ESTIMATION OF HYDROGEN IN ZIRCALOY USING MULTI FREQUENCY EDDY CURRENT.

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ABSTRACT

Hydrogen affects the electrical conductivity of zirconium alloys and electrical conductivity measurements can be used to estimate hydrogen in the metal. The sensitivity and methodology for estimating hydrogen from electrical conductivity in recrystallized Zircaloy-2 laboratory charged specimens using multi frequency eddy current measurements is presented. A model for compensating electrical conductivity changes from other factors including neutron fluence is presented with initial parameters derived from Zircaloy-2 coupons irradiated in the Advanced Test Reactor (ATR) with measurements performed at Idaho National Lab (INL).

1. Introduction

Hydrogen pickup in zirconium alloys from in-reactor corrosion can be a limiting factor in the useful lifetime of zirconium alloy components such as fuel cladding and BWR channel materials. Estimating hydrogen in these components using a nondestructive method has been a goal of the industry. Using electrical conductivity to estimate hydrogen has been considered by many developers [1, 2, 3] and correlations are applicable for limited test cases. Providing a true prediction of the hydrogen content in zirconium alloys from the derived electrical conductivity from eddy current measurements requires more than just establishing an electrical conductivity correlation to hydrogen for a given alloy, since many other factors also influence the electrical conductivity. Separate effects of irradiation damage and annealing of cold work in some heat treatments of alloys will also influence the measured conductivity. In addition, different concentrations of hydrogen through the thickness of a specimen can occur from temperature gradients in-service (e.g. hydride rim) and also from metal composition gradients (e.g. liner fuel). The electrical conductivity of these regions is different and must be accounted for in developing hydrogen correlations and measurement methods.

Application of a multi-frequency eddy current method to irradiated alloys and test specimens are used to measure these separate effects. A predictive tool for estimating hydrogen requires some a-priori knowledge of irradiation conditions and heat treatment of the alloys, along with eddy current data to estimate the electrical conductivity and to detect the presence of a hydride rim.

2. Specimen Conditions

Zircaloy-2 Hydrided Specimens

The material selected for this work was Zircaloy-2 strip with a starting thickness of 1.54 mm and an average equiaxed grain size of 8.5 μm. This material was annealed during fabrication at the relatively high temperature of 700 °C for at least 1 hour after each cold roll

step. Subsequent annealing at temperatures below the eutectoid temperature would induce little microstructural change. Hydrogen concentration targets were as-received (<15), 100, 200, 300, 400, 500, and 600 µg/g (also referred to as parts per million (ppm), by weight).

Three types of specimens were fabricated at each annealing temperature; an as-received, hydrided (with rim on both surfaces), and hydrided and pickled specimen (rim removed). Multiple specimen conditions at each annealing temperature allow for changes in the baseline resistivity due to microstructural changes (i.e. stress relaxation) and the presence of surface hydrides to be quantified, which allows for a more accurate measure of the effect of bulk hydrides.

Hydriding:
Two 10 cm x 10 cm sections of the Zircaloy-2 strip were electrolytically hydrided, resulting in a hydride layer approximately 35 microns thick. The hydriding was performed in a constantly stirred sulphuric acid solution at a temperature of 70°C. The cathode was the Zircaloy plate, while the anode was a lead plate. A direct current of 27 amps was used. Specimens were cut and cleaned in acetone prior to annealing.

Annealing:
Redistribution of the hydrogen was initially done by annealing using temperatures based on Kearns' solubility curve [4] (Figure 1), however, a more applicable curve for predicting the necessary anneal temperatures was generated during this work. This is the 'Anneal Temp vs. [H]' curve in Figure 1. The annealing time was based on Kearns' diffusion equation for Zircaloy to achieve at least 97% homogeneity [5]. The specimen anneals below 400 °C were completed in an air furnace. Homogenization anneals above 400 °C were completed in a more inert atmosphere to minimize oxidation. The furnace was purged with grade 5 argon gas at room temperature and operated in an atmospheric pressure argon environment with a flow rate of approximately 200 cc/min during temperature cycling. A small oxygen concentration (~1 µg/g) in the argon gas was desirable to maintain an oxidized specimen surface to prevent hydrogen escaping to gas by the Sievert's Law mechanism.

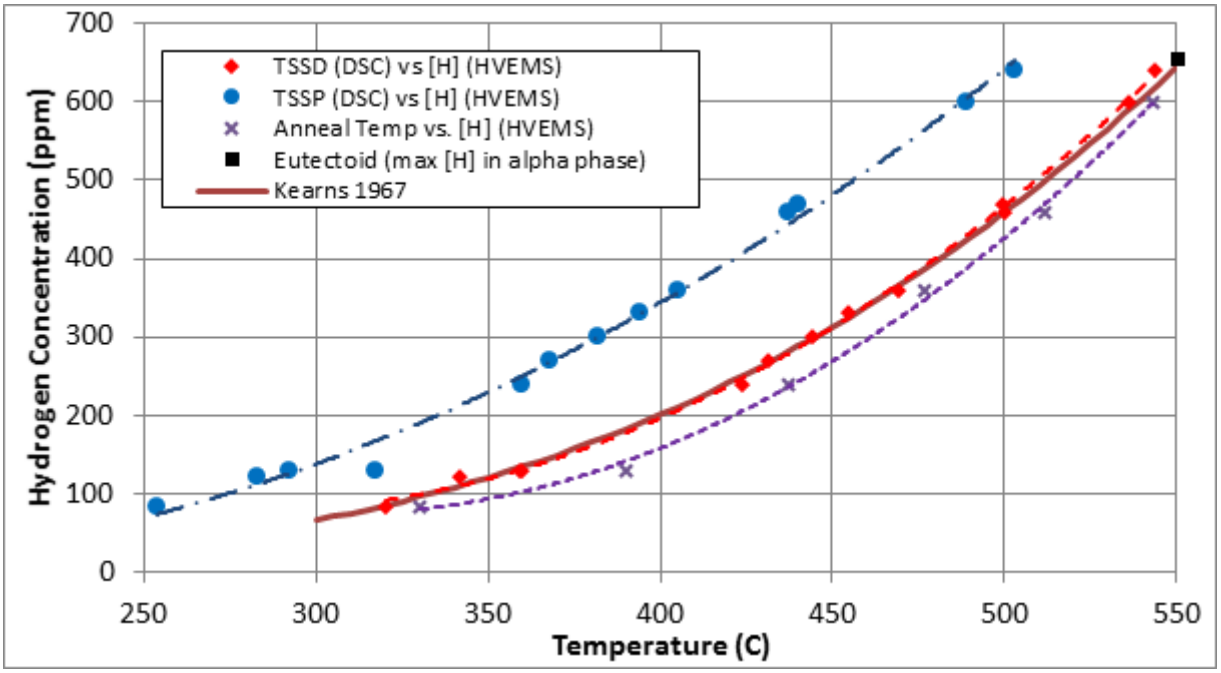

Figure 1. DSC and Anneal Temperature vs. Hydrogen Concentration Results

Surface preparation:
Removing the hydride rim for the 'hydrided and pickled' specimens was completed using mechanical and chemical means. Approximately 0.02 mm of material was wet sanded from each side using 400 grit Carbimet paper. The sample was then immersed in a glycerin-acid pickling solution until the sample thickness was reduced to approximately 1.45 mm.

Metallography:
Metallography was performed perpendicular to the longitudinal normal (LN) and the transverse normal (TN) directions. These designations were nominal; they could not be distinguished from one another. Two directions were imaged to be sure direct comparisons between all specimens could be made. Specimens were prepared using standard metallographic grinding and polishing methods. Zr-hydrides were subsequently revealed using an etchant containing HF, HNO_3, and lactic acid. The microstructure was imaged using bright field illumination. A metallographic image for a 100 ppm target sample with hydride layer present is shown in Figure 2, while Figure 3 shows a metallographic image for a 600 ppm sample with no hydride layer present.

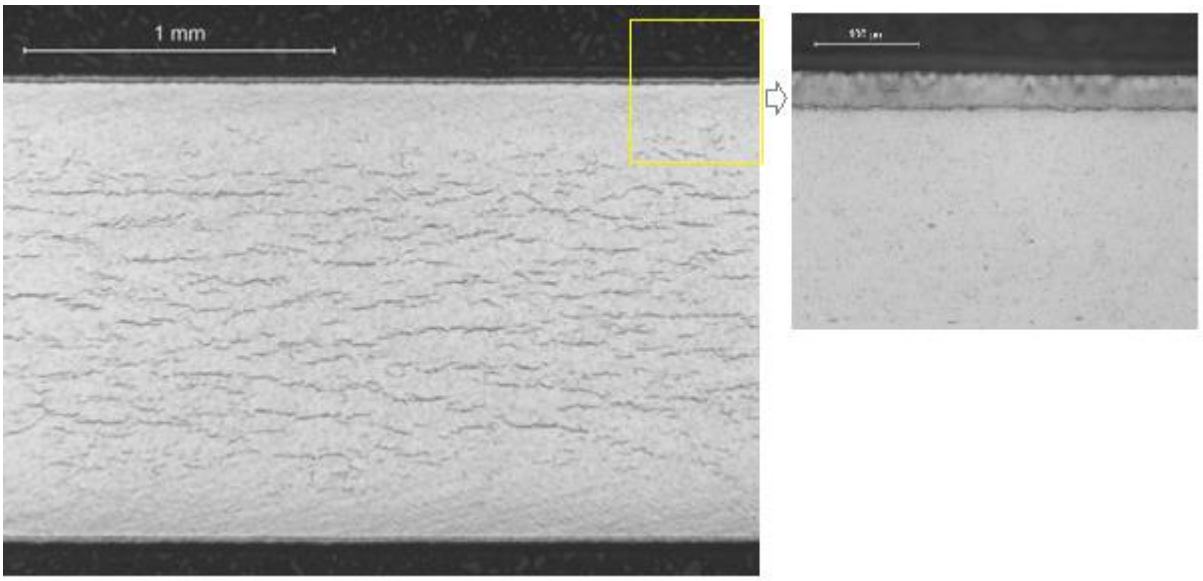

Figure 2. Metallographic image of 100 ppm target with hydride layer

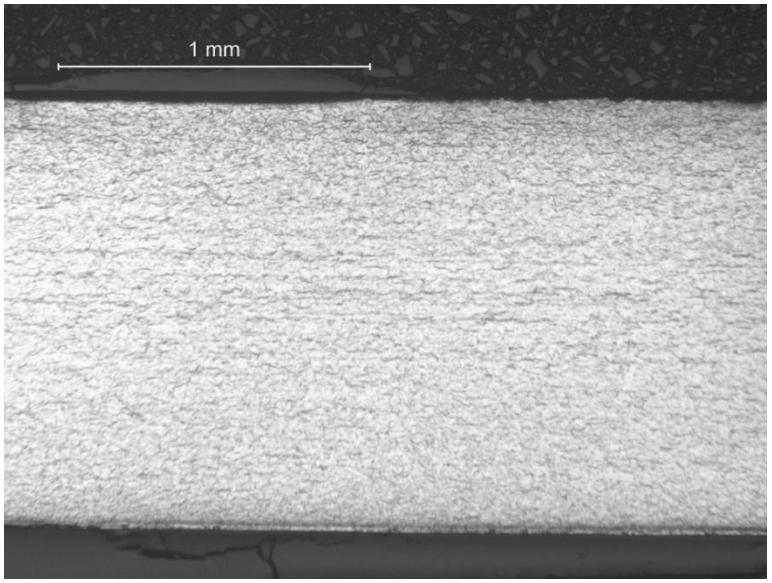

Figure 3. Metallographic image of 600 ppm target with hydride layer removed

Hydrogen Measurements:

Hydrogen concentration in the specimens was measured in two ways: differential scanning calorimetry (DSC), and hot vacuum extraction mass spectrometry (HVEMS). DSC used a heating and cooling rate of 10 °C/min. The terminal solid solubility of dissolution (TSSD) is determined by heating, while the terminal solid solubility for precipitation (TSSP) is defined on cooling. HVEMS is a destructive technique, thus it was performed subsequent to the non-destructive DSC technique. The features of interest on the DSC curves (TSSP and TSSD) are compared with the HVEMS results in Figure 1.

Irradiation Growth Specimens

These specimens are part of the Dimensional Stability Project run by EPRI's Nuclear Fuel Industry Research (NFIR) program. The Zircaloy-2 specimens are from channel material that was cold rolled to 0.8 mm and annealed for 2 hours at 620 °C. The recrystallized microstructure is similar to that for the hydrided specimens referenced above. The Zircaloy-4 specimens are light water reactor spacer material that is also recrystallized. The specimens were irradiated in the ATR as part of the Dimensional Stability Project and subsequently measured using the frequency scanning eddy current technique (F-SECT) [6] at Idaho National Laboratory. The specimens were irradiated at 285 °C in an inert gas environment. The approximate conditions are given in Table 1. All of the standards and irradiated specimens of the same material were from the same sheet stock to eliminate alloying differences.

Table 1: Dimensional Stability Project specimen material conditions

Specimen ID	Material	Fluence (n/cm^2)	Displacement per atom (dpa)	Hydrogen (ppm)
AR30QA10A005	Zry-2	0	0	15
AR30X-2	Zry-2	4.4E+21	6.7	15
AR30Z-1	Zry-2	8.1E+21	12.2	125
AR30Z-10	Zry-2	8.1E+21	12.2	125
AR360A10A006	Zry-4	0	0	15
AR30Y-4	Zry-4	8.1E+21	12.2	40
AR30Y-7	Zry-4	4.4E+21	6.7	40

AR30Z-4	Zry-4	8.1E+21	12.2	125

3. Experimental Setup

Equipment

The frequency-scanning eddy current technique (F-SECT) was used make measurements of normalized eddy current impedance as a function of frequency over the range of 0.4 to 8 MHz. The system uses in internal self-nulling sensor in the probe to compensate for impedance changes relative to cable resonance and minor temperature drift. A specimen holder was used for specimens irradiated in the ATR due to their small size to avoid accidental edge effects. The experiments were performed in air on a table with a configuration shown in Figure 4. A weight of ~ 2 kg is placed on the probe to ensure probe conformance to the surface. Specimens that were not irradiated were measured in a similar manner.

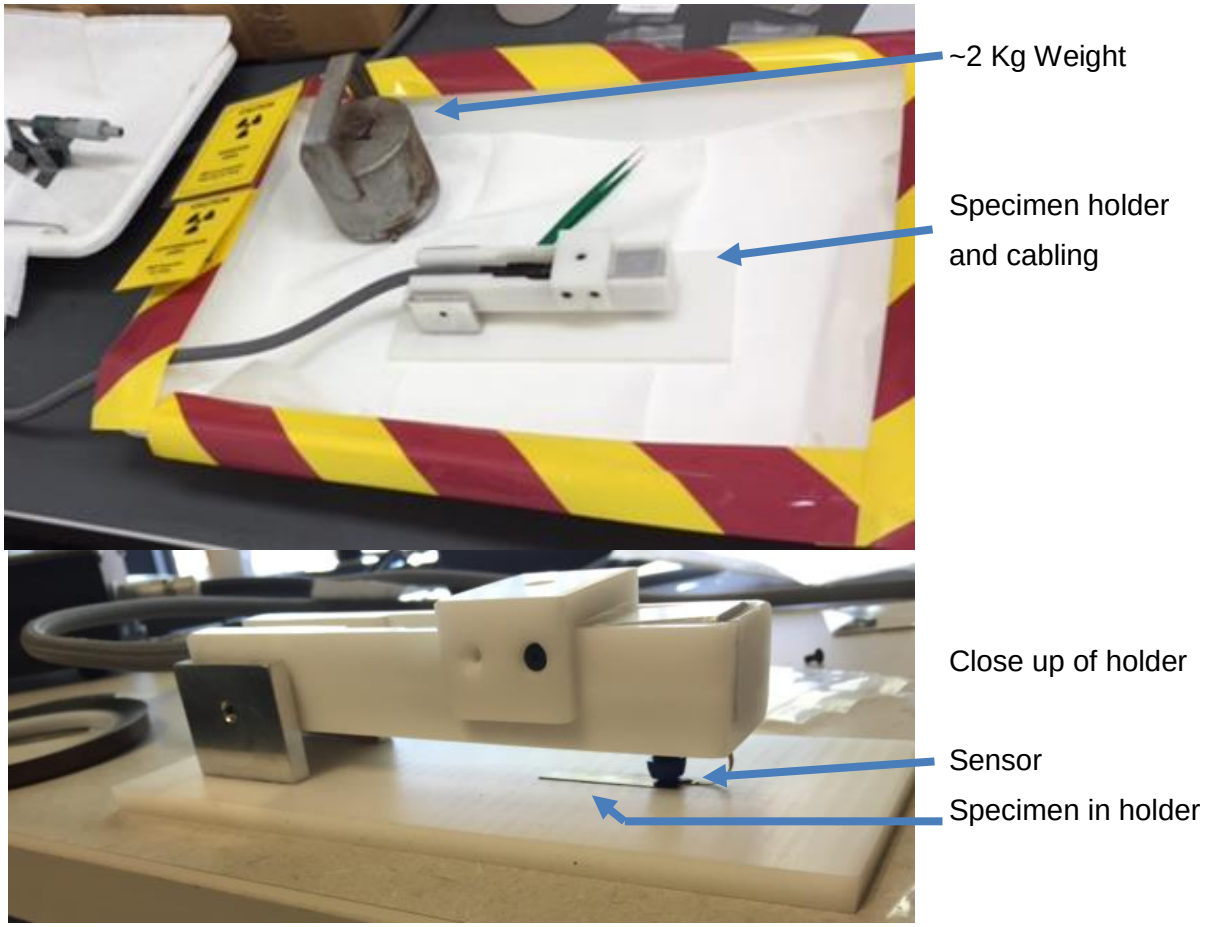

Figure 4. F-SECT probe and holder configuration

Specimen standards are used to provide the normalized impedance measurements. The specimens used as standards were flat sheet specimens (0.8 mm thick) of Zircaloy-2 with an estimated electrical conductivity of 1.45 MS/m and an Inconel 625 alloy with an estimated electrical conductivity of 0.8 MS/m. These values are estimates from comparative study and literature review.

Inversion Model

Electrical conductivity estimates are derived from normalized impedance measurements at multiple frequencies by an inversion model using the vendor supplied F-SECT software described in Reference [6]. A two-layer model (*Figure 5*) is used for most structural materials evaluations (e.g. channel box) provided there is not a ferromagnetic crud present. This model has just 2 unknowns:

Zirconium alloy thickness (L_1), Zirconium alloy conductivity (σ_1).

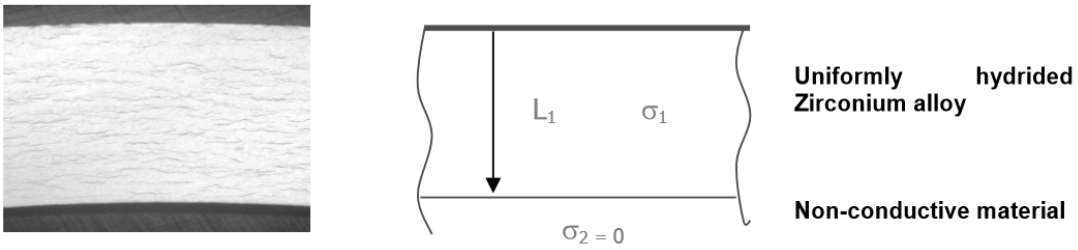

Figure 5. Two-layer inversion model

A three-layer model (*Figure 6*) is used when the presence of a hydride rim or another variation (e.g. liner) is suspected or known. This model has four unknowns:

Hydride rim thickness (L_1), Hydride rim conductivity (σ_1), Wall thickness (L_2), Base alloy conductivity (σ_2)

The raw F-SECT data can be run with several models and both the comparison to model fitting parameters and the reasonableness of the fitted parameters can indicate the conditions of the specimens (e.g. presence of a hydride rim). Other parameters can be computed, such as magnetic permeability, but in the case of the specimens tested here-in it is known that the magnetic permeability is not a variable and more complicated models are not needed.

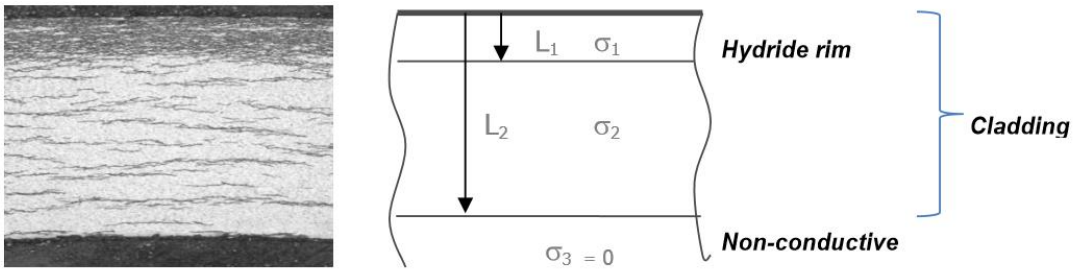

Figure 6. Three-layer inversion model

4. Measurement Results

The change in electrical conductivity of the annealed specimens with no hydrogen addition was small. Three repeat measurements by two different operators on two different systems but the same calibration samples are shown in *Figure 7*. The resolution of the system is 0.001 MS/m and the scatter in computed slopes can be expected for such small measurements differences. As such the annealing effect is considered small for recrystallized Zircaloy-2 specimens but is applied for determining hydrogen sensitivity.

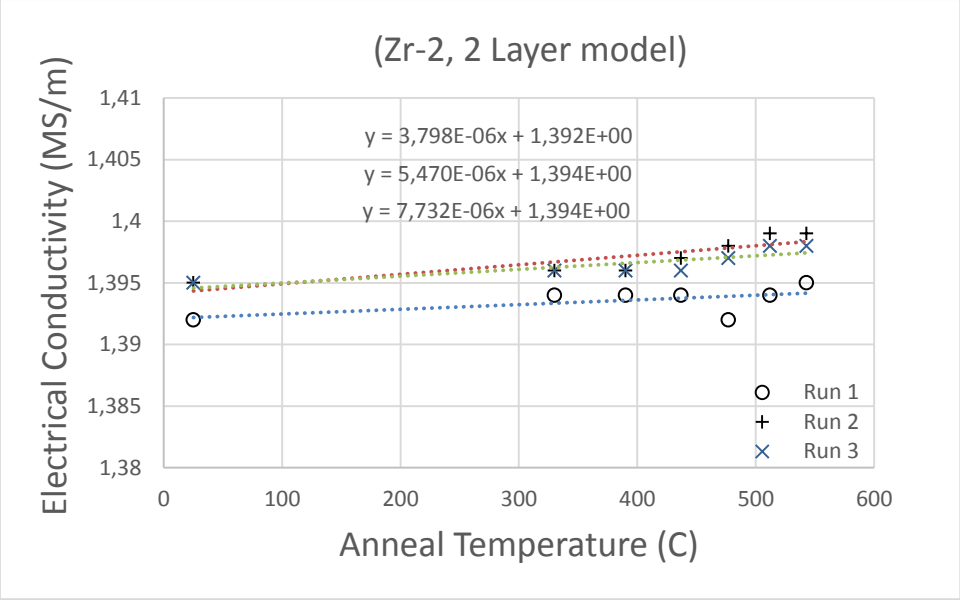

Figure 7. Effect on annealing of samples on electrical conductivity

The repeatability of the raw data for estimating hydrogen sensitivity in uniform hydrided Zircaloy-2 specimens is shown in *Figure 8*. The electrical conductivity data are plotted as a predictor to hydrogen rather than a sensitivity of electrical conductivity to hydrogen because electrical conductivity is the intended independent variable to be measured. It can be seen for these repeat measurements that the x-axis intercept at 0 hydrogen is not a constant but the slopes are similar and linear over the measured range. There is an offset that is dependent on measurement and calibration conditions and it is not modeled explicitly. As such, the offset of the measurements must be determined in the field and is a source of potential bias uncertainty.

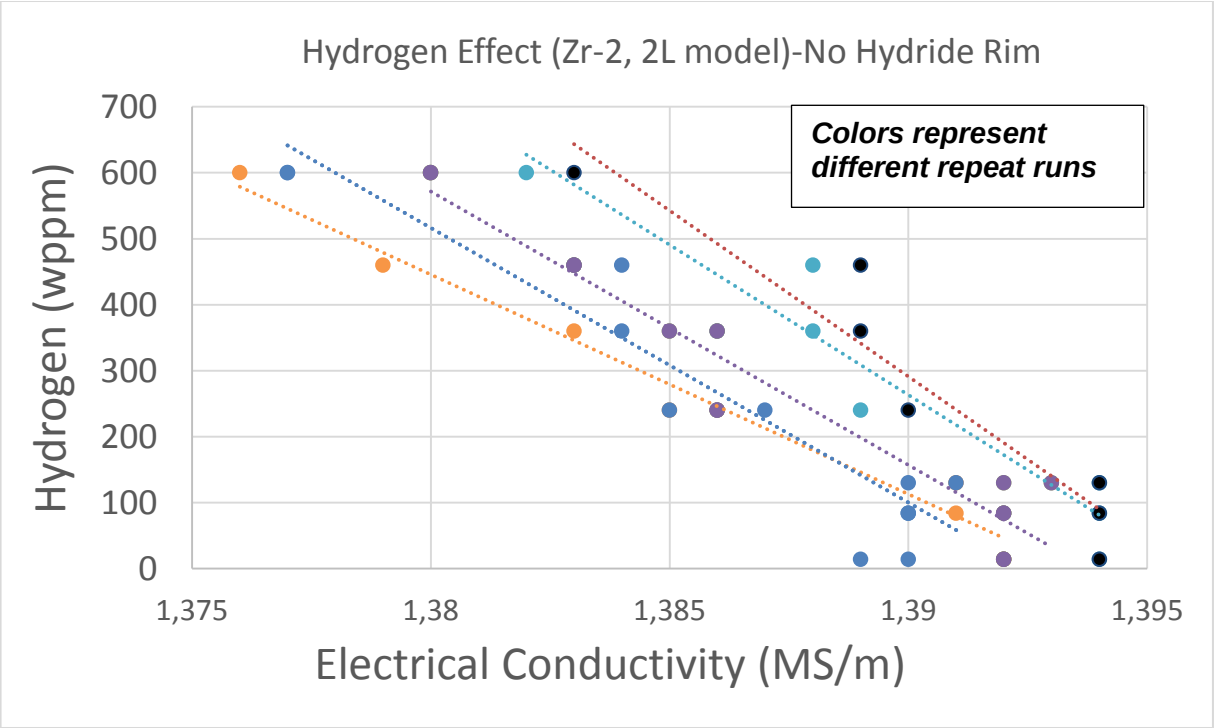

Figure 8. Repeatability of hydrogen sensitivity to electrical conductivity

The sensitivity of hydrogen difference to electrical conductivity change is given for recrystallized Zr-2 using a 2-layer inversion model in *Figure 9*. These data are compensated for differences in electrical conductivity from annealing using an average sensitivity of 5.66e-6 (MS/m/°C) for the annealing temperature parameter from *Figure 7*. To eliminate the offset issues seen in *Figure 8*, the difference in electrical conductivity and hydrogen are used. When as-received specimens have low hydrogen, the hydrogen difference is approximately the total hydrogen content. When comparisons are made on a component, the hydrogen content may be greater than the as-received hydrogen content and so the hydrogen difference is preferred. The standard deviation of the measured vs predicted fit for hydrogen in *Figure 9* is 79 ppm H.

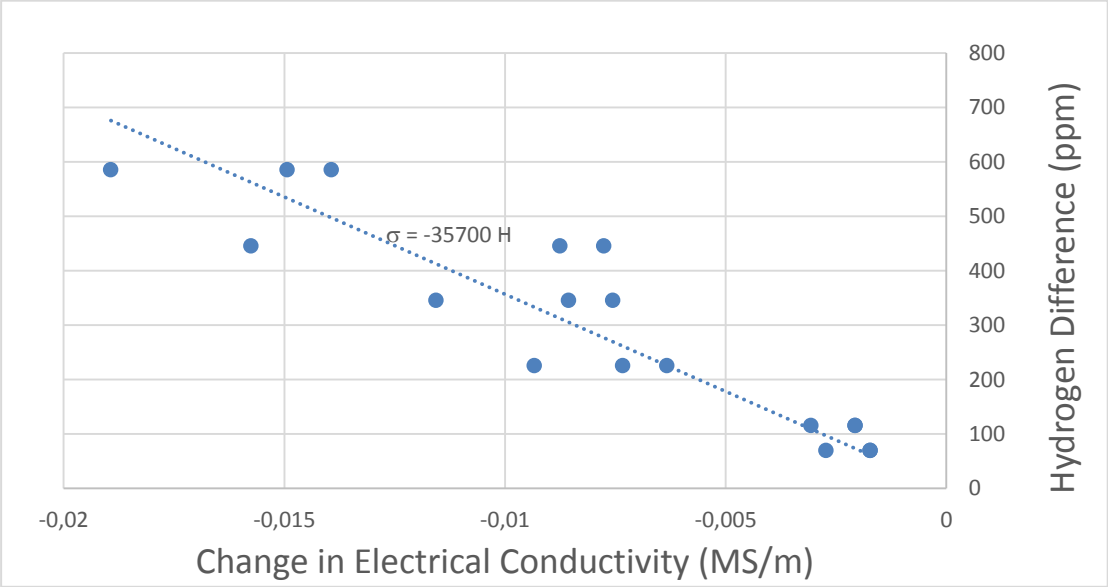

Figure 9. Sensitivity of hydrogen difference to electrical conductivity changes

Irradiation Sensitivity

Recrystallized Zircaloy-2 and Zircaloy-4 specimens irradiated in a gas environment as part of a separate study were measured after irradiation exposure in the ATR. These specimens have < 150 ppm of hydrogen that was added prior to irradiation as part of another experimental goal on hydrogen assisted irradiation growth. The results are plotted in *Figure 10*. For the limited range of fluence, the correlation appears linear for both alloys. Additional specimens are being irradiated but measurements are not anticipated for several more years to determine the potential for continuing linear behavior or reaching saturation.

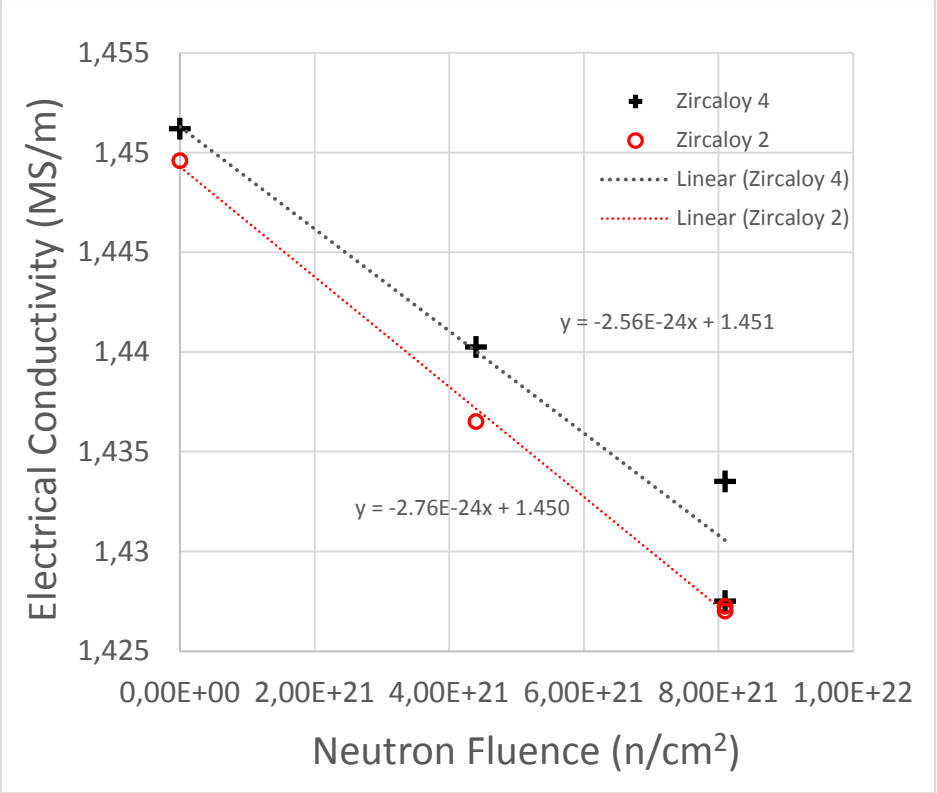

Figure 10. Sensitivity of Electrical Conductivity to Neutron Fluence for Zircaloy-2 and Zircaloy-4

Prior work on a Zircaloy-2 structural material [7] was used to estimate the longer term fluence behavior for the alloy. This material has a significant contribution of electrical conductivity decrease from hydrogen whereas the ATR coupons only have a minor contribution. By compensating the conductivity for the measured hydrogen content using the established sensitivity of -36,000 ppm H / (MS/m) for all specimens, the separate fluence effect derived is plotted in *Figure 11*. No attempt is made to separate contributions to electrical conductivity change due to irradiation from various mechanisms (e.g. precipitate dissolution or dislocation density increase).

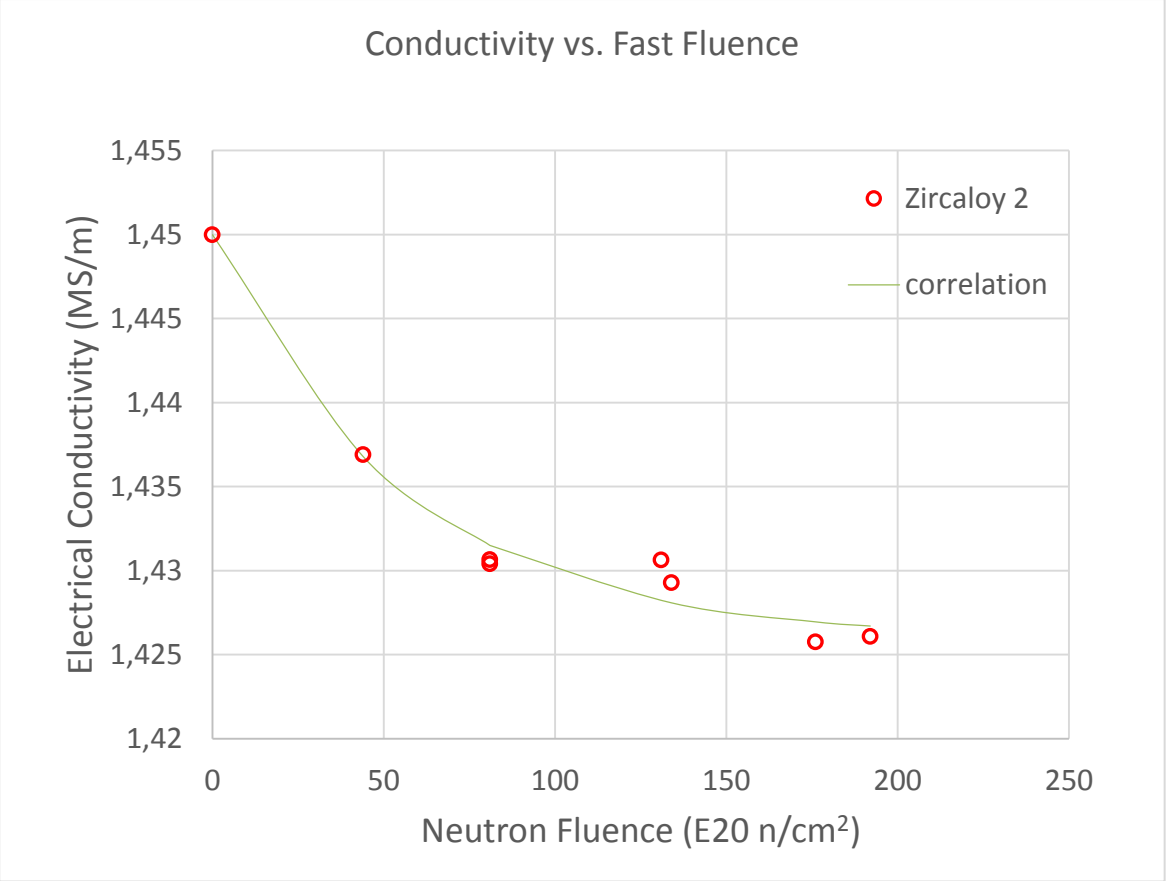

Figure 11. Effect of neutron fluence on electrical conductivity of Zircaloy-2

5. Electrical Conductivity Model to Estimate Hydrogen

Electrical conductivity is affected by several conditions for a given alloy and heat treatment. The factors considered in the current model are alloy, manufacturing heat treatment, in-use temperature and time since manufacturing (i.e. annealing), neutron fluence, hydrogen, and measurement temperature. Simplifications can be made based on a-priori knowledge.

For alpha-annealed recrystallized Zircaloy-2 components, in-service annealing time and temperature are not a primary concern. Measurement temperature is considered a constant offset in the experimental methods used for this study. The primary influences are neutron fluence, alloy composition and hydrogen content.

Because of unknown alloy variations and temperature conditions for the components inspected relative to the standards used, a relative method is used to assess hydrogen content of the components. A region on the component of low measured corrosion and calculated fluence is used as a reference, with hydrogen content estimated relative to this location. In this manner, alloy composition variations are not expected in the component (e.g. fuel rod or channel) and the effect is a constant. Using gamma spectroscopy for the fluence profile estimate in conjunction with the calculated fluence can reduce uncertainty. The mathematical model is

$$\sigma = A\, e^{(-Bf)} - C^{*} H + D, \text{ where,}$$

σ =conductivity (MS/m), f is fluence in E20 n/cm^2 , H is hydrogen in weight ppm

A, B, C & D are fitting parameters that are alloy/heat treatment dependent;

Recrystallized Zircaloy-2 Parameters:
A=0.024 MS/m; B=0.018 (E20 n/cm^2); C=1 / (36000 ppm H/MS/m);
D=condition specific constant to be determined in the field (1.426 MS/m for *Figure 11* fit)
A+D is the initial conductivity and saturation is assumed to occur by 200 x10^{20} n/cm^2.

6. Discussion

For sample preparation, the Zr-H eutectoid temperature (550 °C) [4], was predicted to correspond to a maximum hydrogen solubility in the alpha phase of ~655 µg/g based on the Kearns' equation. It was determined by in-situ annealing in a DSC that the solubility was indeed limited by the eutectoid and that the practical limit of the electrolytic technique for producing uniform hydride was approximately 650 µg/g. The TSSD vs. [H] curve in Figure 1 agrees well with the Kearns' equation and trends towards the eutectoid concentration in the phase diagram, as expected.

Electrical conductivity change with hydrogen for uniformly hydrided specimens can be modeled as a linear function for the range of hydrogen tested. It is an assumption that the relation remains linear to the higher hydrogen contents that can be seen in service. In general, this assumption has been seen to be true [1]. Comparison to electrical conductivity values given in reference [2] (Figure 12) using a different eddy current system shows a similar trend for autoclave hydrided Zircaloy 4 with similar sensitivity that appears to be linear to about 1500 wppm. The data from reference [2] 2-slab experiments are used since the overlapping data matched our experiments well, while other experiments showed different sensitivity.

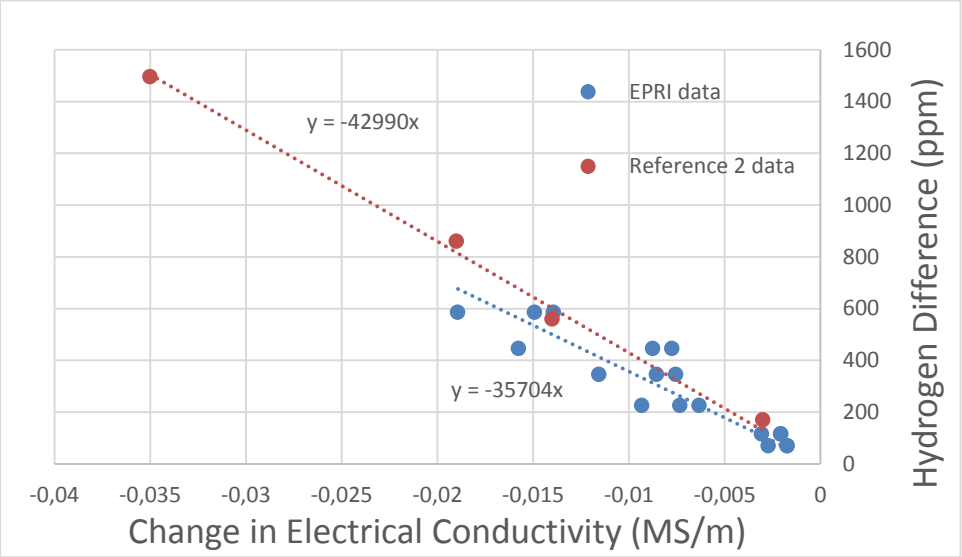

Figure 12. Evidence of continued linear sensitivity from Reference 2

The fluence effect modeled here-in is non-linear and approaches a saturation level somewhat above typical in-service fluence. While fluence data in Reference [1] appear linear based on service components, the components may not yet be approaching saturation fluence where a non-linearity would be observed. This assumption may affect the modeled fluence effect and additional experiments are planned to determine if model modifications are needed.

Hydride rim models and electrical conductivity correlations are under development and are intended to be the subject of a future paper.

7. Conclusion

Modeling parameters for recrystallized Zircaloy-2 components have been developed that account for neutron fluence effects and hydrogen content. Sensitivity parameters for linear dependence of the electrical conductivity on hydrogen content have been established as well as non-linear parameters for fluence sensitivity. The standard deviation of the measured vs predicted hydrogen is 79 ppm for multiple operators using different F-SECT hardware systems. Other sources of uncertainty such as determining the appropriate offsets and neutron fluence corrections are estimated to be larger in magnitude. Application of the model to Zircaloy components is ongoing and subject of a future paper. Planned measurements on additional Zircaloy-2 specimens irradiated in the ATR will be used to confirm or modify the model parameters derived from the component exams to higher fluence.

8. References

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