Preferential Hydrogen Diffusion from Zircaloy-2 Cladding to an Inner Zr Barrier

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GNF has expressed interest in modeling to predict diffusion, precipitation, and dissolution of hydrogen in Zircaloy-2 nuclear fuel cladding during dry storage. To assist in this effort, the following data were obtained from hydrogen-charged Zircaloy-2 samples. Samples were heated and then cooled from 400°C to 200°C over 1, 2, 4, and 15 days. An isothermal test at 440°C for 32 days was also performed. The samples were then analyzed using stereological techniques. No precipitate reorientation was observed and the hydride direction was circumferential as in the as-received samples. The denuded zone thickness grew and then shrank with increasing cooling time. A loss of hydrogen from 340 ppm in the as-received sample to 300 ppm in a 15-day sample was observed by hydrogen analysis.

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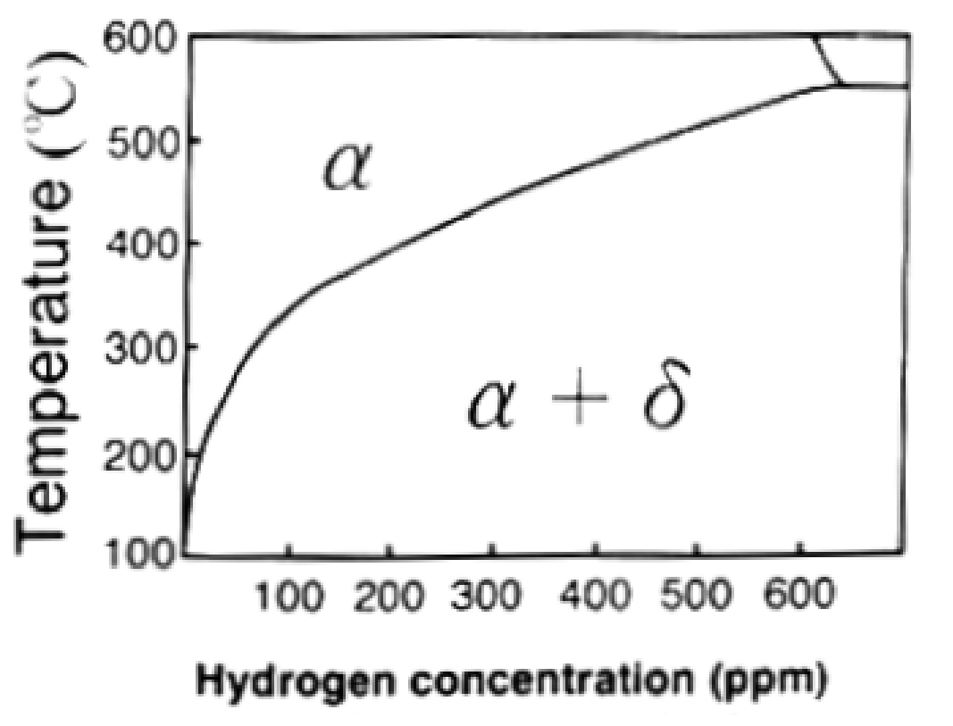
Project Background

- Zircaloy-2 is an alloy of 98.8% Zr and 1.2% Sn with trace Fe, Cr and Ni used for nuclear fuel cladding in boiling water reactors. The precipitation of hydrides in Zircaloy-2 can lead to embrittlement and eventual failure of the cladding.
- Due to the high temperatures reached in the reactor, the metal corrodes, and hydrogen is emitted. This hydrogen diffuses into the cladding and a zirconium hydride phase precipitates once the terminal solid solubility of hydrogen is reached.
- After spent nuclear fuel rods have been cooled in a spent fuel pool, they are moved into dry storage containers for more permanent disposal. During insertion into the dry storage casks, the temperature within the cask peaks at approximately 400°C, then cools to 350°C.
- Previous research (Courty, et al.) suggests that after reaching the solid solubility limit, hydrides prefer to precipitate on the edge of the cladding.
- If orientated radially, the hydrides can be detrimental to the structural integrity of the cladding edge.

Heat Treatments

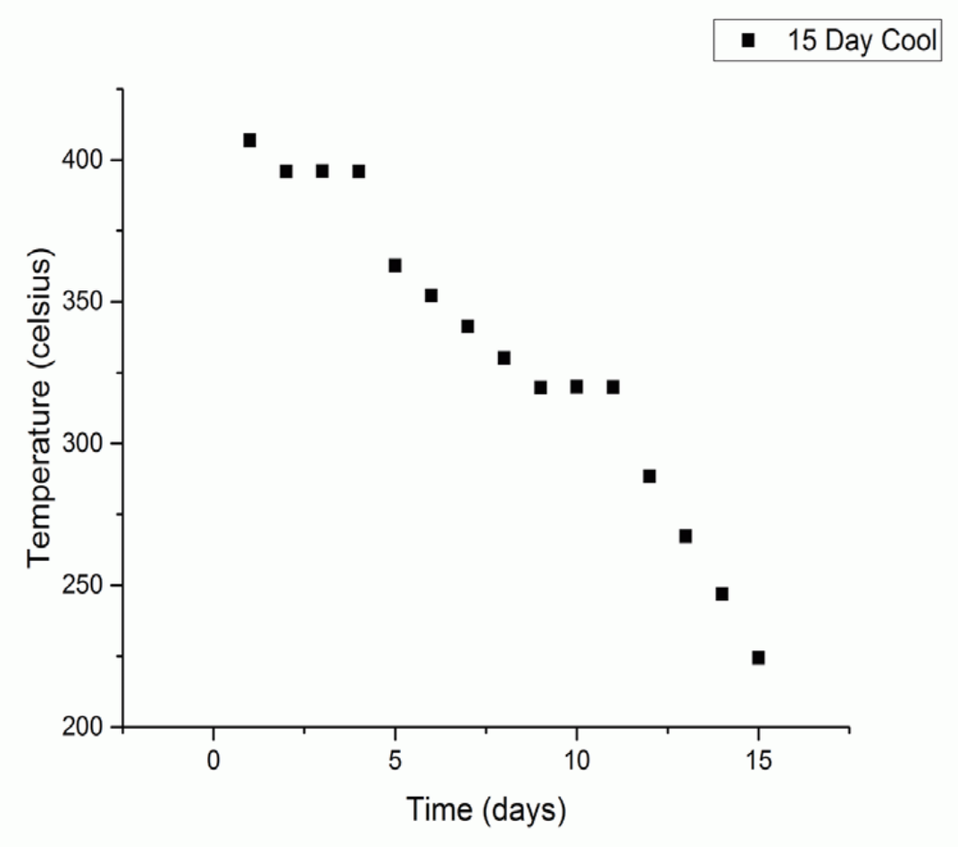


Phase diagram: hydrogen concentration versus temperature. Note terminal solid solubility line. (Sugisaki, et. al.)

Four samples of varying hydrogen content were received for testing.

Sealed ends of borosilicate ampoules. Samples are visible, measuring approximately ⅛ by 1/16 inch.

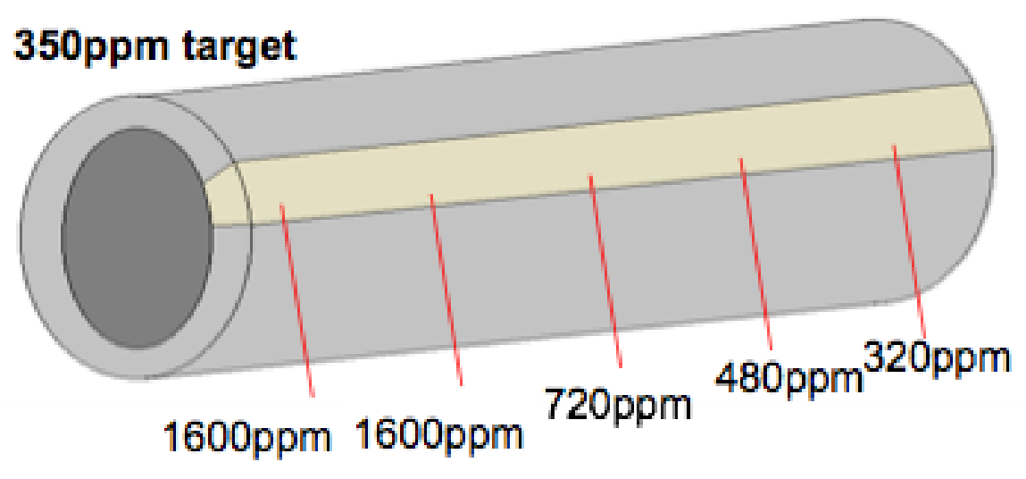
Samples were encapsulated in glass ampoules to allow for heat treatment in an inert environment.



Five total heat treatments were performed: a 32-day isothermal heat treatment at 440°C, and four step-wise slow cools from 400°C-200°C over a period of 15, 4, 2, and 1 days.

The isothermal heat treatment temperature was selected based on the terminal solid solubility temperature. Since samples with a range of hydrogen content were provided, a median temperature of 440°C was chosen.

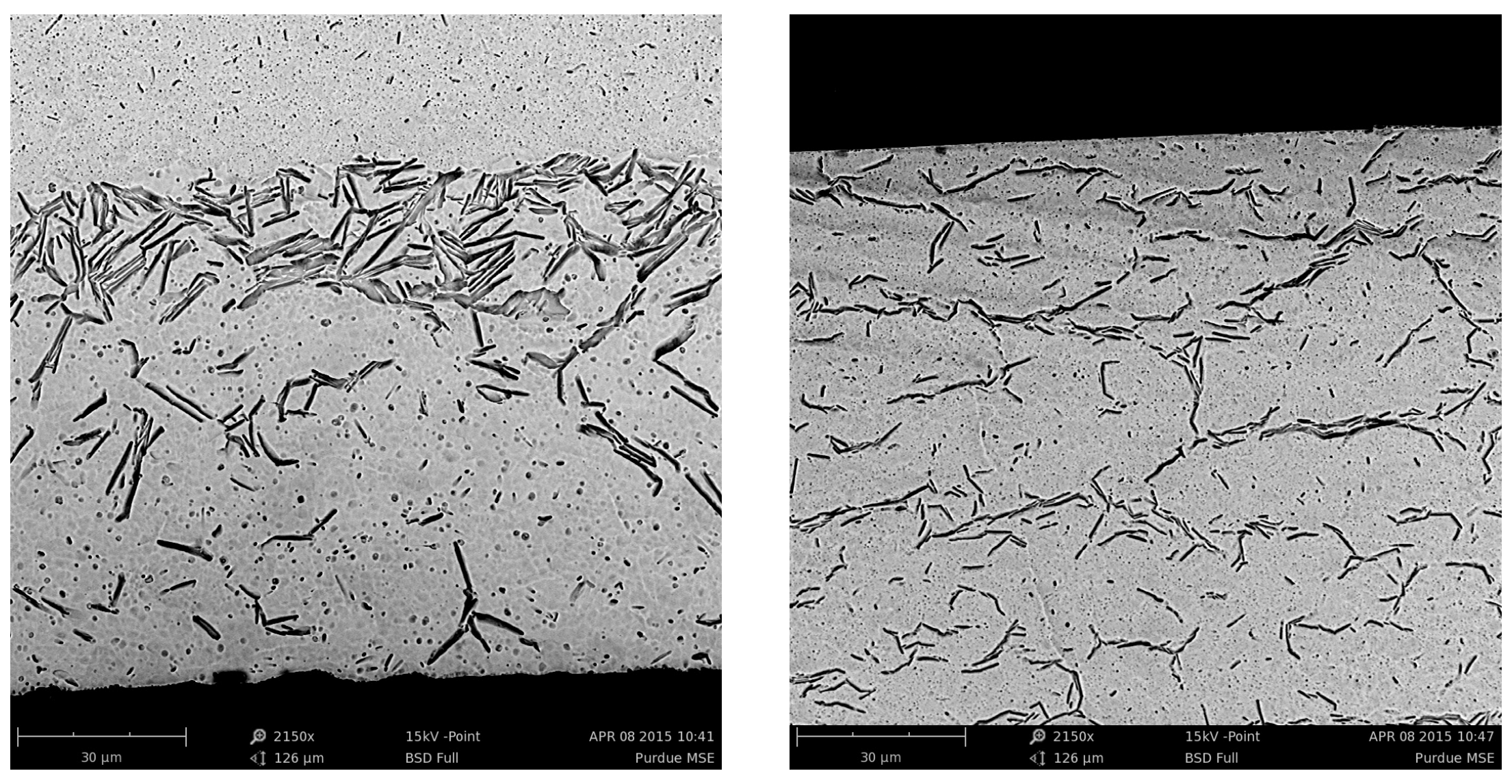
Tubular samples were sectioned and tested along the length of the tube for hydrogen content using testing. Variation in hydrogen content from one end to the other is due to a temperature gradient during loading.



Microscopy

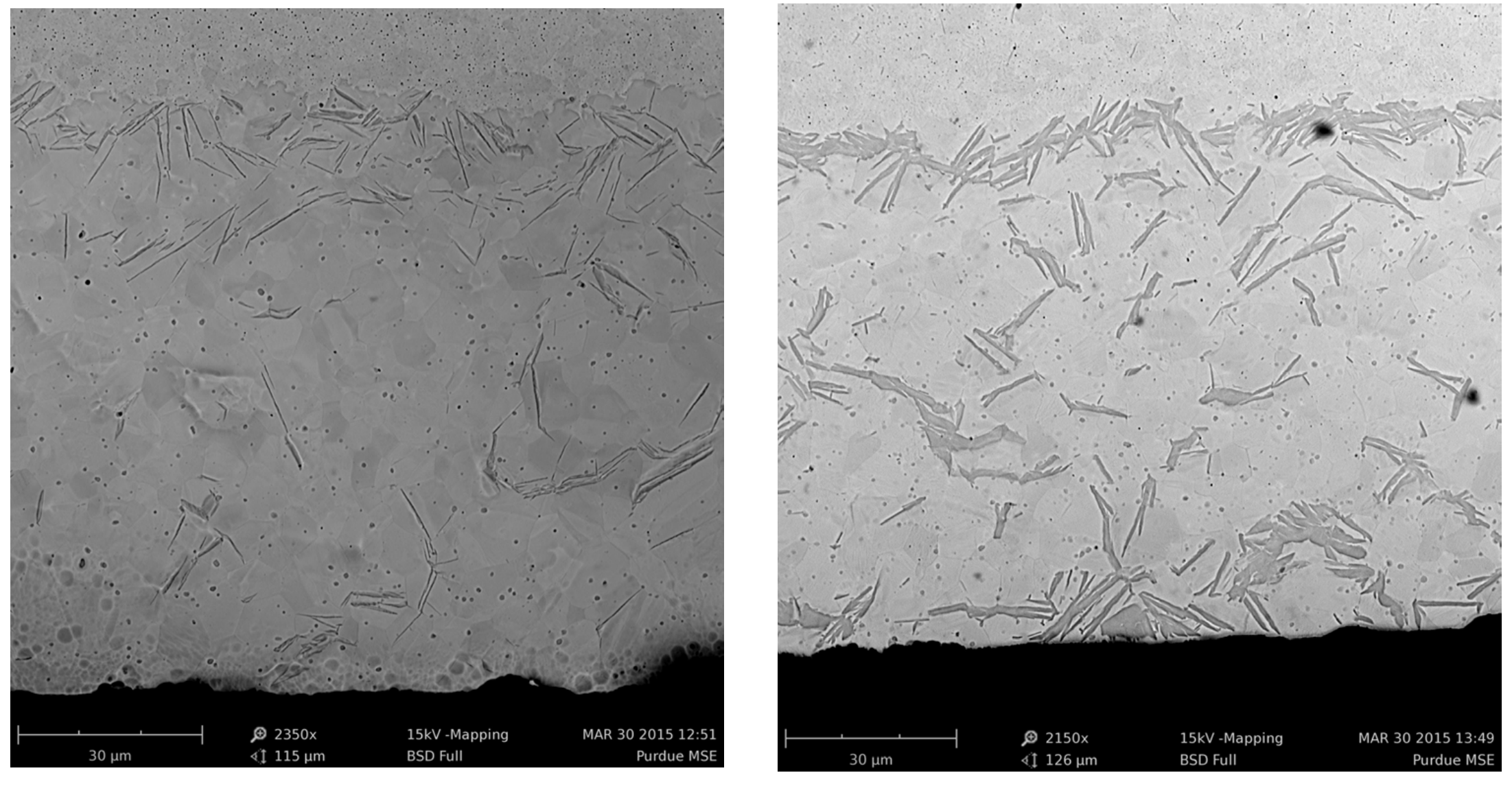
The Zircaloy-2 samples were analyzed with energy dispersive x-ray spectroscopy and confirmed to have the correct composition.

The samples were imaged using back scattered electron detection at maximum contrast and 15 kV to clearly show the hydrides. Hydrides were generally circumferentially oriented, with a thicker band of hydrides in the zirconium - Zircaloy-2 boundary.



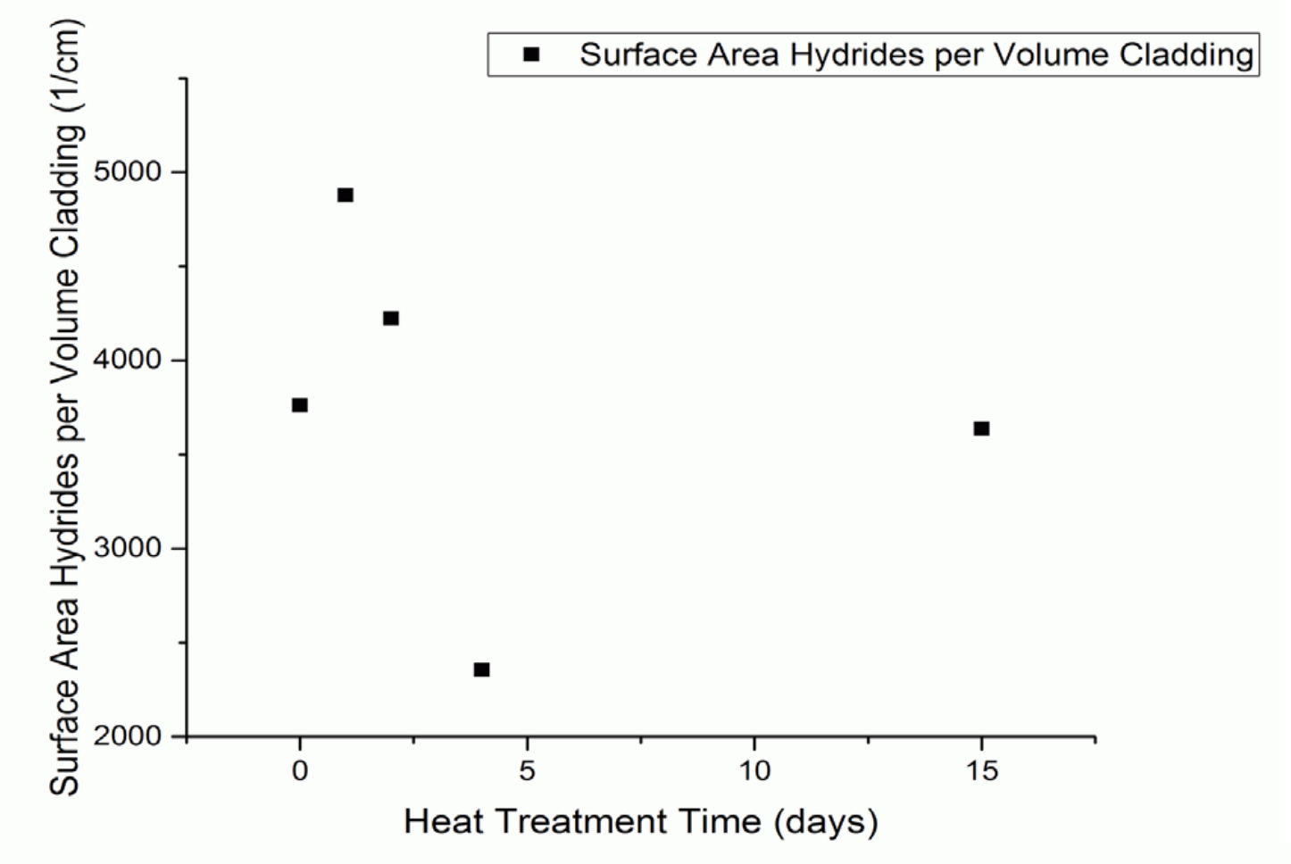
SEM micrographs of sample liner (left) and cladding (right).

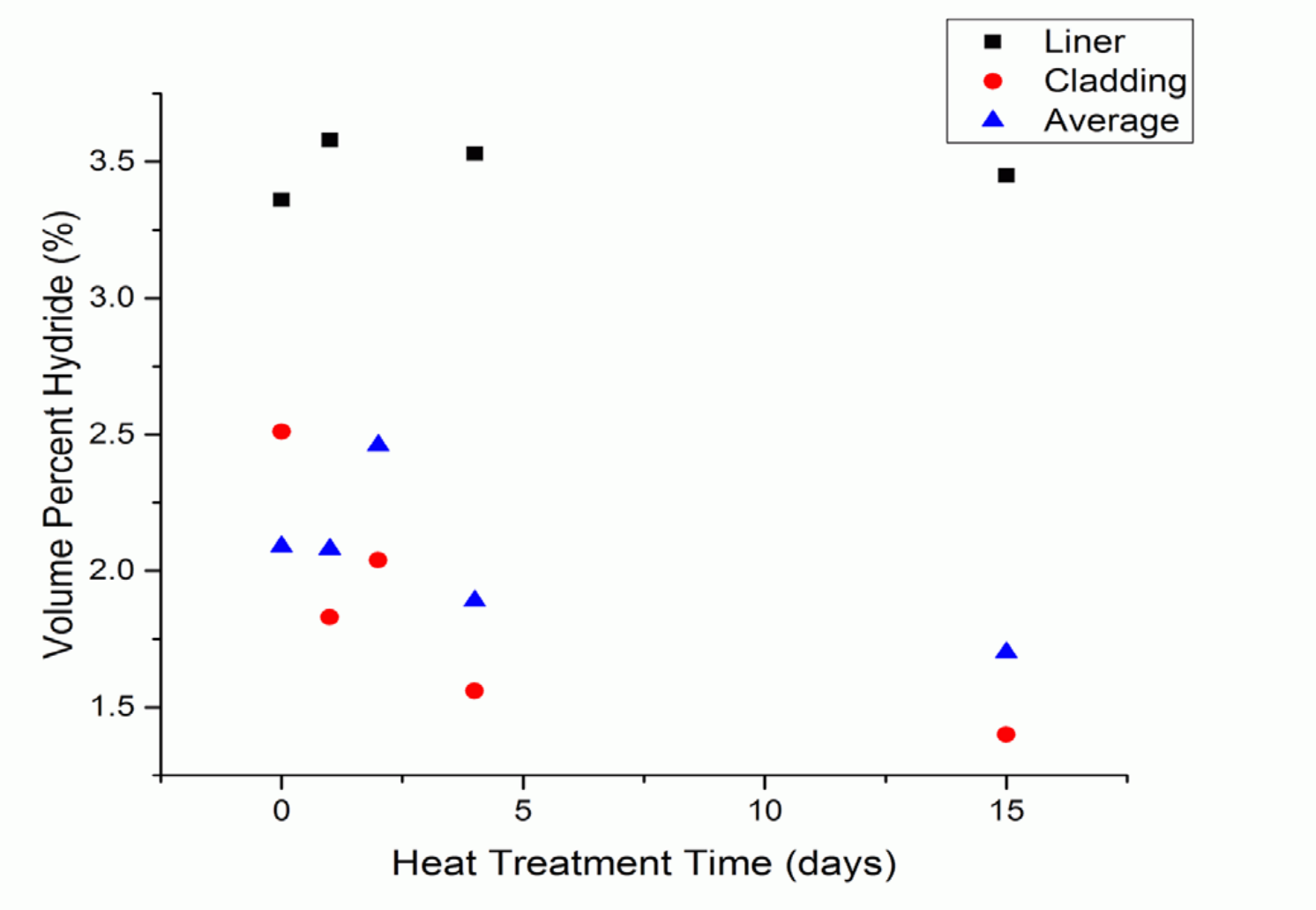
Stereology



SEM micrographs of hydrides in 320 ppm sample, as-received (left) and after a 16-day heat treatment (right).

Quantitative metallographic analysis was used in conjunction with stereology to calculate the volume fraction of delta hydrides and surface area of hydrides per unit volume of cladding. An area lacking in hydrides known as the denuded zone was also monitored.





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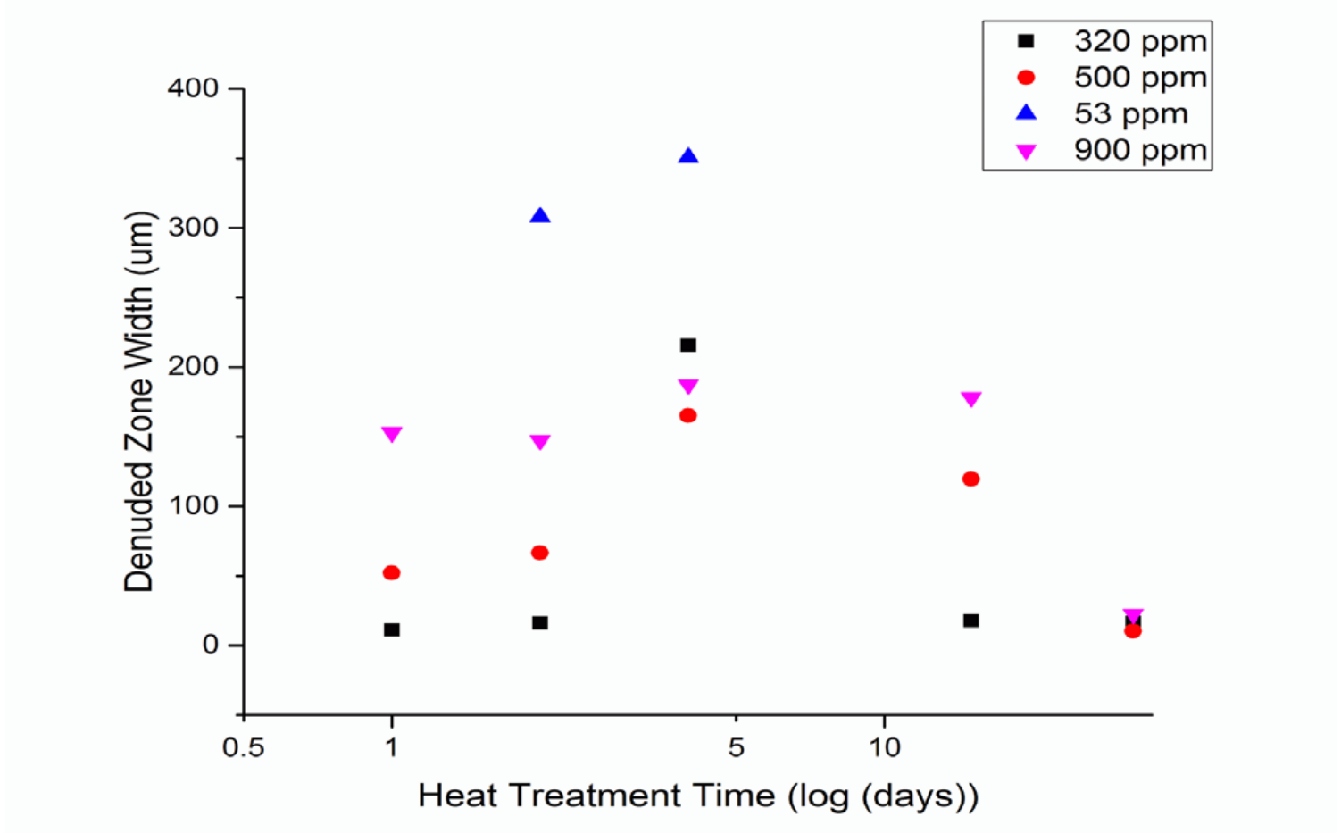
Results & Model

LECO testing of a sample before and after heat treatment showed loss of hydrogen. The sample went from 340 ppm in the as-received condition to 300 ppm after a 15-day heat treatment.



Denuded zone thickness versus heat treatment time for various concentrations.

Denuded zone thickness varies with length of heat treatment. The data does not have a linear fit. The data suggests that hydride precipitation is more favorable in the liner of the samples. Initially, the hydrides prefer to precipitate on the liner-cladding edge and the denuded zone grows. As the sample cools over time, the hydrides super saturate the liner-cladding interface. Precipitation becomes more preferred in the cladding and the denuded zone shrinks. This is supported by images of sample quenched from 400°C where an even distribution of hydrides was observed.

A model was created based on efforts by Courty, et al. to predict hydrogen loss in spent fuel cladding during dry storage. Results from LECO analysis were used to find an appropriate dissolution activation energy to match results for H loss.after a fifteen day controlled cool from 400°C to 200°C Comparisons were made between the developed model and quantitative metallographic analysis. Model results did not align with metallographic analysis.

Recommendations

- Further research is recommended on the effects of terminal solid solubility on temperature at concentrations above 80 ppm.
- Currently, hydrogen loss out of the sample is not considered in any other published research. Further tests need to be completed to monitor both hydride distribution and hydrogen leaving the sample after heat treatments of various lengths. Longer heat treatment times, more representative of long-term storage, should also be considered while monitoring the denuded zone thickness.
- Serial sectioning of samples, as well as further metallurgical analysis is also recommended to get a more accurate picture of the microstructure through the length of the sample tube.

References

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