Modeling of Hydrogen Uphill Diffusion in Dissimilar Titanium Welds

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Outline

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- Modeling Results
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Objectives

- To conduct electrochemical experiments on titanium Grades 7 and 29 to measure corrosion rate

- To determine the role of temperature, corrosion rate, and welding configuration on the hydrogen embrittlement of dissimilar titanium alloys at a welding joint using experimental results

Hydrogen Embrittlement

- Titanium alloys have been proposed for use in nuclear waste management programs
  - Waste containers
  - Drip shields
- A potential degradation phenomenon observed for titanium under certain conditions is hydrogen embrittlement
- Hydrogen embrittlement comes from the formation of brittle titanium hydrides
  - Hydrides form if the hydrogen concentration increases above a critical threshold value in the titanium alloy
  - This leads to a decrease in metal fracture toughness or ductility

Hydrogen Embrittlement at Welds

- Dissimilar welds in titanium alloys are preferential sites where hydrogen embrittlement has been observed to occur
- Hydrogen can concentrate in titanium by uphill diffusion
  - Titanium alloys with different levels of aluminum have different hydrogen chemical activities
  - If two alloys with different hydrogen chemical activities are welded together, a driving force may lead to hydrogen diffusion up a concentration gradient
- Uphill diffusion at weld sites has led to failure of welded vessels

Technical Approach: Experimental

- Measured and compared corrosion rates for two grades of titanium alloys representing two different aluminum contents
  - 0 wt% of aluminum (Titanium Grade 7)
  - 6 wt% of aluminum (Titanium Grade 29)

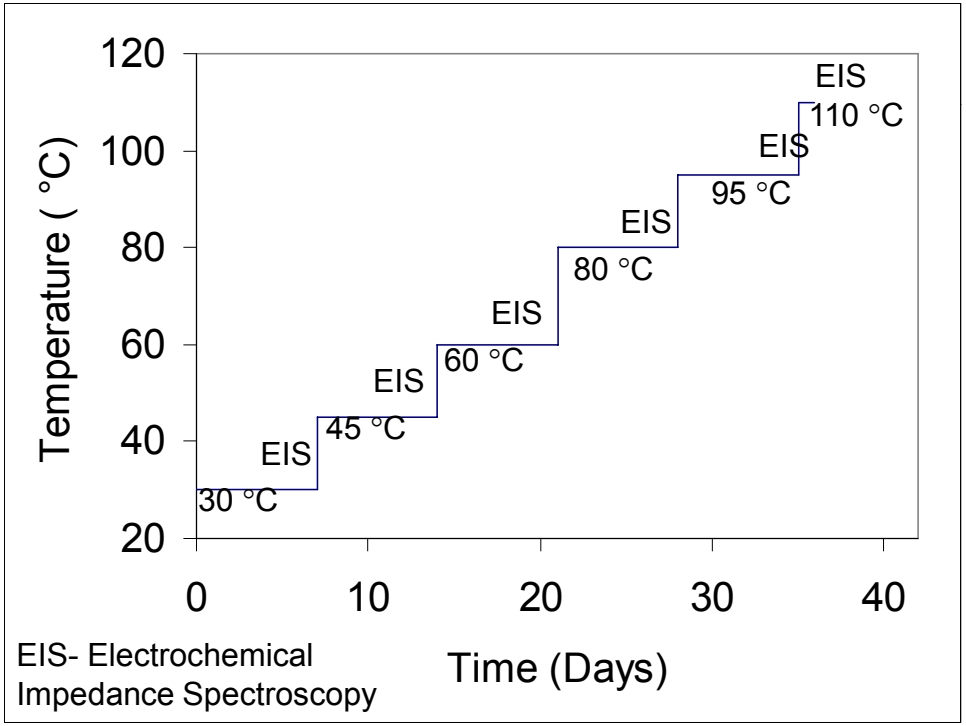
Chemical Composition of Titanium Grades 7 and 29										
Material	Ti*	Pd*	Fe*	C*	N*	O*	H*	Al*	V*	Ru*
Grade 7	99.609	0.16	0.08	0.01	0.01	0.13	0.001	NA	NA	NA
Grade 29	89.773	NA	0.19	0.04	0.006	0.109	0.0021	5.62	4.16	0.10
*Ti–titanium, Pd–palladium, Fe–iron, C–carbon, N–nitrogen, O–Oxygen, H–Hydrogen, Al–aluminum, V–vanadium, Ru–ruthenium										

- Used two techniques to measure corrosion rates
  - Electrochemical impedance spectroscopy (potentiostatic)
  - Potentiostatic polarization tests (95 °C and 0 mV_{SCE})
- Cylindrical test specimens (6.3-mm diameter x 48.6-mm length)

Experimental Details

- Conducted in 2-L glass cell with PTFE lid
- Reference electrode: saturated calomel
- Test solution: 1 M NaCl and 4 M $MgCl_2$
- Solution deaerated with high-purity nitrogen for 24 hours
- Increased solution temperature sequentially from 30 to 110°C*
  - Each temperature held for 7-10 days except the 110* °C [230 °F]

*In 4 M $MgCl_2$ solution only



Uphill Diffusion Model

- Fick's law for diffusion

$$J = -D\nabla C$$

- Gradients, other than concentration, can lead to hydrogen diffusion (even against a concentration gradient), known as uphill hydrogen diffusion

- An aluminum concentration gradient can cause uphill diffusion in titanium, and the uphill diffusion form of Fick's Law is

$$J = -D\left[\frac{\partial C}{\partial x} + CK_a \frac{\partial N_a}{\partial x}\right]$$

Model Parameters

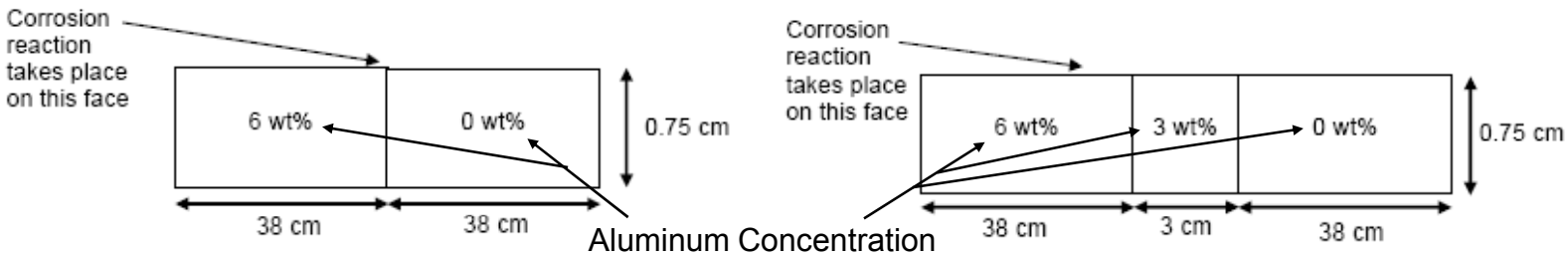
- Initial condition: No hydrogen in the alloys
- Hydrogen forms due to the oxidation of titanium at the exposed surface of the alloys

$$Ti + 2H_2O \rightarrow TiO_2 + 2H_2$$

- Hydrogen absorption coefficient is kept constant at 1.5 percent
- K_a is an experimental constant with value 3.55
- N_a is the concentration of aluminum in the titanium alloy in atomic percent

Model Parameters (Cont.)

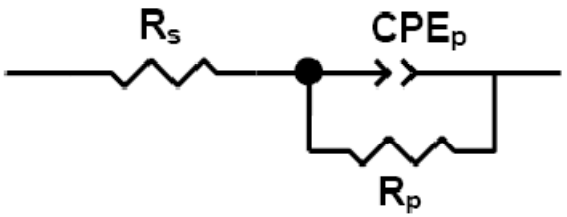
- Developed a one-dimensional model to evaluate hydrogen diffusion across a dissimilar metal weldment
  - Evaluated two weld configurations

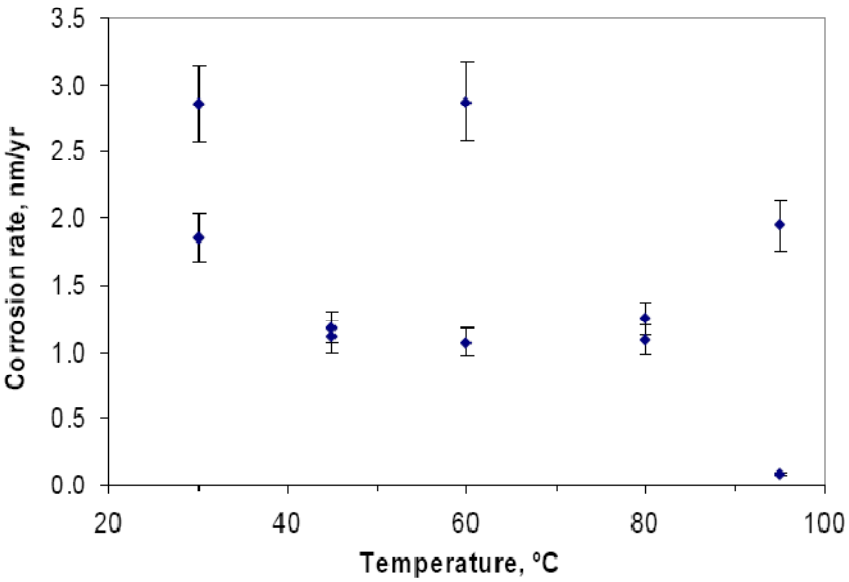


  - Evaluated effect of different corrosion rates
    - Same corrosion rate along all of the titanium alloys
    - Corrosion rate increased in material with higher aluminum content
  - Evaluated effect of temperature
    - Low (25 °C)
    - High (100 °C)

Experimental Results: Electrochemical Impedance

- Electrochemical impedance used a constant phase element analog model to fit the impedance data
- Corrosion values in 1 M NaCl varied from 0.1 to 3 nm/yr [3.9 x 10^{-6} to 1.2 x 10^{-4} mils/yr]
- Corrosion rate in $MgCl_2$ solution were similar to NaCl
- No temperature dependence
- No visual corrosion on the titanium surface





Corrosion Rates in 1 M NaCl

Experimental Results: Potentiostatic polarization

- Anodic current density decreased with time and reached a steady state at approximately 15 days

- In 1 M NaCl and 4 M $MgCl_2$, the passive corrosion rates were 15 and 89 nm/yr [5.8×10^{-4} and 3.5×10^{-3} mils/yr], respectively

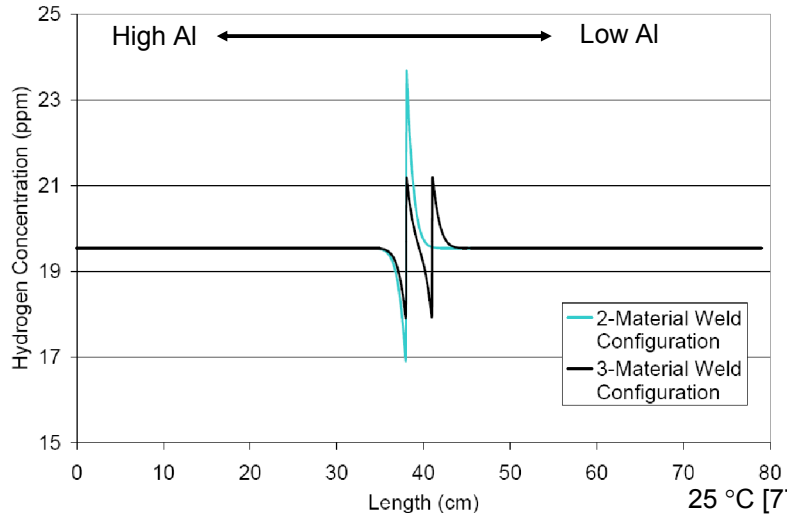
- The anodic current density measured in 1 M NaCl solution for Titanium Grade 29 is similar to that measured for Titanium Grade 7

Estimated Corrosion Rates

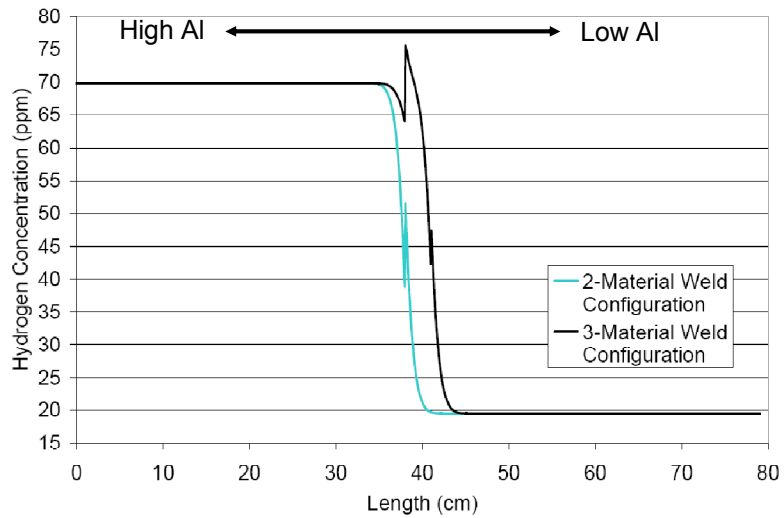
- Corrosion rates measured from potentiostatic polarization are one order of magnitude higher than those measured from electrochemical impedance spectroscopy
- This is due to uncertainty in fitting impedance data
- For diffusion modeling it is assumed that electrochemical impedance data provide a lower bound for the corrosion rate, while potentiostatic polarization rates provide an upper bound

Uphill Diffusion Modeling: Weld Configuration Results

- When corrosion rate is constant across all alloys, addition of a transitional alloy decreases hydrogen concentration
- When varying corrosion rate is used, addition of a transition alloy increases hydrogen concentration
- This occurs at both 25 °C [77 °F] and 100 °C [212 °F]



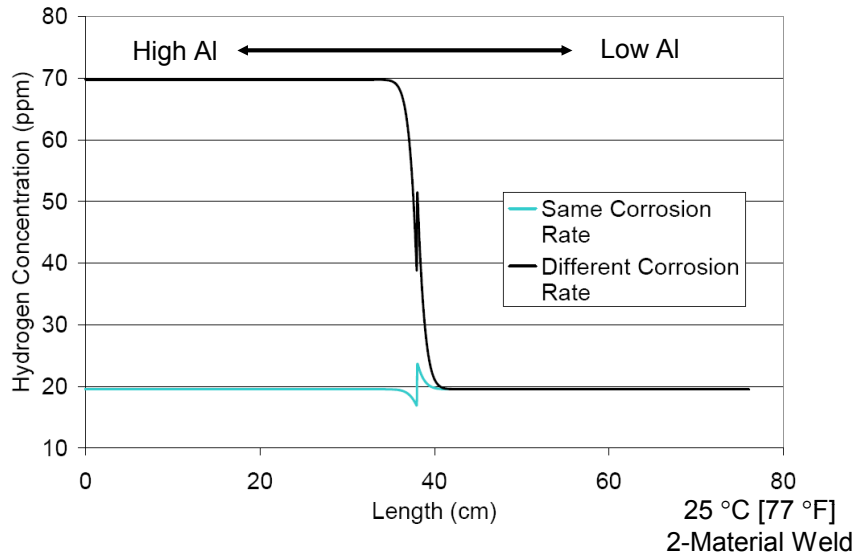
25 °C [77 °F]
Same Corrosion Rates



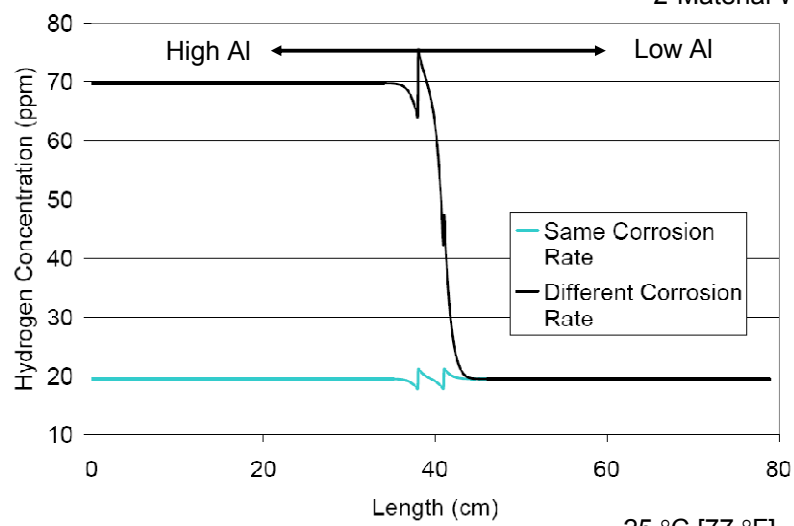
25 °C [77 °F]
Different Corrosion rates

Uphill Diffusion Modeling: Corrosion Rate Results

- When corrosion rates are the same in 0, 3, and 6 wt% aluminum alloys, the peak hydrogen concentration occurs in titanium with 0 wt % aluminum
- When corrosion rates are increased in titanium alloys with 3 and 6 wt% aluminum, peak hydrogen concentration usually occurred in titanium with 6 wt% aluminum
- One exception is the 3-material weld at 25 °C [77 °F], where increased corrosion rate leads to peak hydrogen concentration in transition alloy (3 wt% aluminum)



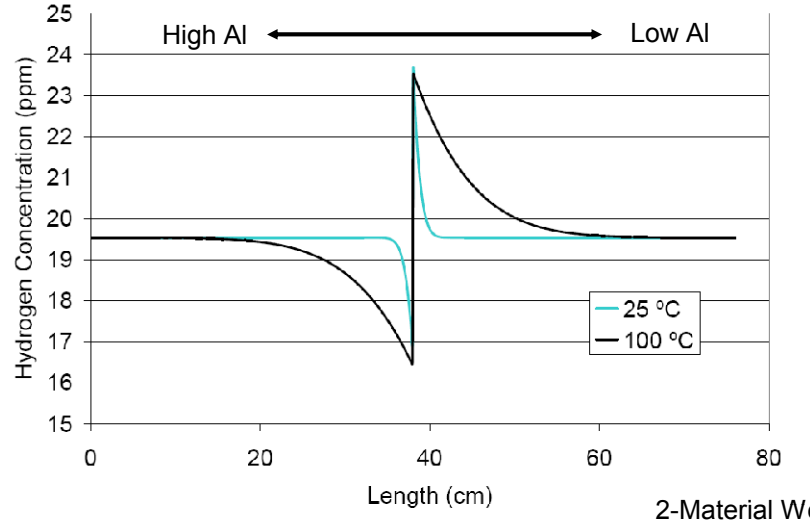
25 °C [77 °F]
2-Material Weld



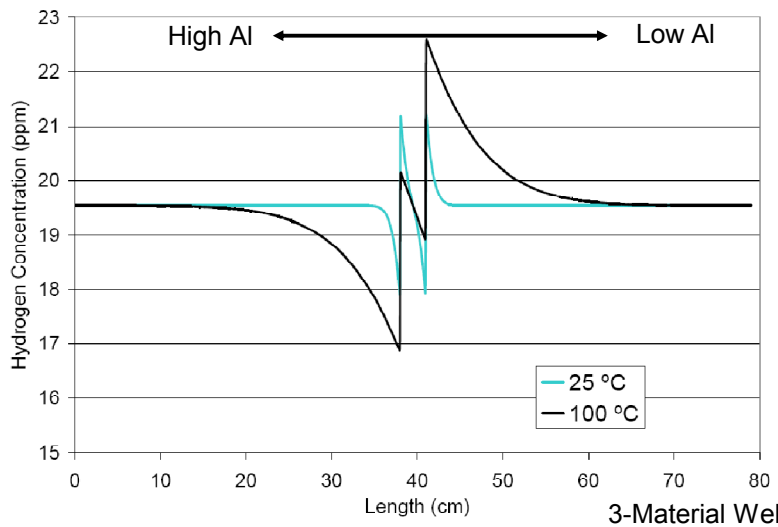
25 °C [77 °F]
3-Material Weld

Uphill Diffusion Modeling: Temperature Results

- When temperature is low (25 °C), the diffusion of hydrogen is restricted to near the weld lines
- When temperature is increased, the diffusion of hydrogen permeates further into the base metal
- There was no difference in temperature effects depending upon the corrosion rates used



2-Material Weld
Same Corrosion Rate



3-Material Weld
Same Corrosion Rate

Conclusions

- In 1 M NaCl and 4 M $MgCl_2$ solutions, there does not appear to be a significant difference in the corrosion rates between Titanium Grades 7 and 29.
- The hydrogen uphill diffusion model indicated that adding a transition alloy may lead to a lower peak hydrogen concentration, but only at the higher temperature evaluated.
- At the lower temperature, adding a transition alloy increases the peak hydrogen concentration.
- Increasing the corrosion rate of the titanium alloys with aluminum moved the peak hydrogen concentration into those alloys.
- Increasing temperature led to an increased hydrogen diffusion in the base alloys.

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