HYDRIDING OF TITANIUM: AN OVERVIEW

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Outline

- Occurrence in Titanium Industrial Usage
- Titanium Oxide vs Hydride
- Hydrogen Absorption Routes & Prevention Methods
- Hydriding vs Embrittlement
- Remediation
- Summary
Industrial Usage of Ti

- **Chemical Processes**
  - Organic acids, chlorinated HC’s, urea
  - Salt production
  - Chlorine, bromine compounds
  - Soda ash

- **Refineries**
  - MEA processes, sour water
  - Crude overhead units (Cl⁻ containing)

- **Others**
  - Condensers
  - Hydrometallurgical

Generally excellent service history for Ti – but hydriding can and has occurred in all these applications.
Titanium Oxide vs Hydride

- Oxide stability
  - Slightly reducing to oxidizing potentials
  - Wide range of pH values

- Hydride stability
  - Reducing potentials
  - Wide range of pH values

- Both can be protective films

- Drastically different diffusion rates cause an issue with hydrides
Hydrogen Absorption Routes

- **Galvanic couples**
  - Usually involves steel corrosion with Ti being cathode
  - Sulfides will increase uptake (recombinant poison)

- **Cathodic protection**
  - Overzealous CP potentials more negative than about -0.8V in sea water
  - Use of Mg or Zn sacrificial anodes

- **Oxide film degradation**
  - Reducing acid corrosion (H reduction)
  - Mechanical abrasion

- **Hydrogen gas**
  - Need high temperature & pressure
Prevention Methods

- **Galvanic couples**
  - Use electrical insulating gaskets
  - Use transition couples more galvanically compatible to minimize driving potentials

- **Cathodic protection**
  - *Always* use potential controlled CP – not current
  - Use Fe or Al based anodes

- **Oxide film degradation**
  - Select a more resistant Ti alloy
  - Limit vibration, apply thermal oxide or wear coating

- **Hydrogen gas**
  - Titanium not generally suitable for use
Prerequisites for Hydriding

Conditions Necessary for Hydriding and Embrittlement – All Must Be Present

- The pH of the solution is less than 3 or greater than 12; the metal surface is damaged by abrasion, or impressed potentials are more negative than -0.8V (vs. SCE)

- The temperature is above ~70°C. Below this temperature only surface hydride films will form which, experience indicates, do not seriously affect the properties of the metal. Failures due to hydriding are rarely encountered below this temperature.

- There must be some mechanism for generating hydrogen. This may be a galvanic couple, cathodic protection by impressed current, corrosion of titanium, or dynamic abrasion of the surface with sufficient intensity to depress the metal potential below that required for spontaneous evolution of hydrogen.
Hydriding vs Embrittlement

- Hydriding can occur at all temperatures
  - In aqueous media nascent hydrogen reacts at surface to form TiH₂
  - Titanium hydride forms crystal plates that appear as dark, needle-like structures in a cross section
  - Can be confused with twinning – special etchants can distinguish, also, twins do not cross grains
  - Hydriding does not typically degrade properties when on the surface
  - Alloying and microstructure can affect hydrogen absorption, solubility, and diffusion rates
  - Difficult to detect except through destructive testing (gas analysis & metallography)
Only one of these Ti components failed, despite having very similar hydrogen concentrations.
Embrittlement requires diffusion of hydrogen
- Typically occurs at temperatures >70°C
- Typically occurs on thin wall tubing or linings
- Orientation of hydride precipitates (which can be affected by stress state) can delay or promote crack initiation
- Migration of hydrogen will occur when stress risers are present
- Solubility of hydrogen increases dramatically with temperature
- Threshold concentrations for degradation can vary
- Concentration of hydrogen is not always the determining factor for failures
Both of these Ti components failed, despite the great difference in hydrogen concentrations.
Hydriding vs Embrittlement

Migration and precipitation of hydrides due to stress riser at crack tip
Hydriding vs Embrittlement

Thin layer of hydrides due to titanium corrosion is common
Hydride precipitates eventually strain the crystal lattice to the breaking point, even in the absence of external stresses.
Remediation

- Hydrogen in titanium is mobile
  - Mobility increases with temperature
  - Need temperature > ~375°C to effectively remove
- Bulk hydrogen removal requires a vacuum
  - Ti does not de-gas in an atmosphere
  - Vacuum de-gassing is very effective
- Hydride film removal
  - Surface films can be chemically or mechanically removed
- Sometimes best solution is to leave the hydrogen

Options are very limited once hydriding has occurred
Titanium has an excellent service history of over 50 years in the CPI.

Hydrogen embrittlement of titanium is one possible mode of failure.

In most cases hydrogen absorption can be minimized or eliminated.

Embrittlement failure factors can be related to concentration, temperature, microstructure, and stress state.