On the origin of the hydride precipitation-dissolution hysteresis in zirconium: Comments on Short Communication of G.A. McRae and C.E. Coleman published in Journal of Nuclear Materials 568 (2022) 153889

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Abstract

This is a comment paper on the work of McRae and Coleman recently published in Journal of Nuclear Materials 568 (2022) 153889, where the diffusion of H atoms in to and away from "hydride-stabilising clouds" upon thermal cycling was deemed the sole origin of the precipitation-dissolution hysteresis. Here I explain why the nature of the transformation itself would lead to a thermal hysteresis, and discuss the possible reasons why the model of McRae and Coleman does not align with experimental results.

In a recent publication by McRae and Coleman [1], the conventional interpretation for the hydride precipitation-dissolution hysteresis in zirconium by Puls [2] was challenged. The key point is that if the peak temperature for each thermal cycle is not high enough for the misfit strain-induced dislocations to annihilate, then the number of dislocations produced per cycle should decrease with number of cycles due to the memory effect [3], which would lead to variation of the energy associated with the hysteresis. The fact that this is not observed

experimentally indicates the plastic work is not the true origin of the hysteresis, and instead it may be attributed to the diffusion of hydrogen atoms in to (upon precipitation) and away from (upon dissolution) “hydride-stabilising clouds” around the hydrides.

While I find this argument constructive for improving the understanding of the hysteresis, I disagree with it. Firstly, it is not yet clear whether the misfit dislocations from prior cycles may only act as nucleation sites for hydride precipitation in subsequent cycles, and hence a comparable number of new dislocations could be generated upon hydride growth. Secondly, I am doubtful about whether the damage created by these dislocations is significant enough to induce failure of the material after a number of cycles (as suggested by McRae and Coleman [1]). Furthermore, this argument only focussed on the misfit strain and dislocations which are all by-products of the phase transformation, but how about the energy associated with the transformation itself?

There has been substantial ambiguity over the mechanism through which the HCP-structured α-Zr transform into FCC/FCT-structured δ/γ-hydride and vice versa, but the most widely accepted one to date is that proposed by Carpenter [4] (and later developed by Weatherly [5]) where the transformation takes place in a martensitic manner *via* the glide of $\frac{a}{3} < 1\bar{1}00 >$ partial dislocations on alternate $\{0001\}$ basal planes, leaving behind stacking faults thereby changing the stacking sequence of the atomic layers, illustrated in Figure 1 (from Ref. [6]).

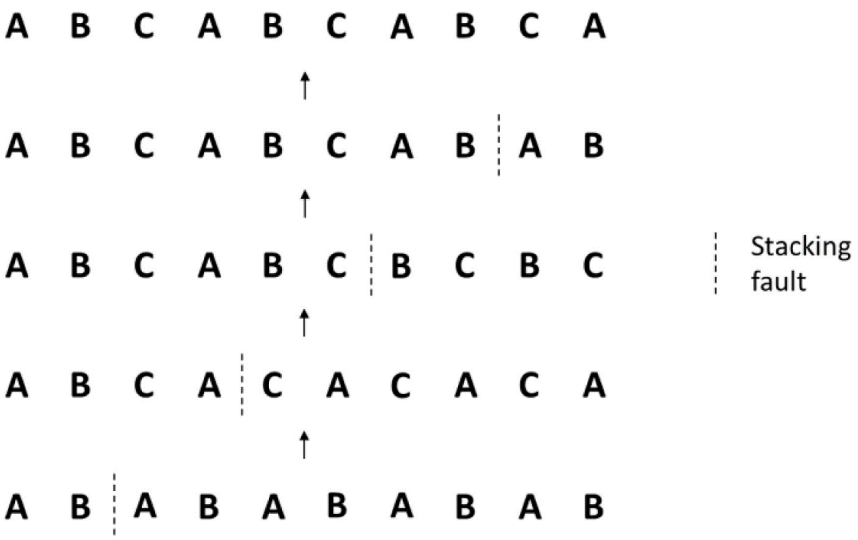


Figure 1 Schematic illustration of the HCP α-Zr to FCC δ-hydride phase transformation, adapted from Ref. [4]. Figure from Ref. [6].

If the Carpenter-Weatherly's explanation (mechanism) is true, then necessarily there is energy associated with the glide of the partial dislocations upon precipitation/dissolution (effectively movement of the hydride-matrix interface [7]) and the stacking faults, which could also contribute to the formation of the hysteresis at least partially. Note that these dislocations should be distinguished from the dislocations generated outside the hydride core to accommodate the misfit between the hydride and the matrix, though there might be intrinsic relations between these two types of defects, and upon hydride precipitation/dissolution they may interact and/or react with one another. Additionally, there might be a difference in the driver of the movement of these transformation dislocations upon precipitation and dissolution: their movement could be driven by a thermal stress and/or simply a mechanical stress exerted by the orderly arranged H atoms in the lattice upon precipitation, but upon dissolution the stress is more likely completely thermal.

It is therefore not logically correct to claim that if the hysteresis is not due to plastic work associated with the misfit dislocations, then it should be attributed to a diffusion process. Furthermore, the hypothesis made by McRae and Coleman that hydride precipitates in Zr are surrounded and stabilised by μm-scale clouds of hydrogen solute atoms disagrees with experimental results obtained *via* atom probe tomography (APT) reported in Ref. [8,9].

Based on a transmission electron microscopy (TEM) image in Ref. [10], McRae and Coleman [1] postulated that the thickness of the hydrogen clouds, if exist, should be over 1 μm, and within the ~1 μm region the local H content should be the same as that in the hydride. However, as shown in Figure 2 here (from Ref. [8]) which gives the concentration profile of deuterium across an interface between δ-deuteride and α-Zr in Zircaloy-4, the thickness of the transition layer (in terms of D content) is only up to 60 nm. It is worth noting that the position of the boundary of the δ-deuteride was confirmed by scanning transmission electron microscopy-high angular annular dark field (STEM-HAADF) imaging (see Figure 2 of Ref. [8]), and therefore the high D content region in the APT results is indeed the δ-deuteride rather than a "hydrogen/deuterium cloud" in the matrix. More examples of this can be found in Figure 13 of Ref. [9] for example, where two hydride (as opposed to deuteride)-matrix interfaces were studied and similar transition layer thicknesses were observed.

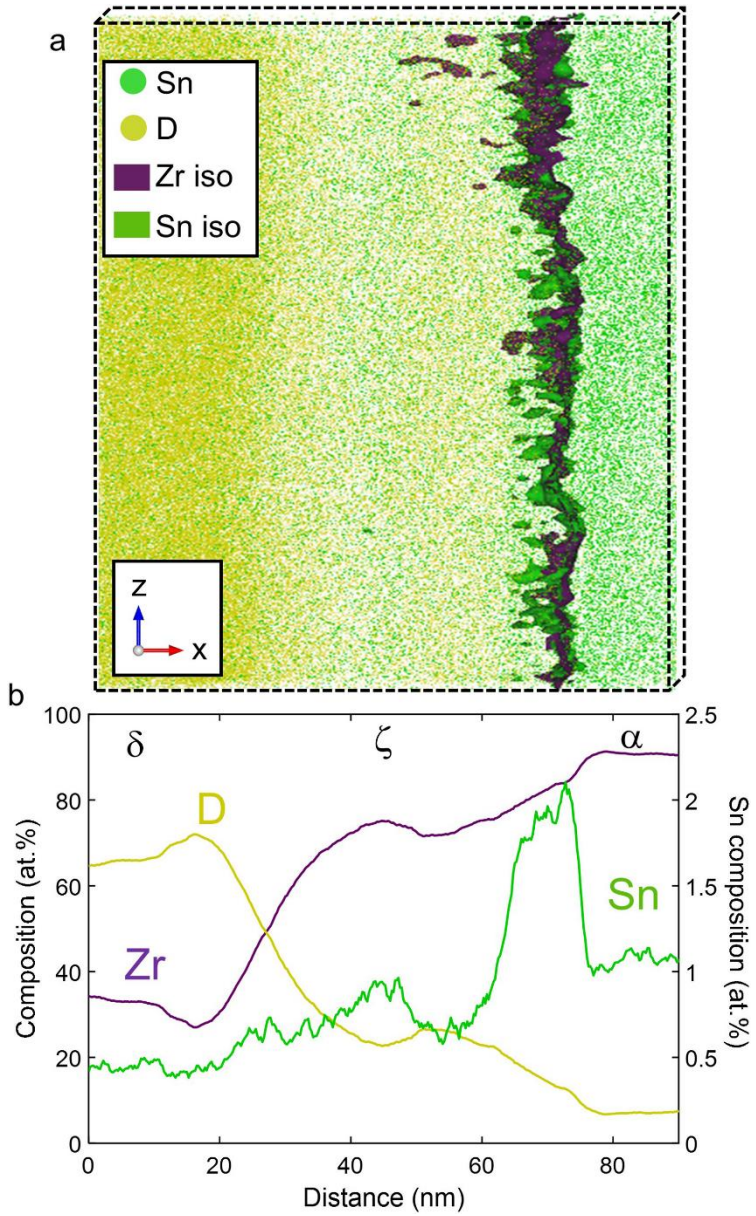


Figure 2 (a) APT reconstruction atom map cross-section of region of interest across deuteride/α-Zr interface. A Zr isocomposition surface (85 at.%) and a Sn isocomposition surface (1.9 at.%) have been used to highlight the interface. (b) 1D composition profile of Zr, D and Sn in the x-direction [8].

Note that this discrepancy between experimental results and the model of McRae and Coleman does not necessarily suggest that their theory is completely incorrect. Experimentally, hydrides in Zr were indeed found to be surrounded by stress fields and dislocations [11], which is deemed the origin of their auto-catalytic nucleation inside grains [12] and across grain boundaries [6]. It also makes sense that the diffusion of H atoms near hydrides is driven by the competition between concentration and stress gradients, and a similar model by McRae *et al.* based on the Nernst–Einstein equation published earlier [13]

can explain delayed hydride cracking in certain aspects, but what might be wrong given their postulation is not supported by experimental results?

While the McRae-Coleman model appreciated the existence of plasticity around hydrides to accommodate misfit, it simplified the problem by regarding the dislocated regions adjacent to hydrides as locally yielded areas and did not explicitly take into account the stress fields around individual dislocations. Plausibly, this simplification of the model would lead to: a) a more uniform stress distribution and therefore H atom distribution around the hydrides and b) an overestimate of stress and hence H content as no plastic relaxation was considered. This could contribute to the experiment-simulation discrepancy mentioned earlier. Consistently, recent work by Reali *et al.* showed that incorporating the effect of plastic relaxation on the local H profile around hydrides can substantially change the simulation results [14]. It is therefore essential for the model of McRae and Coleman to be further developed before it can accurately calculate the local H profile around hydrides and the energy associated with diffusion, thereby becoming useful for working out the true origin(s) of the precipitation-dissolution hysteresis.

To conclude, exploring the origin of the hydride precipitation-dissolution hysteresis in zirconium is a work in progress. Contributions from the energy required to move the transformation dislocations upon hydride precipitation and dissolution should be taken into account (as per other martensitic transformations [15]), along with energy associated with misfit strain and diffusion to quantify their relative significance experimentally and numerically. The model of McRae and Coleman does not describe accurately the H profile around hydrides likely due to ignorance of local plastic relaxation of the stress field, and further development is needed in order to properly predict local diffusion.

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