

# Materials for Hydrogen Compression



Thermo-Mechanical-Chemical Energy Storage Workshop  
SwRI - August 10-11, 2021



*The world turns to Elliott.*

# Introduction

- Hydrogen can have an embrittlement effect upon metallic materials
  - While the strength of the material remains unchanged, the ductility of the material can be significantly reduced
    - From a fracture mechanics or fit-for-service perspective, defects that are acceptable without Hydrogen may become unstable in the presence of Hydrogen

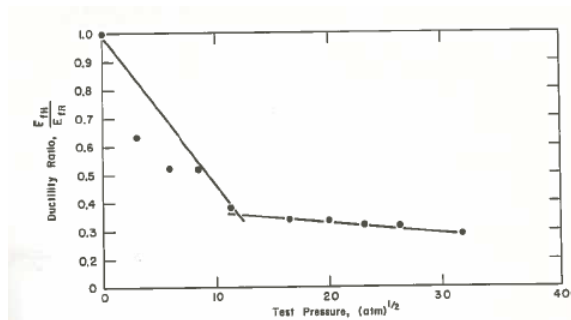


Figure 6. Effect of Hydrogen Pressure on Ductility of Type 304L Stainless Steel Tested to Fracture in Hydrogen Gas at Room Temperature

Effect of Hydrogen Pressure on Ductility of 304L Stainless Steel Tested to Fracture in Hydrogen Gas at Room Temperature

Source: Hydrogen in Metals, ASM, 1974

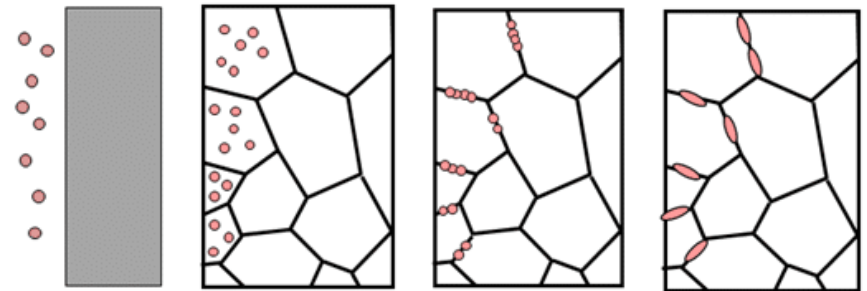
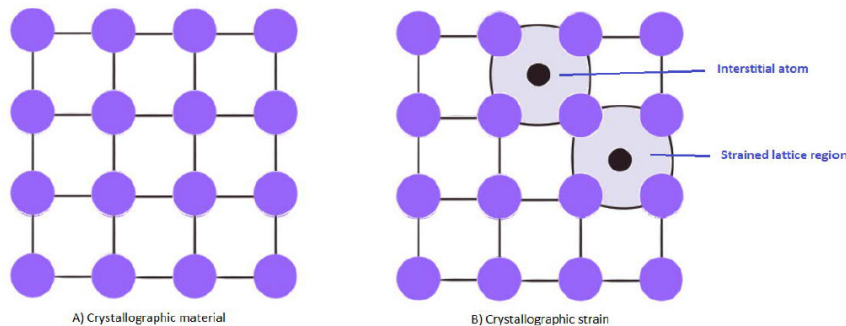


Illustration showing diffusion of atomic Hydrogen to grain boundaries within steel  
Source: [www.imetllc.com](http://www.imetllc.com)

# Why Does Hydrogen Make Metals Brittle?

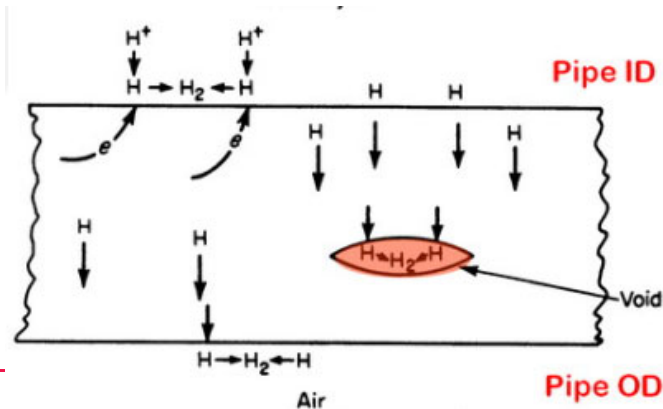
- Diatomic hydrogen ( $H_2$ ) does not readily diffuse into steels
- Atomic Hydrogen generated in the cathodic reaction penetrates the steel resulting in the loss of ductility
  - Leading theory is that the atomic Hydrogen recombines within the metal to form  $H_2$ , react with carbon, accumulate at impurities
  - Requires a corrosion reaction occurring within the process
  - Hydrogen atoms can insert themselves at interstitial sites and does not allow dislocations to move



Lattice strain in a metallic material caused by an interstitial hydrogen atom

# Hydrogen Embrittlement

- Atomic Hydrogen
  - Generated as part of a corrosion reaction which generates free hydrogen atoms
    - Atomic Hydrogen is the smallest known particle, it can diffuse through anything
    - Atomic Hydrogen then combines with another hydrogen particle to form  $H_2$ 
      - This results in a build up of internal pressure contained within the steel
  - HIC occurs when chemicals that prevent the combination of Hydrogen atoms into molecules are present. The cathode of a corrosion cell produces atomic hydrogen as part of the chemical reaction. If it does not immediately form gas molecules, this hydrogen diffused through the steel wall. Hydrogen atoms within the steel have a number of harmful effects, including embrittlement and accumulations of gas blisters, especially in laminations.

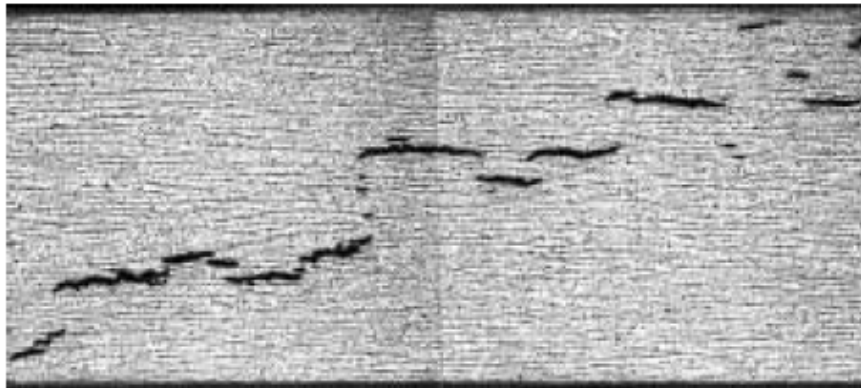


Diffusion of atomic hydrogen to defects within a steel pipe

Source: [www.corrosionclinic.com](http://www.corrosionclinic.com)

# Hydrogen Induced Cracking (HIC)

- NACE TM0103 defines this as stepwise internal cracks that connect adjacent hydrogen blisters on different planes of the material or to the surface
  - High stress fields interact to connect and form a stepwise appearance
  - No externally applied stress is required for this type of cracking to occur!



HIC in Carbon Steel Under no Applied Stress

Source: NACE TM0103



# Hydrogen Induced Cracking (HIC)

- Development of cracks along the rolling direction of the steel
  - Cracks on one plane tend to link up with cracks on adjacent plans to form steps across the thickness
  - Components processed through a uni-directional thermo-mechanical process such as plates, pipes, tubing
  - NACE TM0284
    - Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen Induced Cracking
    - Hydrogen absorption from aqueous sulfide corrosion
  - Linepipe steels can be susceptible when  $H_2S$  is present
    - Accumulation of Hydrogen at inclusions or areas of microstructural segregation



# HIC Testing per NACE TM0284

Testing for susceptibility to Hydrogen Induced Cracking

## NACE TM0284 Testing Apparatus

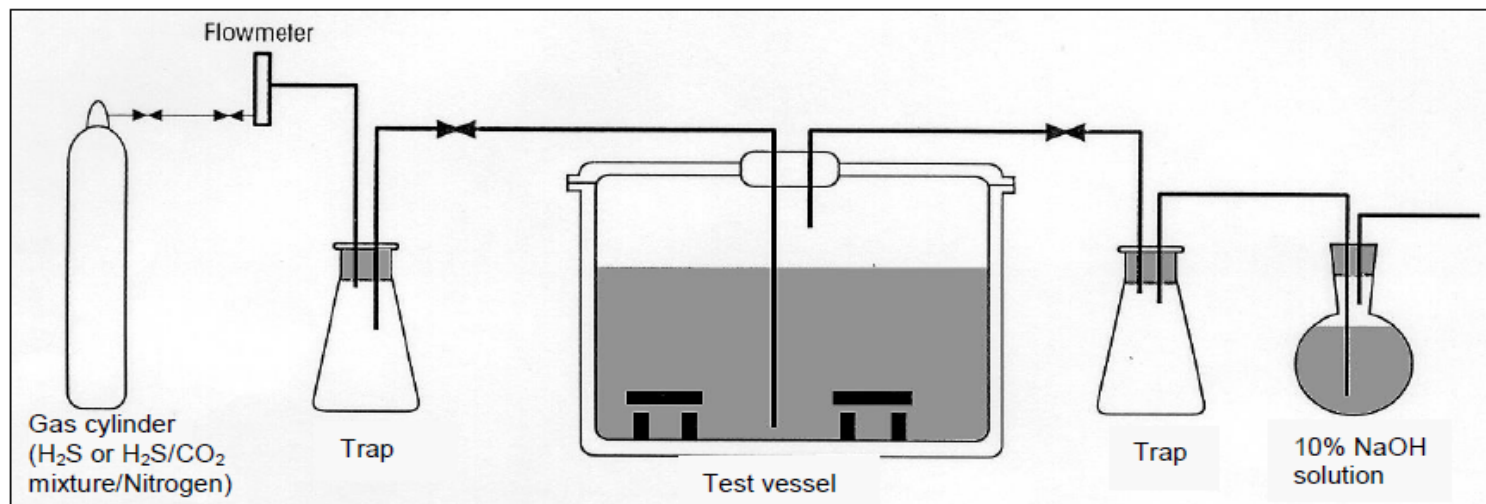


Figure 1: Schematic Diagram of Typical Test Assembly

# HIC Testing per NACE TM0284

- Testing setup per NACE TM0284

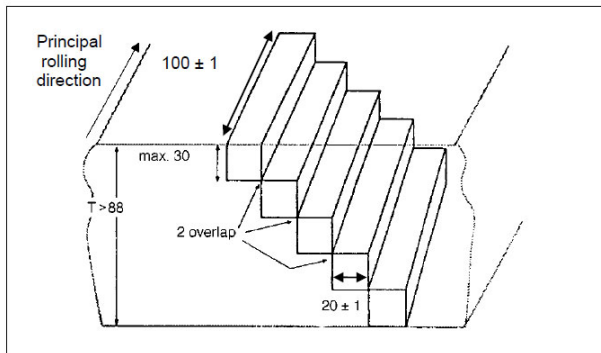


Figure 9: Test Specimen Location for Plates over 88 mm (3.5 in) Thick (All Dimensions in mm [1 in = 25.4 mm])

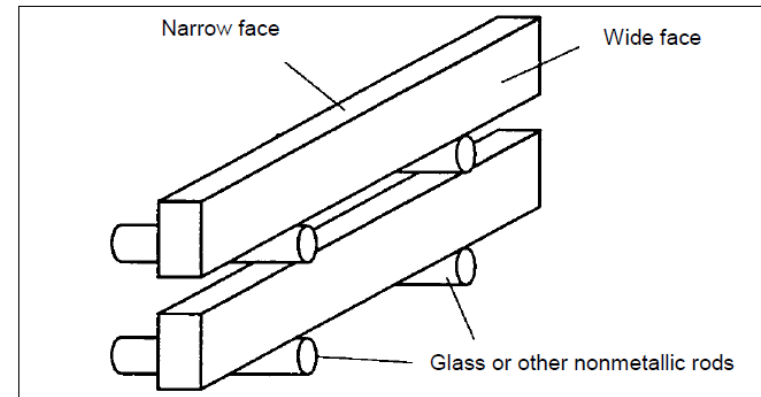


Figure 10: Orientation of Test Specimens in the Test Vessel



# HIC Testing per NACE TM0284

## Testing Results and Acceptability

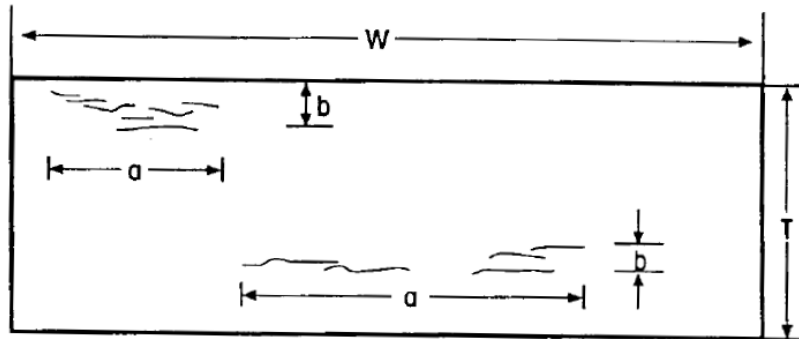
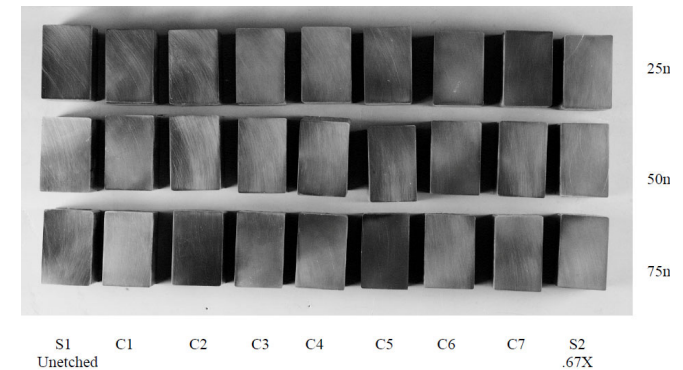
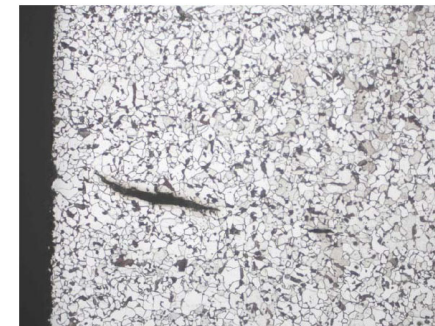


Figure 11: Test Specimen and Crack Dimensions to Be Used in Calculating CSR, CLR, and CTR



Cross-sectional samples for evaluation in metallograph at 100X magnification

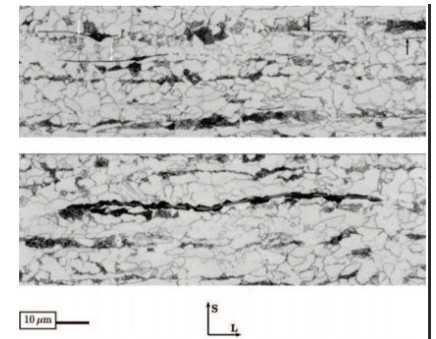


5% Nital etch Original @ 200X  
Photomicrograph of typical cracks  
Heat R0811 Slab 02



# Material Susceptibility to HIC

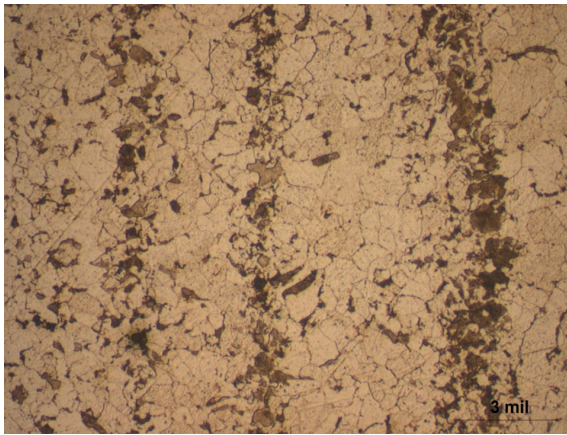
- Steel cleanliness
  - Keep Sulfur levels low (less than 0.002%)
- Alloying element segregation
  - Limit number of interfaces available for the accumulation of Hydrogen
- Manganese Sulfides and Silicates are typical initiation sites
  - Elongated inclusions have a high stress concentration at tip
  - Limit the number of these through cleaner steel
  - Inclusion shape control provides significant help
- Material toughness
  - Heat treatment for highest resistance to fracture



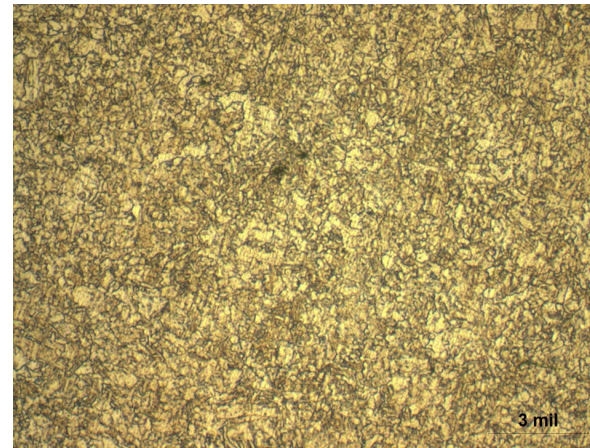
Manganese Sulfide  
Inclusions in Steel

## Heat treatment

- By increasing the fracture toughness of the material, this increases the resistance to HIC
  - Elimination of banding in microstructure



Double Normalized ASME SA516 Grade 60 Plate



Normalized + Accelerated Cooled + Tempered  
ASME SA516 Grade 60 Plate

Impact toughness increased from 150 ft-lbs to 250 ft-lbs in accelerated cooled and tempered material



# Rotating Equipment

- API 617
  - Axial and Centrifugal Compressors and Expander-compressors
  - Paragraph 4.5.1.11
    - Materials that have a yield strength in excess of 827 MPa (120psi) or hardness in excess of Rockwell C 34 are prohibited for use in hydrogen gas service where the partial pressure of hydrogen exceeds 689 kPa (100 psi gauge) or the hydrogen concentration exceeds 90 molar percent at any pressure
    - ***This restriction is applied to all materials! No exceptions are provided.***
  - No other restrictions are placed on materials used for any component
    - The yield strength limit has an effect on the materials used for the rotating components which controls the spin speeds
      - Impellers and shaft
      - Higher rotational speeds needed for achieving desired transport pressure of Hydrogen



# Rotating Equipment

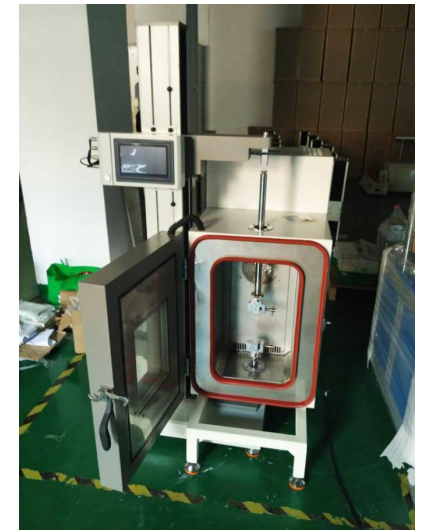
- Effort by a number of companies to find higher strength materials that are not subjected to Hydrogen embrittlement
  - No industry-recognized standard set as a fit-for service test
  - Development of materials and testing conditions are reviewed as a case-by-case basis
    - High pressure Hydrogen chambers
      - Slow strain rate testing or applied load for a set time
      - Corrosion cell generating Hydrogen



Brittle Fracture due to Hydrogen  
Source: TPS 2020, Lecture 196



Ductile Tensile Failure





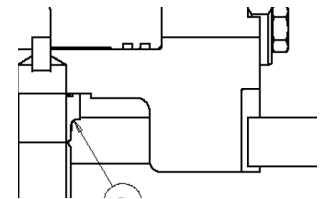
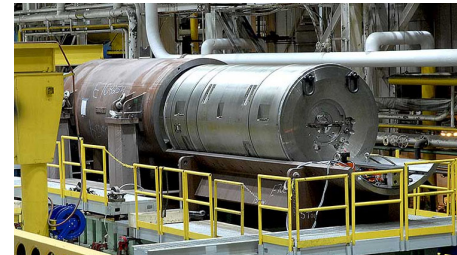
# Common Alloys for Compressors

- Casing and internal stationary components
  - Carbon steel (ASME SA516 Grade 60/70)
    - If H<sub>2</sub>S is present, NACE TM0284 HIC Testing may be required
    - Forgings per ASME SA350 Grade LF2 can be utilized
      - Forging process avoids unidirectional thermomechanical processing
    - Shafts – UNS G43400
      - Quench and tempered, 827 MPa maximum yield strength
  - Impellers
    - UNS S17400 (17-4 PH) or UNS S15500 (15-5 PH)
      - Solution treated and double aged to 827 MPa maximum yield strength
    - UNS S42400 (13Cr-4Ni or F6NM)
      - Quench and tempered to 827 MPa maximum yield strength



# Centrifugal Compressors – Auxiliary Components

- Shaft Seals
  - Standard abradable or rub-tolerant seal materials
    - Mica-filled PTFE
    - PEEK or PAI
    - Aluminum seals
- O-rings
  - Hydrogen gas does not influence the selection
    - FKM, FFKM, FEPM all have a “1” rating in Hydrogen gas
    - Other process gas constituents usually influence the selection for chemical compatibility
    - Rapid Gas Depressurization rating is not influenced by Hydrogen
- Process Gas Piping and gaskets
  - Typically carbon steel
    - ASME SA106 Grade B, SA333 Grade 1
      - As a rule-of-thumb, match the casing material
    - No limitation on gasketing material for Hydrogen



## Coating Options

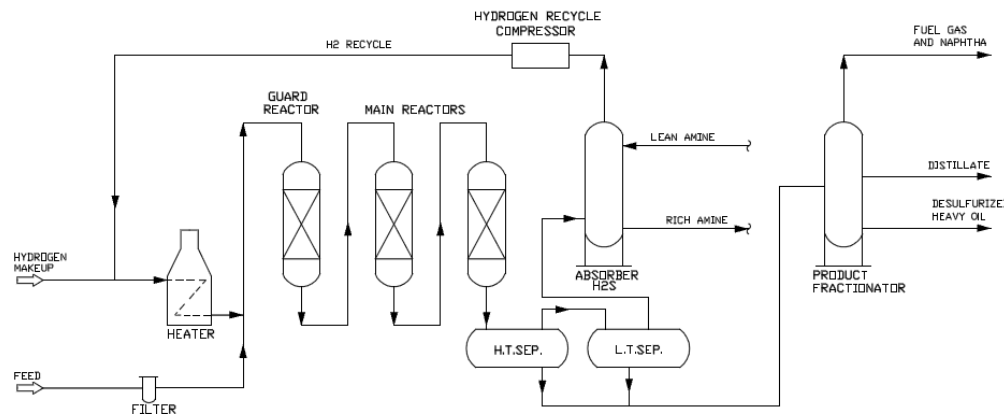
- Base material must be suitable for Hydrogen service
  - Coatings can be compromised
  - Hydrogen will always find a way to diffuse!
- Coatings can be helpful when hydrogen is generated because of a corrosion process
  - Can be used to extend the life of rotating equipment





# Hydrogen Compression in Refinery Applications

- Common purifying process within refineries
- H<sub>2</sub> recycle stream from H<sub>2</sub> recycle compressor combines with make-up gas and it is introduced into the reactors
- Process gas is over 90% H<sub>2</sub>
- Typically discharge pressures are less than 1,000 psi (70 Bar)



# Hydrogen Compressors in Refinery Applications

- Failure by Hydrogen embrittlement is not common
  - Meet API requirement for 120 ksi maximum yield strength
- Most problems associated with ammonium chloride carryover into the compressor

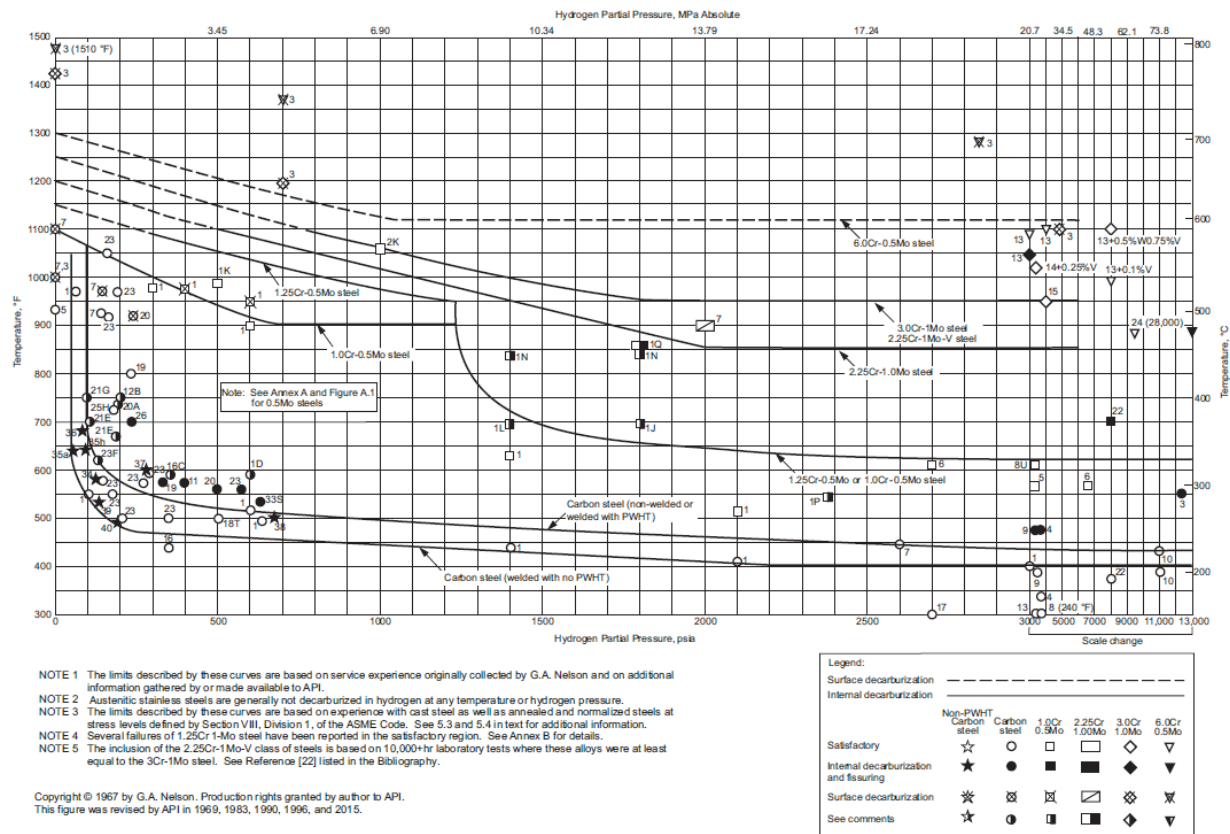


# API 941

- API 941 provides guidelines
  - Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants
    - When postweld heat treated, carbon steel pressure vessels have been used successfully up to 10,000 psi (69 MPa) and temperatures up to 221°C.
      - Highly stressed and hardened steels are susceptible to hydrogen embrittlement
    - At higher pressures and temperatures, High Pressure Hydrogen Attack (HPHA) can occur
      - Atomic hydrogen can permeate steel and react with carbon

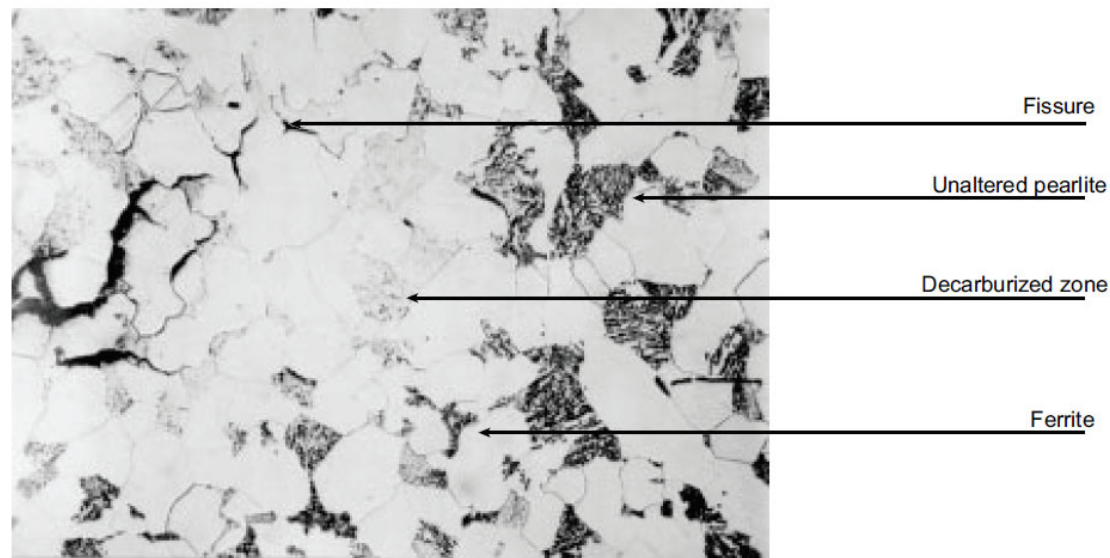


# Guideline from API 941



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# High Temperature and High Pressure Hydrogen Service Effects on Carbon Steel



NOTE Service conditions were 65,000 hours in a catalytic reformer at a temperature of 790 °F (421 °C) and a hydrogen partial pressure of 425 psia (2.9 MPa). From Reference [11] in the Bibliography. Magnification: 520X; nital etched.

**Figure 2—C-0.5Mo Steel (ASTM A204 Grade A) Showing Internal Decarburization and Fissuring in High Temperature Hydrogen Service**



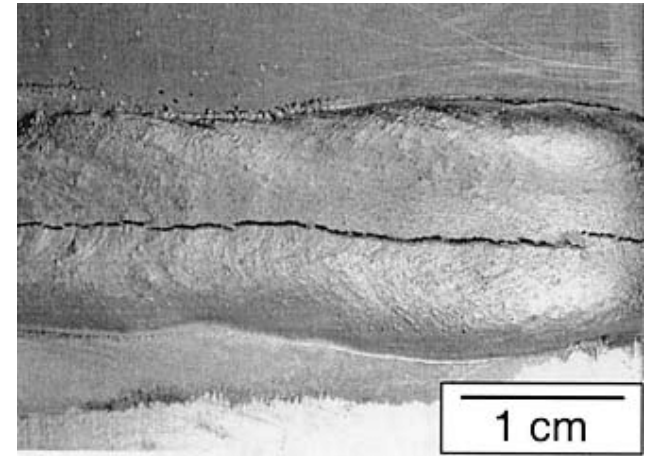
# Ammonia, Hydrogen and Hydrocarbons

- Ferrous alloys are generally not corroded by  $\text{NH}_3$  or  $\text{NH}_4\text{OH}$  at ambient or at elevated temperatures
  - At normal atmospheric temperatures, gaseous hydrogen does not readily permeate steel, even at high pressures.
  - General corrosion rate of carbon steel in ammonia is less than 0.05 mm/year
- Stress corrosion can be controlled
  - Eliminate moisture and free oxygen
  - Stress relieve welds
  - Avoid high stress concentrations or residual stresses
    - Cold bending of piping should not be utilized



# Fabrication Considerations For Hydrogen

- “A weld is essentially a casting with all the usual intense thirst for Hydrogen in the molten state.”
  - Hydrogen in Metals, ASM , 1973
- Hydrogen is a notorious enemy of weldments
  - This is a leading cause of cracking in high-strength steel weldments
- Can be controlled through processing
  - Hydrogen limits on weld consumables
  - Preheat temperatures and slow cooling allow Hydrogen to escape and not be trapped inside the weldment



# Summary

- Pipelines
  - Carbon and carbon-manganese steels are suitable for hydrogen service
    - Avoid high stressed locations
    - Postweld heat treatment of weldments should be required
    - Temperature below 400°F (204°C),
    - Partial pressure below 10,000 psi (69 MPa)
- Centrifugal Compressors
  - Carbon steel is suitable for pressure containing and internal components
  - Low alloy steel and martensitic stainless steels may be used with a maximum yield strength of 120,000 psi
  - Same temperature and pressure restrictions as pipelines apply
- Ammonia service
  - Limit the amount of moisture and impurities included in the process gas







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