Reply to ‘Comments on “Evidence of the hydrogen release mechanism in bulk MgH₂”’

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In a comment on our Article “Evidence of the hydrogen release mechanism in bulk MgH₂”, Surrey et al. assert that the MgH₂ sample we studied was not MgH₂ at any time but rather MgO; and that the transformation we observed was the formation of Kirkendall voids due to the outward diffusion of Mg. We address these issues in this reply.

The comment by Surrey et al.¹ on our recently published study² contains two main assertions:

1. The MgH₂ sample we studied was not MgH₂ at any time but rather MgO.
2. The transformation we observed was the formation of Kirkendall voids due to the outward diffusion of Mg.

These are dealt with below.

The presence of MgH₂
It is possible that MgO [001] could have a good fit to the pattern compared with the MgH₂ [101] zone axis. However, we are confident the diffraction pattern is from MgH₂.

Firstly, MgO is most likely to exist in a nanocrystalline form on the outer surface of the bulk specimen under atmospheric exposure and hence, ring patterns would have been found in the SAD instead of diffraction spots (See for example Figure 2 of the comments by Surrey et al.)¹.

Furthermore the detailed crystallography of our sample can be found from the supporting Synchrotron XRD data which is discussed in the supplementary section of our paper (as Figure S3)². This confirms that the as-prepared bulk sample contains mainly MgH₂ and a small amount of other phases including Mg, Mg₂Ni, Mg₂NiH₄ but not MgO. Refer to Fig. 1 below for a more detailed XRD peak profile and Rietveld refinement for a sample tested under 0.1 MPa in-air, at 26°C³.

Dehydrogenation of MgH₂ or diffusion of Mg and Kirkendall void formation
We are confident we observed dehydrogenation in our samples using ultra-high voltage transmission electron microscopy (UHV-TEM). Firstly we have provided two additional independent measurements of dehydrogenation occurring at a temperature in the vicinity of 400°C in the material we used. The first is based on synchrotron XRD as in Fig. S3 of our paper⁴ and the second on DSC as in Figure S5 of our paper². For comparison, literature reported results for hydrogen desorption of MgH₂ are in the range of 320–450°C dependent on the presence of various catalysts (e.g. NaNH₄⁵, Fe⁶, FeCl₃⁶ or graphite⁷, respectively) and the heating rate. In the UHV-TEM the temperature range of the transformation we observed was between 400–455°C, consistent within reason for the transformation of MgH₂ to Mg.

The question that then remains is what was the difference between the samples and observation techniques used by Surrey et al.¹ which made the MgH₂ so unstable and the dehydriding reaction so fast as to make observation difficult? The answer of course is that we studied large samples a few microns in size that were relatively free of deformation in UHV-TEM (1,000 kV), while Surrey et al.¹ studied small 100 nm samples that were produced by high-energy ball-milling in low voltage TEM (300 kV).

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The bulk samples we used were prepared by conventional casting and machining methods which contrast greatly with other severe deformation methods (e.g. ball milling). As a result, our sample could be handled under normal atmosphere without any significant oxidation as compared to materials processed by ball milling methods. In fact, several of our previous works have been carried out using this approach\textsuperscript{2,8,9}. Reference 16 provided by Surrey et al.\textsuperscript{1} relates to their interpretation of our data that the transformation we observe is the formation of voids. This interesting publication shows this is a mechanism that operates in Mg particles of size 15–20 nm over a time period of hours but that Mg particles >50 nm are stable. The transformation in our sample takes place in a period of 10–20 minutes and, as the length scale is a few microns, it would seem to make this mechanism unlikely.

Secondly, conventional TEM with an accelerating voltage of 200 kV–300 kV has disadvantages including inelastic incident beam interactions with the samples, and the sample dimensions (typically less than 100 nm in thickness) make surface effects more prominent\textsuperscript{10}, which becomes particularly important in small samples with a high specific surface area. In this aspect, UHV-TEM is more favorable for determining the mechanism of hydrogen release in real-time. A true comparison of our observations can only be made with similar experimental regimes, namely large samples (1–2 micrometers) and UHV-TEM conditions.

Summary

Surrey et al.\textsuperscript{1} have raised some interesting points. Their interpretation can be expected from experiments using nanocrystalline samples and conventional TEM at low voltages. This was in fact the main contribution of our paper, understanding the dehydriding mechanisms in large samples which was facilitated by \textit{in-situ} viewing using ultra-high voltage TEM. The dependence of dehydriding on sample size and observation conditions highlights the need for our publication. The dehydriding behavior of our material was further confirmed with independent Synchrotron XRD and DSC experiments.

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Additional Information

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