively eliminate the H signal caused by water vapor inside the 6 cm^3 volume defined by the neutron beam and the field of view of the gamma-ray detector. The background with the PGAA shutter closed indicates that part of the background for PGAA analysis is due to a constant neutron source from the neutron guide 30 mm above the sample position. The inset in Fig. 1 shows the expected significant Mg peak when the Mg chamber was used. Surprisingly, the other spectra have the same level of Mg background signal. However, flowing He gas in the Teflon tent is still preferred for Mg measurements because the 2,828 keV Mg peak has an interference with one N line at 2,831 keV, which becomes problematic when the sample is irradiated in air.

Measurement of H at increasing of hydrogenation times by PGAA

The change in H content in thin films as a function of its exposure time as measured by PGAA reveals trends that are

Fig. 1 Comparison of H and Mg background spectra under four sample environments, the spectrum labeled as neutron shutter closed was obtained with the neutron shutter for PGAA closed while the main beam shutter for neutron guide is open for adjacent guide



not seen by inferential methods. The H content has not fully saturated in the film until at least 48 h of hydrogenation, as shown in Fig. 2. In contrast, the change in the IR emissivity showed the saturation after less than 5 h of hydrogenation using the same set of samples. Additional investigations using Fourier transform infrared (FTIR) and transmission electron microscopy (TEM) are under way to address the discrepancy raised by two methods. PGAA therefore, as expected, allows one to quantify changes in the films throughout the hydrogenation process, and provides a benchmark against which other techniques may be compared.

In addition to determining H contents by comparing samples with polypropylene and Mylar thin film, the mass of H in the sample was also calculated based on comparison of PGAA count rate of a mass fraction of 3.171% H and a mass fraction of 12.55% Ti in a urea-titanium-graphite standard and a pure Ti metal foil. As shown in the Fig. 2, the H contents obtained with all three standards agree well within 1 s of uncertainty.

Variation of H, Mg, and Ti along a thin $Mg_yTi_{(1-y)}$ hydride gradient film

A total of nine regions along the graded thin hydride film were measured for their H content using PGAA exclusively. INAA was used to give concentrations for the Mg in each sample. The Ti was found to be well determined by both techniques. The Mg, Ti and H mole fraction in the Mg–Ti

thin films using results from INAA and PGAA are shown in Fig. 3. A smooth variation of composition gradient was confirmed in Mg–Ti thin films prepared by sputtering technique described above. The H/Mg ratio of the ninth sample is close to 1 indicating a partially completed hydrogenation process. Figure 4 shows that substituting Mg by Ti affects the H absorption in Mg–Ti thin films. A jump of H retention at about $Mg_{0.8}Ti_{0.2}$ suggests a favorable Mg–Ti composition for H storage that might lead to further investigation on its kinetic properties. Research conducted by Vermeulen et al. [12], using electrochemical hydrogenation of electron-beam deposited Mg–Ti alloy pointed out that $Mg_{0.8}Ti_{0.2}$ alloy presents a superior reversible H storage capacity, along with high rate-capability.

Use of the He-filled Teflon sample environment during PGAA measurement improves the detection limit for Mg. The comparison of Mg and Ti concentrations evaluated by PGAA and INAA is shown in Fig. 5 with 1 s of uncertainty. Even though the associated uncertainty is large, PGAA measurement of Mg is in agreement with trends of the Mg concentration observed by INAA. Both analytical techniques agree well with Ti determination.

Conclusion

Cold neutron PGAA was used to determine the level of hydrogenation after exposing metal thin films to H_2 for

Table 1 Comparison of H and Mg background in four sample environments by PGAA

Conditions	H (2,223 keV) (counts s ⁻¹)	Equivalent mass of H (μg)	Mg (2,828 keV) (counts s ⁻¹)	Equivalent mass of Mg (μg)
Neutron shutter closed ^a	0.020 ± 0.001	1.51 ± 0.08	0.019 ± 0.001	710 ± 37
Teflon tent flushed with He gas	0.032 ± 0.002	2.48 ± 0.16	0.019 ± 0.002	710 ± 74
Mg vacuum chamber	0.043 ± 0.002	3.27 ± 0.19	0.083 ± 0.002	3,101 ± 74
In air	0.092 ± 0.002	7.02 ± 0.23	0.019 ± 0.002 ^b	710 ± 74

^a The shutter for PGAA chamber is closed, the main shutter continues allows for neutron in adjacent guide

^b Interference with one N peak at 2,831 keV, value determined by ratio with another N peak at 2,520 keV

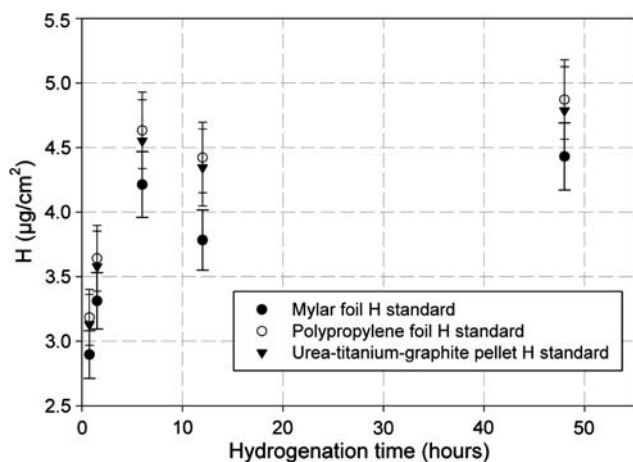


Fig. 2 H concentration with 1 s uncertainty in MgH_x thin films versus hydrogenation time

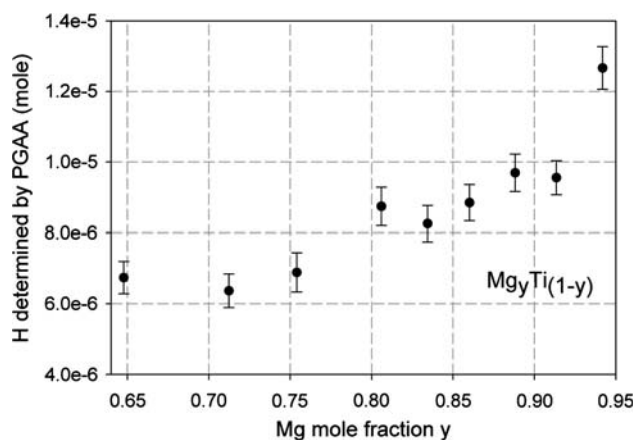


Fig. 4 The changing H contents with 1 s uncertainty determined by PGAA in thin Mg_yTi_(1-y) hydride films, y is the mole fraction of Mg in the Mg–Ti thin films

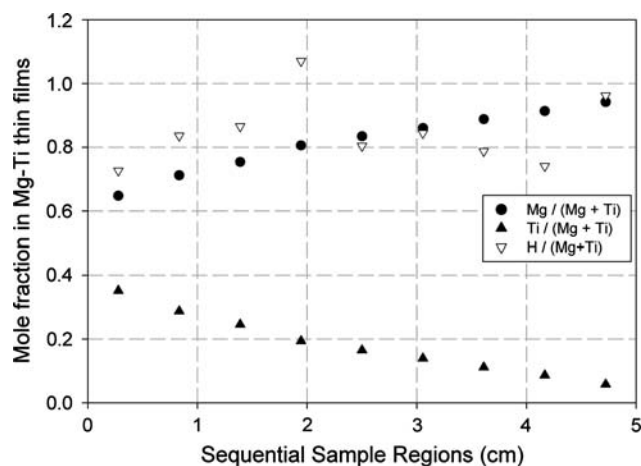


Fig. 3 The changing composition gradient of Mg and Ti with H content in Mg–Ti thin films, the Mg and Ti are determined by INAA and the H is determined by PGAA

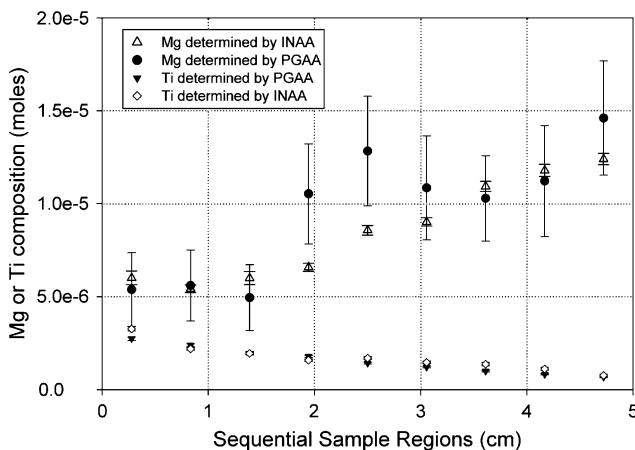


Fig. 5 Comparison of Mg and Ti composition with 1 s uncertainty determined by PGAA and INAA in Mg–Ti thin films

times ranging from 0.75 to 48 h. The results suggest that the IR emissivity may be only valid for H determination to shallow depth. To establish a methodology for combinatorial study of hydride thin films by PGAA, the thin Mg_yTi_(1-y) hydride film was prepared and analyzed by both PGAA and INAA to measure the change in molar ratio of

Mg, Ti and H for nine small regions. Even though INAA provides better detection limits for Mg, the need to break samples for spatially resolved concentration mapping encourages the pursuit of PGAA for combinatorial thin film hydride screening. The replacement of the Mg vacuum chamber with a He gas environment reduced the H

background by 25%, and the analysis of Mg was made possible. However, unless the local neutron intensity was increased by one or two orders of magnitude, e.g., by using neutron focusing lens [13], the ability to resolve Mg and H spatially with practical resolution is still limited by low mass of hydrides in thin film samples.

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