

**First round of review**

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Report of Referee A -- LU16933/Baldi

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The work presents H<sub>2</sub> pressure versus optical transmission isotherms of Mg-Pd binary alloys across a range of compositions via combinatorial analysis. Analysis of these data are used to draw conclusions regarding the effect of Pd on the plateau pressuring and plateau width within the miscibility gap of the binary system. The conclusions are somewhat inconclusive, but the analysis and interpretation does make a significant contribution to the field of hydrogen phase behavior in dimensionally constrained systems. I recommend publication in PRL with minor revision based on the points below. I did not review the supplemental material.

**1. The authors do not indicate how  $x$  (the composition) was measured. This should be included in the manuscript since it is an important experimental detail. I suspect  $x$  was derived from either the sputter gun current or from the geometry of the gun-target system. If this the case, then  $x$  really was not measured directly but inferred and this should be stated explicitly.**

AUTHOR REPLY

The composition of the thin film alloys are derived from a calibration of the sputtering rates of pure Mg and Pd targets. This calibration procedure can be vetted by measuring the local composition of the gradient films using Rutherford backscattering spectrometry on films grown in the same deposition run on amorphous carbon substrates and it is known to provide reliable composition values. To explain this aspect we have added the following sentence in the main text:

*“The thickness of the Mg<sub>1-x</sub>Pd<sub>x</sub> gradient alloy layer is measured with profilometry, while its composition is derived from the calibrated sputtering rates of pure Mg and Pd targets. Such calibration procedure has been validated using Rutherford backscattering spectrometry and it is known to provide reliable composition values [12].”*

**2. The statement is made that the thickness varies slightly with composition. This is not true; the variation is approximately 60%. The authors should discuss any implications of the thickness vs.  $x$  dependence on the measurements.**

AUTHOR REPLY

We have removed the word “slightly” from the mentioned sentence. The influence of the thickness variation across the compositional gradient is implicitly mentioned in our discussion of Figure 2a, but we have made it more explicit by changing the following text

*“From Fig. 2a we also observe that the width of the pressure plateau depends on the Pd concentration in the Mg-Pd alloy. The decrease in plateau width with increasing Pd content is however only partially due to the variation in thickness across the Mg-Pd alloy sample. The solid line in Fig. 2a shows the plateau width expected under the assumption that Pd does not affect the hydrogen storage capacity of the Mg-Pd alloy and all Mg atoms hydrogenate to form MgH<sub>2</sub>.”*

into

*“From Fig. 2a we also observe that the width of the pressure plateau depends on the Pd concentration in the Mg-Pd alloy. As expected from the fact that the film thickness decreases with palladium composition, the plateau width also decreases with increasing palladium content. Such decrease in plateau width, however, is only partially due to the variation in thickness across the Mg-Pd alloy sample. The solid line in Fig. 2a, in fact, shows the plateau width expected under the assumption that Pd does not affect the hydrogen storage capacity of the Mg-Pd alloy and all Mg atoms hydrogenate to form MgH<sub>2</sub>.”*

**3. The authors indicate the films have a (002) preferred orientation and that the “degree of crystallinity” decreases with x. The authors should state what degree of crystallinity means exactly. Presumably it refers to peak broadening with x (I think this is stated later in the manuscript).**

AUTHOR REPLY

By “degree of crystallinity” we indeed mean that the 002 peak, as measured with x-ray diffraction, becomes broader and less intense with higher Pd concentrations, as shown in section 3 of the supplemental materials. Following the reviewer’s advice we have changed the following sentence:

*“Thin films of Mg-Pd alloys have a 002-oriented crystalline structure with a degree of crystallinity that decreases with higher Pd concentrations and an average lattice parameter roughly corresponding to a Vegard mixture [15] (see also SM3).”*

into

*“Thin films of Mg-Pd alloys have a 002-oriented crystalline structure with x-ray diffraction peaks becoming broader and less intense with higher Pd concentrations and an average lattice parameter roughly corresponding to a Vegard mixture [15] (see SM3).”*

**4. The authors state that hydrogen absorption and associated large  $\Delta V/V$  “must” lead to porosity. Plan view TEM is used as proof of porosity. However, the authors do not indicate which features in the TEM micrographs are the porosity (or voids). I note that the presence of voids or bubbles is demonstrated with TEM by performing both over focus and under focus; this evidently was not performed. It is therefore unclear how the TEM images demonstrate the existence of voids/porosity.**

AUTHOR REPLY

During TEM analysis the presence of voids is routinely determined using Fresnel fringes that occur around their edges during underfocus and overfocus of the objective lens. This occurs due to interference of the scattered electron wave from the edges of the void and the non-scattered electron wave coming from the gun. Also in the present study, we confirmed the presence of voids by performing such underfocus and overfocus analysis. We did not however record the associated underfocused and overfocused images and we cannot therefore add them to the manuscript or the supplemental material. To make this aspect more explicit we have added the following underlined sentence:

*“These TEM images reveal drastic microstructural changes in the metal films upon hydrogen cycling, with coarsening of the grains and the formation of a large number of voids, as confirmed by the appearance of Fresnel fringes while imaging at over and under focus (not shown here).”*

Related to the appearance of structural defect upon cycling, we have added the following sentence before the concluding paragraph:

*“Finally, a similar asymmetric behavior between hydrogen loading and unloading has already been observed for palladium nanoparticles and interpreted as due to the formation of defects during hydrogen desorption [29].”*

**5. The first two sentences of the first full paragraph on page four attempt to explain the analysis of the results. The first sentence states the alloying effect can be fully accounted for by the volume contraction. The second sentence states that alloys partially accounts for the high hydrogen pressures. I think a bit more explanation is necessary here.**

AUTHOR REPLY

Indeed, our original wording of the reasoning in its present form is confusing and we have simply removed the second sentence, which was unclear and redundant.

**6. In the second to last paragraph second sentence of the manuscript the authors state that in light of their experimental evidence hydrogen absorption and desorption cannot be treated solely within an elastically constrained model. They should state exactly which experimental evidence they refer to in making this statement.**

AUTHOR REPLY

We have followed the reviewer's advice and changed the sentence

*"In light of the experimental evidence presented here, however, it is clear that [...]."*

to

*"In light of the composition-independent unloading isotherms shown in Fig. 3a, however, it is clear that [...]."*

**7. In the last paragraph of the manuscript the authors bring in a Pd-capped Mg reference and state that their binary results cannot explain the former. They state this is demonstrated by the current work, but why this is true is not made clear. A bit more explanation is required I think.**

AUTHOR REPLY

We have again followed the reviewer's advice and changed the sentence

*"Our elastic clamping model, however, while quantitatively describing the observed increase in loading pressures, fails to take into account the large structural rearrangements and plastic deformations occurring upon hydrogen absorption in Mg-rich films. Future efforts [...]"*

to

*"Our elastic clamping model, however, while quantitatively describing the observed increase in loading pressures, fails to explain why unloading isotherms do not show any composition dependence. Accurate modeling of the hydrogenation process of magnesium-based nanomaterials will have to include the large structural rearrangements and plastic deformations occurring upon hydrogen uptake. Furthermore, future efforts [...]"*

**8. The Figure 3 caption incorrectly states the as-deposited TEM image is before the 10th cycle—it is actually before the 1st cycle.**

AUTHOR REPLY

We believe the reviewer simply misread the caption, which currently correctly reads

*"b) Planar view TEM images of a Mg<sub>0.9</sub>Pd<sub>0.1</sub> film (left) before and (right) after 10 hydrogenation and dehydrogenation cycles."*

**9. Finally, I wonder if the authors thought about performing a FIB lift out of the samples on glass as opposed to growing special films on a nitrate window for TEM. I think this would have been a**

**better route; it would have allowed a better picture of the microstructure in cross section (vs the plan view shown) and even though the grain size is small, it may have been possible to image dislocations after several hydrogen cycles. However, given the small grain size SAD probably would not be possible. Still it would have been worth the effort.**

AUTHOR REPLY

This is a great suggestion and we did think about performing a cross-sectional TEM analysis on a FIB lamella, as we have done, for example, for Mg/Ti multilayer films in [Baldi et al., Physical Review B 81, 224203 \(2010\)](#). Given the intensive sample preparation involved in the preparation of FIB lamellae and the fact that the composition in our films is homogeneous across their thickness, however, we found it sufficient for the purpose of the present study to perform planar view TEM imaging.

**Second round of review**

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**Report of Referee B -- LU16933/Baldi**

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**The work presents a new explanation on the different reactions and effects of Mg-Pd film vs bulk Mg towards H<sub>2</sub> absorption at high pressures. I believe the authors reasonably addressed the important questions raised by the reviewers and therefore recommend publication in PRL.**

**AUTHOR REPLY**

We thank the reviewer for her/his assessment and for recommending publication.

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Report of Referee C -- LU16933/Baldi

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The manuscript "Elastic versus alloying effects in Mg-based hydride films" by A. Baldi et al. addresses the question whether the high hydrogen absorption pressure in Pd capped Mg layers is caused by clamping or by alloying. Therefore, the authors investigated hydrogen adsorption/desorption isotherms of Pd doped thin Mg films, separating alloying effects from clamping. The paper is scientifically sound and the experiments seem to be carried out carefully with great accuracy.

The authors conclude that alloying Pd with Mg does indeed lead to an increase of loading pressure. However, this alloying effect cannot explain the strong increase of loading pressure in Pd capped Mg films. The authors show that a clamping model reasonably describes hydrogen loading of the Pd-capped thin films but fails to explain the unloading curves. The authors correctly mention that an elastic model is inaccurate as it leaves out plastic deformations. In their concluding remarks they say that "accurate modeling ... will have to include the large structural rearrangements and plastic deformations..." In this respect, the paper keeps the promise to "resolve the controversy" between alloying and clamping, by stating neither effect is responsible for the observed increase of equilibrium hydrogen pressures in Pd capped Mg films vs. bulk Mg.

This is a bit unsatisfactory as the role of plastic deformation is highlighted, but not further explained, this should be the topic for further investigation in the future. Therefore I understand the 1<sup>st</sup> reviewer saying "The conclusions are somewhat inconclusive" I also agree with his conclusion "the analysis and interpretation does make a significant contribution to the field of hydrogen phase behavior in dimensionally constrained systems."

I think the paper should be accepted for publication in PRL after the authors elaborate more on the effect of plastic deformation. Without going in details and numbers, the authors should outline how a model would take plastic deformation into account. How do the plastic deformations influence the hydrogen uptake. How are plastic deformation in the case of thin Mg films quantified? What values would be realistic? What relation to the pressure would you expect? Do you expect saturation effects? Would it be possible to tailor the hydrogen uptake (and release) of hydrogen by a prior deformation step?

AUTHOR REPLY

The referee asks to elaborate *qualitatively* on the effect of plastic deformations on the hydrogenation properties of Mg-based thin films. This is an excellent remark and it is the reason we had already added the section "SM6. Elastic energy versus plastic deformation energy" in the Supplementary Material.

This section, which was perhaps not properly "advertised" in the main text, effectively already answers all the referee's comments and perhaps goes beyond her/his recommendations, by providing a *quantitative* analysis of the plastic energy dissipated upon hydrogen absorption and desorption.

In view of length restrictions, we prefer to keep this discussion in the supplementary material (which we have slightly edited for clarity), but we have highlighted it in the main text by adding the following underlined sentence:

"Accurate modeling of the hydrogenation process of magnesium-based nanomaterials will have to include the large structural rearrangements and plastic deformations occurring upon hydrogen uptake (see [31] and the discussion in SM6)."