Enhanced oxidation resistance of magnesium nanorods grown by glancing angle deposition

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Oxidation behavior of magnesium thin films and nanorods were investigated in the temperature range of 25–550 °C by using thermal gravimetric analysis. Arrays of vertical magnesium nanorods were deposited by the DC magnetron sputtering glancing angle deposition technique, while the magnesium thin films were deposited using the same system but at normal incidence. The morphologies and corresponding crystal structure of the samples were analyzed by scanning electron microscopy, transmission electron microscopy and X-ray diffraction methods, respectively. We report that the Mg thin films showed oxidation induced weight gain starting from room temperature. On the other hand, Mg nanorods did not show any indication of significant oxidation at temperatures below 350 °C. Enhanced oxidation resistance of Mg nanorods was also confirmed by quartz crystal microbalance measurements. At temperatures higher than 350 °C, Mg nanorods started to get oxidized and their weight increased at a similar rate to that of Mg thin films. We argue that reduced oxidation of Mg nanorods is mainly attributed to their single crystal nature. Magnesium nanorods’ reduced oxidation can potentially play a key role in hydrogen storage and gas sensing applications.

1. Introduction

Magnesium is among the lightest of all metals and as a result it is used in an increased number of industrial applications and processes as well as for products for which reduced overall weight is essential, such as automobile parts, sporting goods, and aerospace equipment [1]. Magnesium and its alloys have also generated a high interest as advanced materials for hydrogen storage and detection [2–11]. However, the oxidation resistance of magnesium is rather low and can lead to poor material properties especially at elevated temperatures. Several researchers have studied the oxidation properties of magnesium and magnesium alloys [12–15]. The oxide layer that can form at low temperatures on the surface of magnesium and magnesium alloys is generally in the form of MgO. The morphology of MgO layer is porous and therefore it cannot act as an efficient barrier to prevent the further oxidation of the metallic structure [16–19]. Notable weight gain due to the oxidation process was reported for Mg alloys at temperatures higher than...
200 °C [20–22] for Mg ultrafine particles and Mg thin films [23] at temperatures higher than 400 °C, respectively [24]. Studies on the oxidation rate of magnesium and its alloys also reported that they get further enhanced at temperatures higher than about 400 °C [19,20,22–25]. However, there have been reports indicating that thin films of Mg have been observed to significantly get oxidized at temperatures as low as 160 °C [26].

One of the most promising applications of the magnesium based material systems is their use for solid-state hydrogen storage environments because of their high storage capacity (7.6 wt% for Mg), low material density, low cost, and vast availability [27]. However, typical hydrogen absorption/desorption temperatures of magnesium are elevated (≥300 °C) due to the poor kinetics [28]. Recently, nanostructured magnesium fabricated by the glancing angle deposition (GLAD) technique [29–31] has been an attractive structure. GLAD Mg nanostructures and nanostructures also incorporating catalyst additives [36–39] have been on the focus of research for hydrogen storage and have significantly lower absorption temperatures. Recently, Cansizoglu and Karabacak reported significantly lower absorption temperatures of hydrogen in Mg nanotrees produced by GLAD, where a hydrogen storage value of ~4.8 wt% was measured at temperatures as low as 100 °C [40]. On the other hand, these hydrogen storage experiments on nanostructured Mg either with or without catalyst additives have been performed under oxygen-free environments. There is a concern that high surface area Mg nanostructures with small feature sizes can seriously suffer from surface oxidation when exposed to ambient or oxygen rich environments leading to low interaction with gaseous hydrogen and poor absorption/desorption kinetics. Therefore, there is a need to investigate the oxidation properties of magnesium nanostructures in the presence of oxygen, which will be quite critical especially for hydrogen storage applications. It has been previously reported that atomic hydrogen cannot diffuse trough the crystalline structure of the magnesium oxide films [26,41–43] which makes MgO a diffusion barrier for H. In addition, Pranevicius et al. [44] found that even small impurity levels of oxygen during hydrogenation could result in the formation of a surface oxide barrier.

The aim of the present study is to provide a detailed investigation of oxidation properties of magnesium nanorods fabricated by GLAD technique and compare this to that of conventional magnesium thin films. Oxidation behavior of magnesium samples has been studied using thermal gravimetric analysis (TGA) in dehumidified dry air supplied by Airgas at temperatures ranging from room temperature (~25 °C) to 550 °C. Mg nanorods and thin films have also been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results of this study are believed to be significant in elucidating the thermal behavior and stability of GLAD-generated Mg nanostructures under various temperature conditions. Such an understanding of the behavior of various Mg structures in gaseous environments could provide solutions to the current limitations faced by this material for large scale usage in energy related applications with a focus on their usage as the active component in high efficiency hydrogen storage systems.

2. Experimental details

Glancing angle deposition (GLAD, also known as oblique angle deposition) has been an effective technique to produce arrays of various 3D nanostructures, in the form of nanospirals, nanobeads, and nanorods [32–35]. During GLAD, the incident beam of atoms is sent at a high angle (typically larger than 70°) as measured from the surface normal of a rotating or a stationary substrate. Due to geometrical “shadowing effect”, the incident vapor is preferentially deposited onto higher surface features, which are better exposed to incident beam of atoms. This preferential growth dynamic gives rise to the formation of well-separated nanostructures, with dimensions typically ranging from tens to hundreds of nanometers, depending on the detailed growth parameters and material being deposited.

In our experiment, samples of Mg thin films and GLAD nanorods were deposited using a DC magnetron sputter deposition unit. The substrates were polished alumina pieces that were annealed at about 200 °C for 5 h under ambient conditions before deposition in order to fully oxidize any impurities present in the substrate. During the sputter deposition of Mg, the base pressure was about 7.0 × 10⁻⁷ mbar, and argon pressure was 2.7 × 10⁻³ mbar. The DC power used was 80 W and the distance between the center point of the substrate holder and the Mg source (diameter of about 5 cm) was about 20 cm. Conventional thin films samples were deposited at an angle of θ = 0° and nanorods were deposited using GLAD method at a deposition angle of θ = 84° as (measured from the substrate surface normal). In addition, both types of deposits were accompanied with an azimuthal substrate rotation around the central substrate surface normal axis with a speed of 1 rpm. Deposition rates were measured to be 10.8 Ao/sec and 2.8 Ao/sec for normal incidence and GLAD experiments, respectively. Silicon wafer pieces have been used as substrates for the samples to be analyzed for SEM and XRD. For TEM analysis, nanorods deposited onto alumina substrates were scrapped off into isopropyl alcohol and sonicated. Later this suspension was placed on to holey carbon grids.

Thin films and nanostructured samples of Mg were analyzed using SEM (FESEM-7000F, JEOL) for the morphological investigation and XRD system (Bruker D8 discover) for the crystal orientation (texture) investigation. TEM analysis was performed by a JEOL JEM 2100F. Film thicknesses were measured using the cross sectional SEM images.

Oxidation experiments of the Mg nanorods and Mg thin films were performed by using TGA (METLER TOLEDO 815e) at temperatures ranging 25–550 °C in dry air. A heating rate of 3 °C/min was used for the experiments. The weight change was recorded as a function of time (for isothermal TGA measurements) or temperature (for variable temperature measurements). Isothermal TGA experiments were carried out at constant temperatures of 150, 250, 300 and 350 °C. The final mass values presented in this work were obtained by subtracting the bare alumina weight data from that of coated alumina samples of identical dimensions.

As it will be discussed in the following section, during some of the TGA experiments, we observed a weigh loss for our
nanorod samples. Mg has a high vapor pressure and may show evaporation around 400 °C [23,52]. The origin of weight loss although not entirely clear is believed to be due to either the sublimation of Mg (due to magnesium’s high vapor pressure at low temperatures) or the evaporation of water vapor adsorbed onto the high surface area of the nanorod samples. In order to investigate this observation, we utilized a new quartz crystal microbalance (QCM) system that enabled us to measure possible weight changes of the Mg nanorod coatings under vacuum (i.e. free of water vapor on the surface of nanorods) conditions. QCM crystals are typically used in conventional thin film thickness monitoring units and are sensitive to very small changes in the mass of a coating as small as in the scale of nanograms. To perform the mass change detection vs. temperature experiments using QCM crystals as a substrate for our nanorod and thin film coatings, we have developed a custom made chamber that can operate at temperatures ranging from room temperature up to 500 °C as well as at pressures from vacuum (10⁻³ bar) up to 50 bar. The chamber has a dual QCM sample holder configuration. One holder is reserved for a bare QCM crystal used for the control sample while a 2nd holder is for the actual sample measurements. We deposited Mg nanorods onto QCM crystals using GLAD as described above. Before Mg deposition, the oscillation frequency of the bare QCM crystal was measured at atmospheric pressure and at a pressure of 10⁻³ bar while at room temperature in order to calculate the pressure effect on the crystal. The total Mg deposition amount on the crystal was calculated comparing the frequency values before and after deposition. The sample to be tested was placed inside the chamber and evacuated for 2 days at 10⁻³ bar of pressure. This enabled us to remove the water present on the sample surface and inside the chamber. Once the frequency stabilization was achieved in both QCM crystal oscillations, the temperature was increased from room temperature to 250 °C in 3 h at a steady rate. Then the system was cooled down to room temperature. The initial and final mass values before and after QCM tests were compared under the same conditions in order to calculate the weight percentage changes in the mass of Mg nanorod coatings.

3. Results and discussion

Both thin films and nanorod-structured samples of Mg were grown with various thicknesses in order to understand their morphological and crystal orientation evolution. Fig. 1 shows the top view and cross sectional SEM images of some of the Mg thin film samples deposited at normal incidence. Mg thin films quickly form a rough morphology during the early deposition stages (Fig. 1a). As the film gets thicker (Fig. 1b), a highly textured microstructure incorporating a cheese like fine porosity was found to develop. This porosity might be due to the limited mobility of the Mg atoms during the sputter deposition process, while the substrate temperatures are typically low (i.e. lower than about 50–100 °C), which is correlated to lower adatom mobility values [45] Sputtered thin films also show a columnar microstructure as can be seen

![Fig. 1](image_url)

Fig. 1 – Top view (top row) and cross section view (bottom row) scanning electron microscopy (SEM) images of Mg thin films of thickness about a) 250 nm and b) 1700 nm that were deposited at normal incidence.
from the cross sectional SEM images in Fig. 1 (bottom row). In addition, the XRD analysis presented in Fig. 2a for the sputter-deposited Mg thin films show a pattern that promotes a texture formation in the (002) direction which is independent of the film thickness value.

On the other hand, GLAD Mg nanorods show a different morphology than that of the Mg thin films. Unlike continuous Mg films, as can be seen in Figs. 4 and 5, the nanorods form in the shape of isolated columnar arrays with an average diameter of about 120 nm, and separated by gaps in the range of a few tens of nanometers. In addition, the XRD patterns of the GLAD nanorods differed significantly from that of the thin films deposited at normal incidence (Fig. 2b). Contrary to strongly (002) oriented Mg thin films, the crystallographic analysis of the nanorods presents peaks corresponding to the crystalline directions of (101), (102) and (103) in addition to the (002) peaks. These peaks other than (002) become more intense when the nanorods get longer, while the change in (002) orientation is minimal for thicknesses larger than 900 nm. The formation of crystal orientations other than the preferential (002) texture in sputtered GLAD Mg nanorods is believed to be due the shadowing effect and limited adatom mobility of these crystal orientations [46,47]. During the initial stages of GLAD, Mg atoms can form randomly oriented islands. Some of these islands have higher vertical growth rates due to the lower adatom mobility on their crystal planes (e.g. due to a more atomically rough crystal plane), where others have faster lateral growth rate due to higher adatom mobilities (e.g. on a atomically smooth closed packed crystal plane like for example on Mg (002)). Due to shadowing effect, obliquely incident atoms preferentially deposit on higher islands of lower adatom mobility and higher vertical growth rates, leading to nanorods with energetically un-preferential crystal orientations. However, in our case it seems that roughness of the GLAD Mg samples, and therefore the shadowing effect couldn’t develop strong enough at thicknesses smaller than 900 nm, leading to still a dominant (002) texture. As the nanorods get longer and surface gets rougher, shadowing effect can become more effective to promote the growth of nanorods with other crystalline orientations.

TEM analysis on the GLAD Mg nanorods revealed a single crystal structure (Fig. 3). In Fig. 3, single set of spots in the selective area diffraction (SAD) pattern and high resolution TEM image of a single nanorod both show that individual nanorods of Mg have a single crystal formation. SAD pattern corresponds to the hexagonal crystal structure on the sidewall where the diffraction pattern was taken. Single crystal nature of the individual Mg nanorods is similar to the previously reported results on metallic nanorods deposited by GLAD [46,48–50]. Single crystal structure is an important property in explaining the oxidation behavior of the Mg nanorods.

Variable temperature TGA result of a conventional Mg thin film is shown in Fig. 6. TGA data was recorded for Mg thin films with a thickness of about 1100 nm. Actual mass values were normalized to the initial value of the Mg thin film. These films were found to continue gain weight due to the oxidation for temperatures of up to 550 °C, with the exception of a small plateau between 250 and 350 °C. Total change in the weight was as high as about 85 wt% (weight percent) indicating an oxygen rich stoichiometry compared to the crystalline MgO. The rate of weight gain slightly slowed down as the temperature increased from room temperature. This parabolic behavior takes place due to the slower oxidation rate of Mg, which originates from the diffusion barrier properties of the oxide layer [23,52]. As the oxide layer gets thicker, it impedes the oxygen from passing through and reaching the metallic magnesium underneath the oxide layer [22,51]. The plateau observed between temperatures of about 250–350 °C may also be ascribed to the competing reactions of already slowed down oxidation rate (i.e. smaller weight gain) and evaporation of water vapor trapped in the small pores of Mg film (i.e. weight loss).

The weight change profile of Mg nanorods (1050 nm in height and morphology similar to the one shown in Fig. 5b), for variable temperature TGA has a quite different behavior than that of the Mg films. In Fig. 6 it is observed that the weight of the Mg nanorods decreased by about 2 wt% as the temperature increased from 25 to 150 °C. This slight weight loss is believed to be the result of the evaporation of water vapor adsorbed on the surface of the magnesium nanorods. The possibility of sublimation of magnesium has been

![Fig. 2 – X-ray diffraction (XRD) profiles of (a) Mg thin films deposited by magnetron sputtering at normal incidence and (b) Mg nanorods deposited by glancing angle deposition (GLAD) show the evolution crystal orientation as a film gets thicker. Line profiles have been off-set in the y-axis for clarity.](image-url)
discarded after our QCM tests performed at temperatures from 25 to 250 °C (described above) where no measurable mass loss has been observed under water vapor free conditions. Fig. 7, showed that the mass of the nanorods remained relatively constant between temperatures from 150 to 350 °C. Above 350 °C, magnesium nanorods begin to gain weight with increasing temperature up to 550 °C. This weight gain of about 6 wt%, corresponds to an oxidation process which is much smaller than that of conventional Mg film (~85 wt%). We also have recorded a weight gain due to the structural oxidation of the Mg nanorod samples of about 12 wt% during the QCM measurements. Although the QCM experiments were performed under vacuum (10⁻³ bar) we believe that this level of vacuum was not high enough to avoid oxidation.

Reduced oxidation values of Mg nanorods compared to conventional thin films are believed to mainly originate from their single crystal property. In a single crystal structure, there are no grain boundaries present and therefore the diffusion rate of oxygen is significantly reduced. In addition, possible crystal orientation on the sidewalls of the nanorods might present a less reactive plane for oxygen penetration and oxide formation. For example, Mg basal (001) plane is about 25% more reactive than (100) prismatic plane [23] in oxidation. On the other hand, some of the Mg nanorods have un-preferential crystal orientations (Fig. 2) with non-closed pack crystal planes, which could normally enhance diffusion of oxygen, yet it seems that single crystal property dominated the process leading to enhanced resistance to oxidation.

In addition, isothermal TGA analyses were carried out to examine weight changes of the Mg nanorods at constant temperatures of 150, 250, 300 and 350 °C. The TGA results for these temperatures are shown in Fig. 7 for up to 180 min. All the isothermal lines show a similar behavior. At the initial times there is a mass loss mainly due to the evaporation of water vapor followed by a slightly fluctuating behavior especially at temperatures higher than 150 °C. The fluctuation at later times can originate from the competition between the

Fig. 3 — Transmission electron microscopy (TEM) results of an individual GLAD Mg nanorod are shown: (a) TEM selective area diffraction (SAD) pattern showing an hcp crystal structure, (b) High resolution lattice imaging, and (c) TEM image.

Fig. 4 — Top view (a) and cross section view (b) SEM images of Mg nanorods by GLAD of thickness about 200 nm.
weight gain due to the low oxidation of nanorods and evaporation of trapped water vapor in the smaller gaps of the structures. However, the final weight gain after the initial release of the water vapor is still insignificant (max value being about 3 wt% at 300 °C). These results also show the reduced oxidation property of Mg nanorods produced by GLAD, which is consistent with the variable temperature TGA and QCM results discussed above.

Fig. 5 – Top view (top row) and cross section view (bottom row) SEM images of Mg nanorods by GLAD of thickness about a) 900 nm and b) 1050 nm.

Fig. 6 – Thermogravimetric analysis (TGA) results of magnesium thin film and magnesium nanorods are shown as a function of temperature. Actual mass values of the coatings were normalized to their initial values for comparison.

Fig. 7 – Isothermal TGA plots of magnesium nanorods at 150, 250, 300, and 350 °C show the change in dynamic weight of nanorods as a function of time. Actual mass values of the coatings were normalized to their initial values for comparison.
4. Conclusions

In this study, we report that Mg thin films showed significant oxidation with weight gains of as high as about 85 wt%, in temperature ranges from 25 to 550 °C. On the other hand, the oxidation of Mg nanorods grown by GLAD was minimal with a weight change of as little as 6 wt% in similar conditions. Our QCM studies also further confirmed the reduced oxidation of Mg nanorods. Because of their nanostructured large surface area morphology, one might normally expect an enhanced oxidation in nanorods of Mg. The unusual resistance of Mg nanorods to oxidation is believed to originate mainly from their single crystal nature where no grain boundaries for fast-diffusion of oxygen are present. In addition, possible crystal orientation on the sidewalls of the nanorods might present less reactive planes for oxygen penetration and oxide formation. These results suggest that GLAD Mg nanorod arrays with or without catalyst additives, or their alloys can be attractive candidates especially for hydrogen storage applications where reduced oxidation property is highly desirable.

References


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