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Mechanisms of Hydrogen-Assisted Fracture in 21-6-9 Stainless Steel

Brian Somerday
Sandia National Laboratories
Livermore, CA, USA

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000

Austenitic stainless steels provide excellent performance in H_2 containment components

- High ductility and fracture toughness
- Yield strength up to ~100 ksi
- Environmental compatibility
  - Resistant to hydrogen-assisted fracture

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Objective

- Identify variables that potentially compromise hydrogen-assisted fracture resistance of stainless steels
  - Temperature
  - Alloy composition (e.g., Ni, N concentrations)
  - Ferrite content (e.g., welds)
  - Forged microstructure
- Establish mechanisms of hydrogen-assisted fracture in stainless steels
- Evaluate steels under conditions that are relevant for H_2 gas containment

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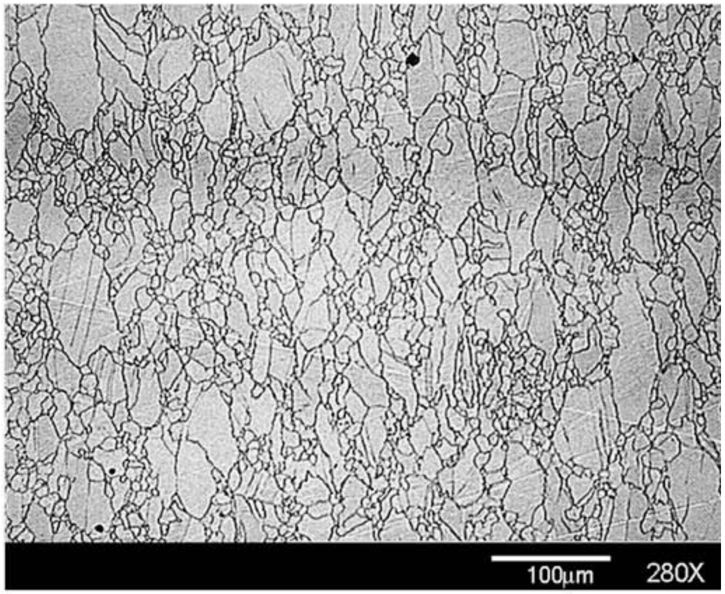
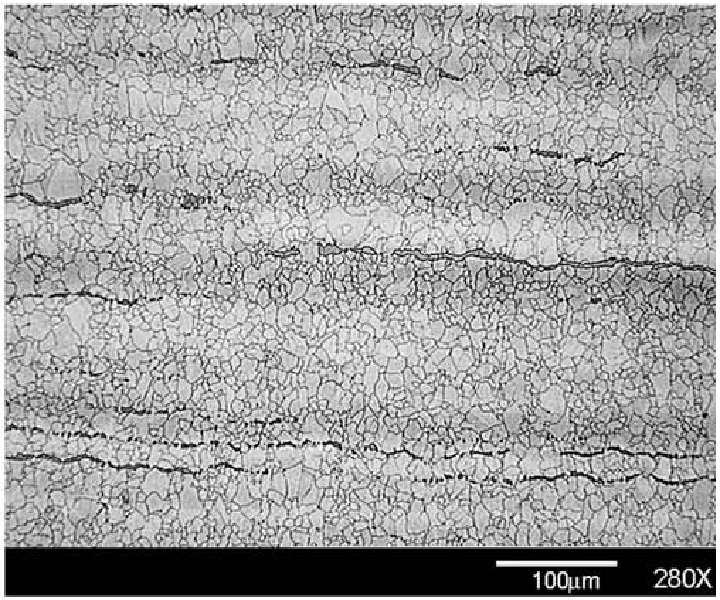
Materials: 21Cr-6Ni-9Mn forgings

- Fe-Cr-Ni-Mn-N stainless steels
  - FCC austenite matrix with possible discontinuous BCC ferrite
  - No strain-induced martensite at near-ambient temperatures

21Cr-6Ni-9Mn
(0 vol% ferrite)



21Cr-6Ni-9Mn
(2 vol% ferrite)



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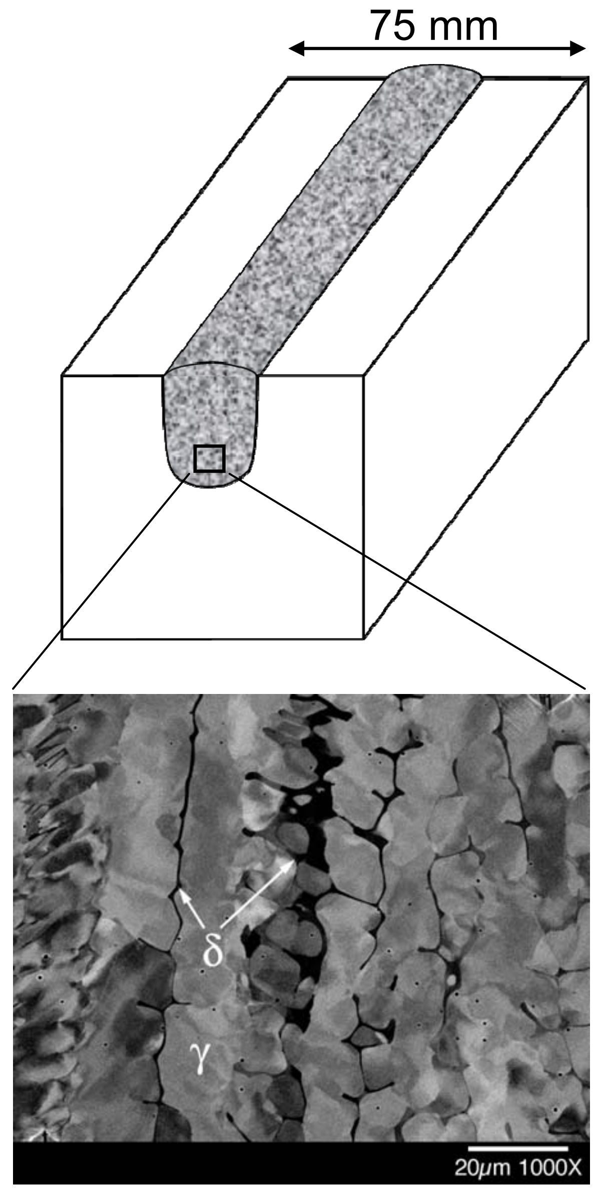
Nibur, Somerday, San Marchi, Balch, Acta Mat, 2009

Materials: 21-6-9/21-6-9 gas-tungsten arc weld

- Base metal
  - 19.07 Cr, 6.96 Ni, 9.78 Mn, 0.26 N, 0.018 C
  - 19.6 Cr_{eq}, 13.0 Ni_{eq} (WRC-1992 Diagram)
  - σ_{ys} ~485 MPa
  - Ferrite number ~0

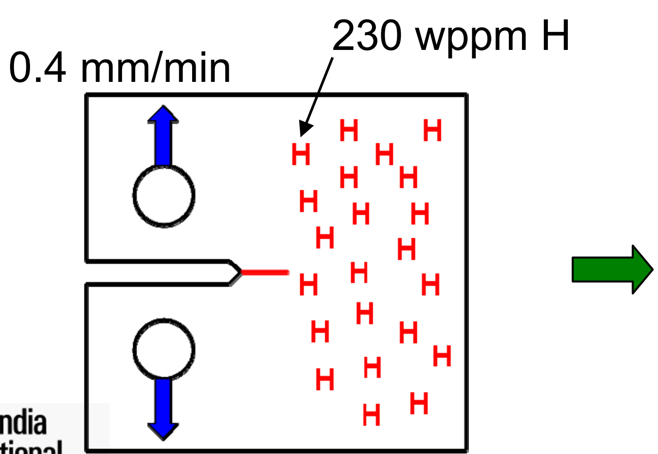
- Weld fusion zone
  - 19.54 Cr, 6.81 Ni, 9.39 Mn, 0.19 N, 0.030 C
  - 19.6 Cr_{eq}, 11.7 Ni_{eq} (WRC-1992 Diagram)
  - Ferrite number ~7 to 9

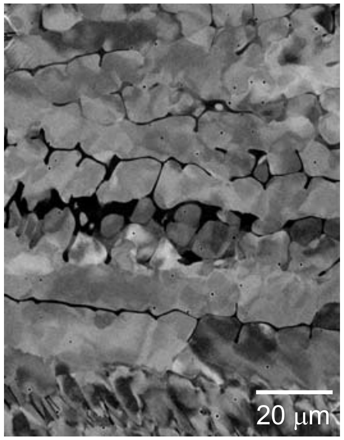


Somerday et al., <u>Met Trans A</u>, 2009

Mechanical testing: fracture mechanics methods

- Conducted fracture toughness tests on compact tension specimens following elastic-plastic methods in ASTM E1737
  - Two crack orientations for forgings, only one for GTA welds
- Measured effect of hydrogen on fracture using thermal charging in H_2 gas technique
  - Exposed to 138 MPa H_2 gas/300 ºC for ~30 days
  - Fracture toughness measured in air at room temperature





crack parallel to dendritic structure in welds

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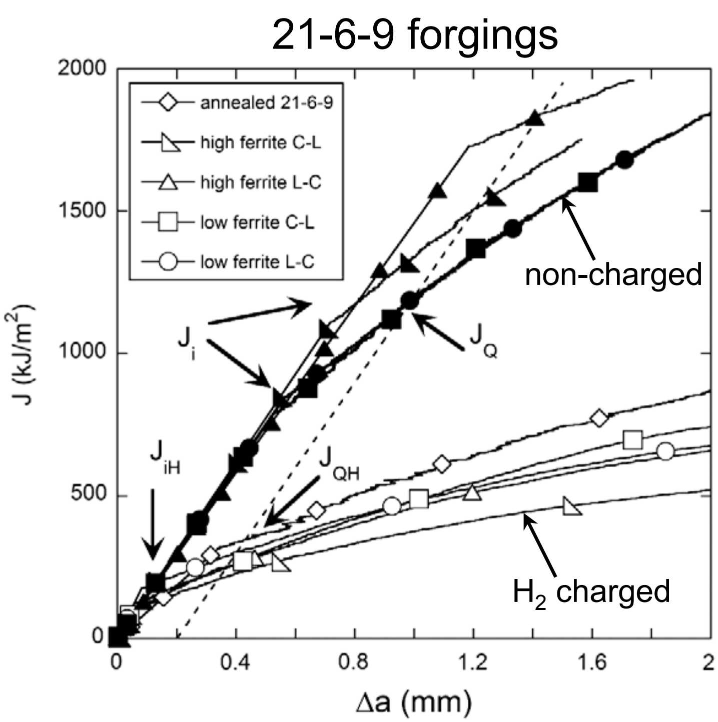
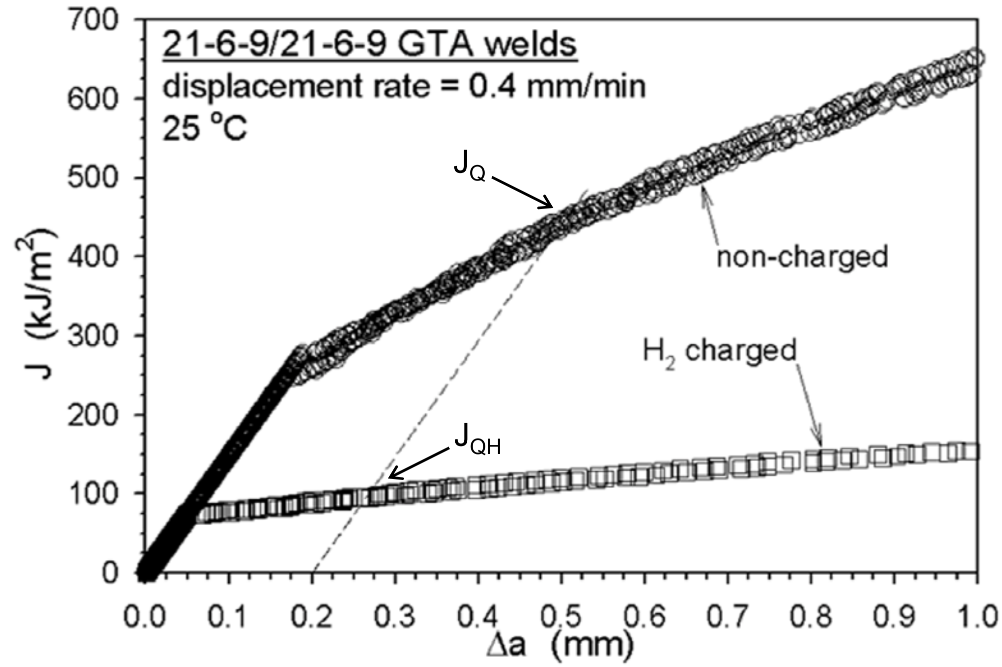
Crack-growth resistance curves show that hydrogen reduces fracture resistance





Absolute values of fracture toughness lower in H_2-charged welds compared to H_2-charged forgings

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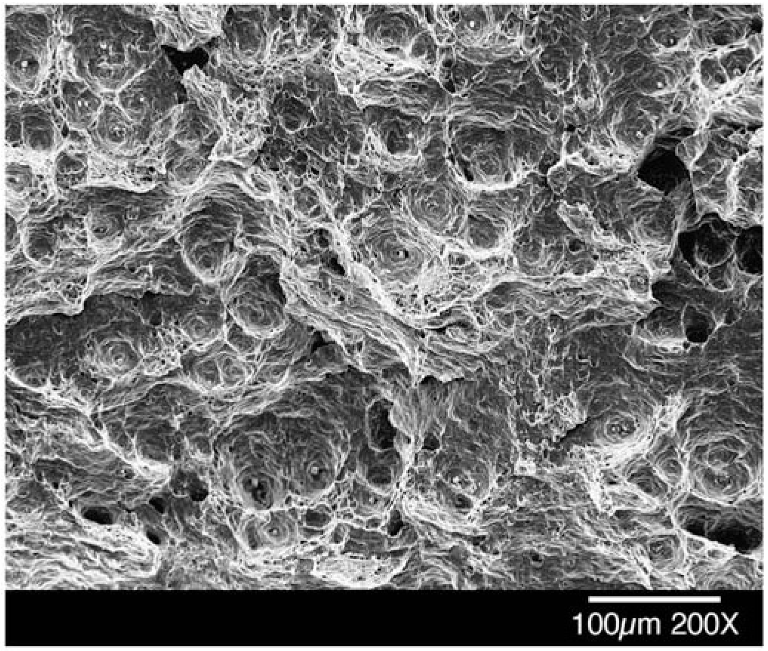
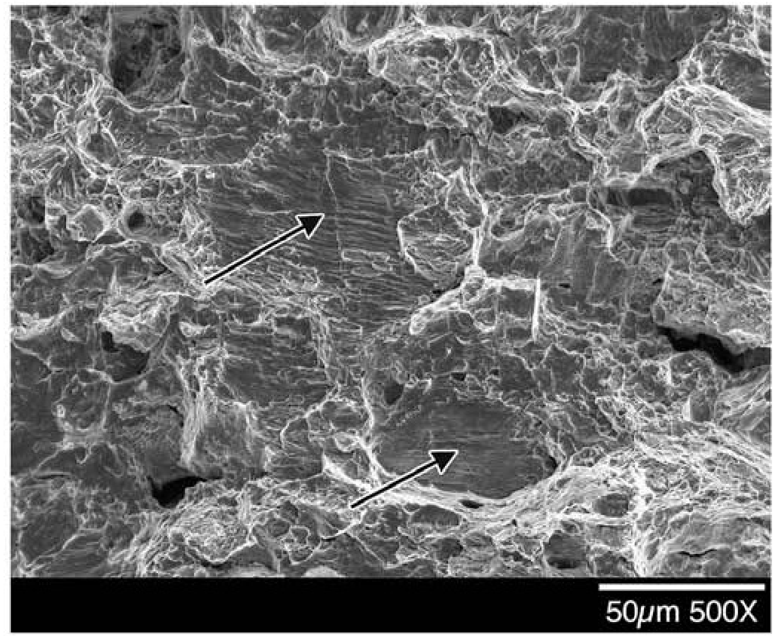
Hydrogen alters fracture mode: forgings

Non-charged



H_2-charged



- Non-charged fracture surfaces show equiaxed dimples
- H_2-charged fracture surfaces exhibit facets
  - Equiaxed dimples almost absent

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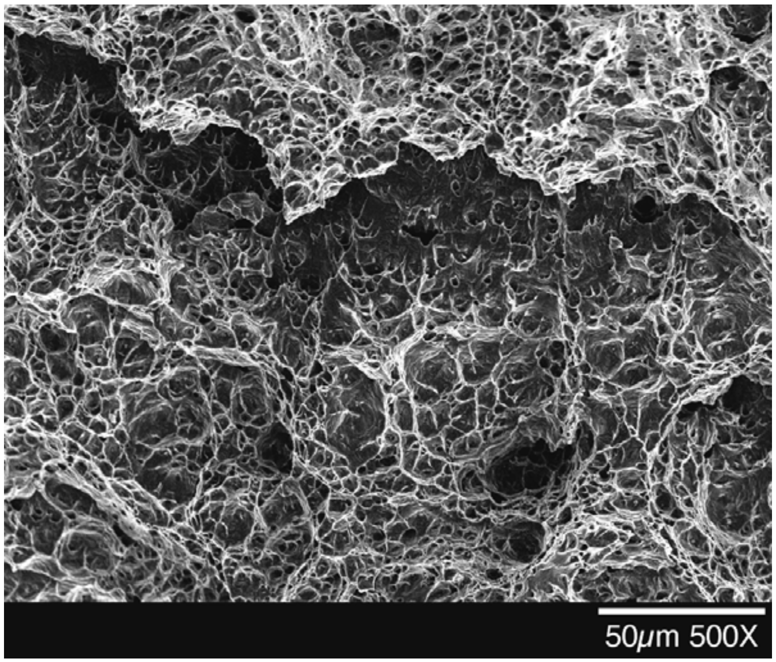
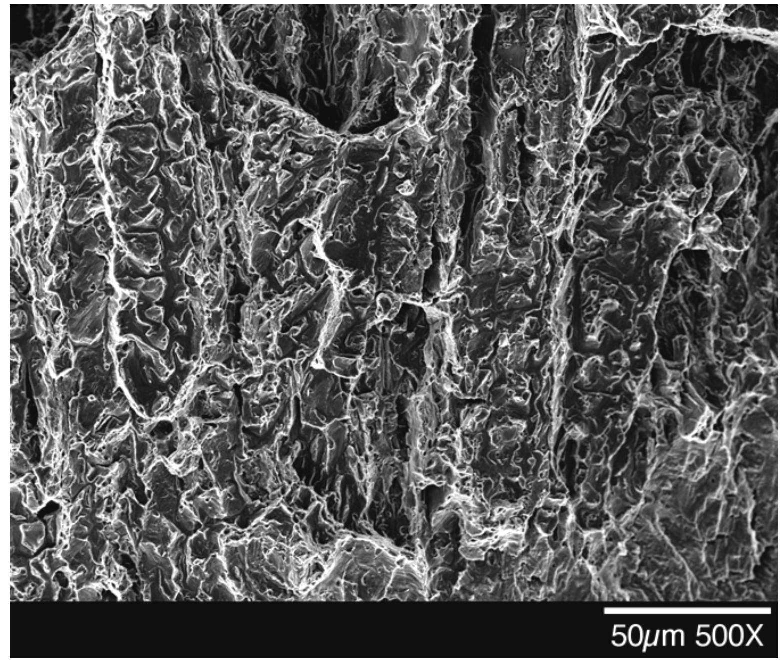
Hydrogen alters fracture mode: GTA welds

Non-charged



H_2-charged

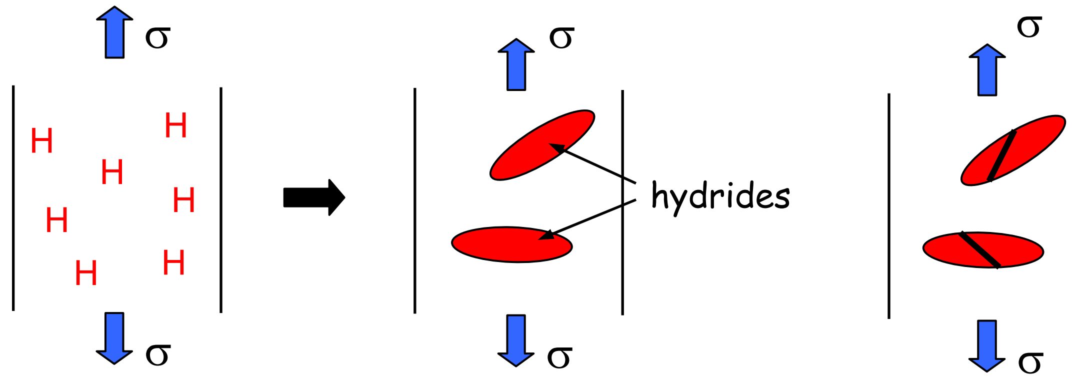


- Non-charged fracture surfaces show equiaxed dimples
- H_2-charged fracture surfaces display oriented structure
  - Equiaxed dimples almost absent

Hydrogen embrittlement mechanisms

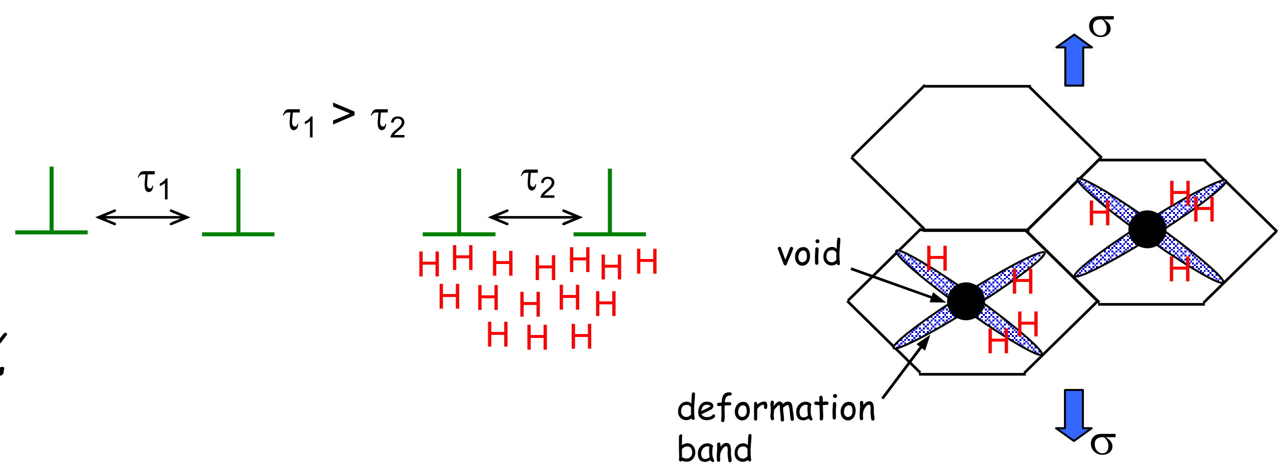
Hydrides

D. Westlake,
H. Birnbaum



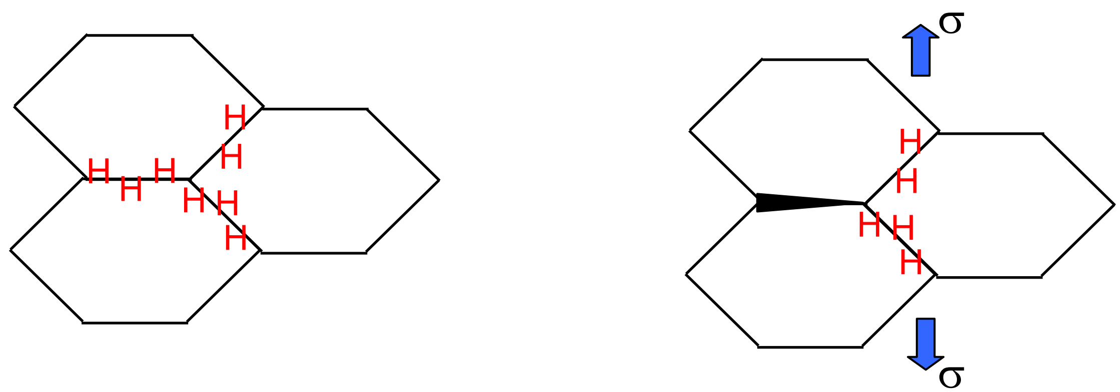
Hydrogen-Enhanced Localized Plasticity (H.E.L.P.)

C. Beachem, H. Birnbaum,
I. Robertson, P. Sofronis



Hydrogen-Enhanced Decohesion

A. Troiano, R. Oriani



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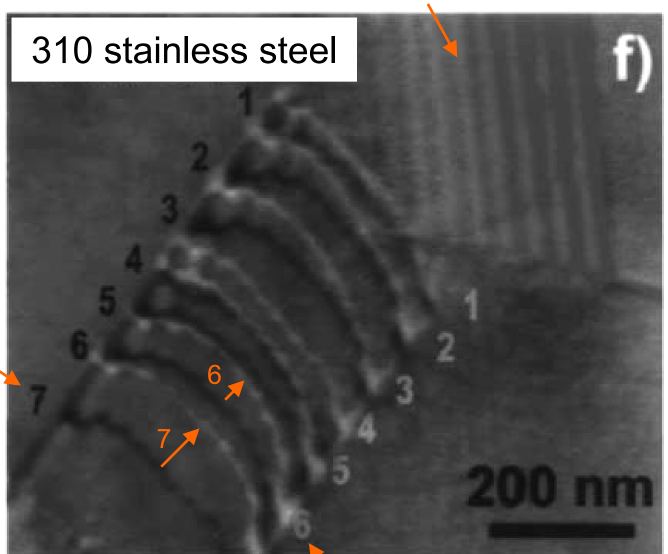
Hydrogen-enhanced localized plasticity (HELP) conclusively demonstrated for numerous metals



I. Robertson, Eng. Fract. Mech., 2001

- Enhanced dislocation mobility (softening) and stress shielding concept demonstrated through *in situ* TEM experiments
- Other observations:
  - H stabilizes edge component of mixed dislocations
  - H promotes localized deformation

Unresolved issue: "What is the detailed mechanism by which the enhanced dislocation mobility causes fracture in *bulk* specimens?" *H. Birnbaum, CDI 96, 1997*

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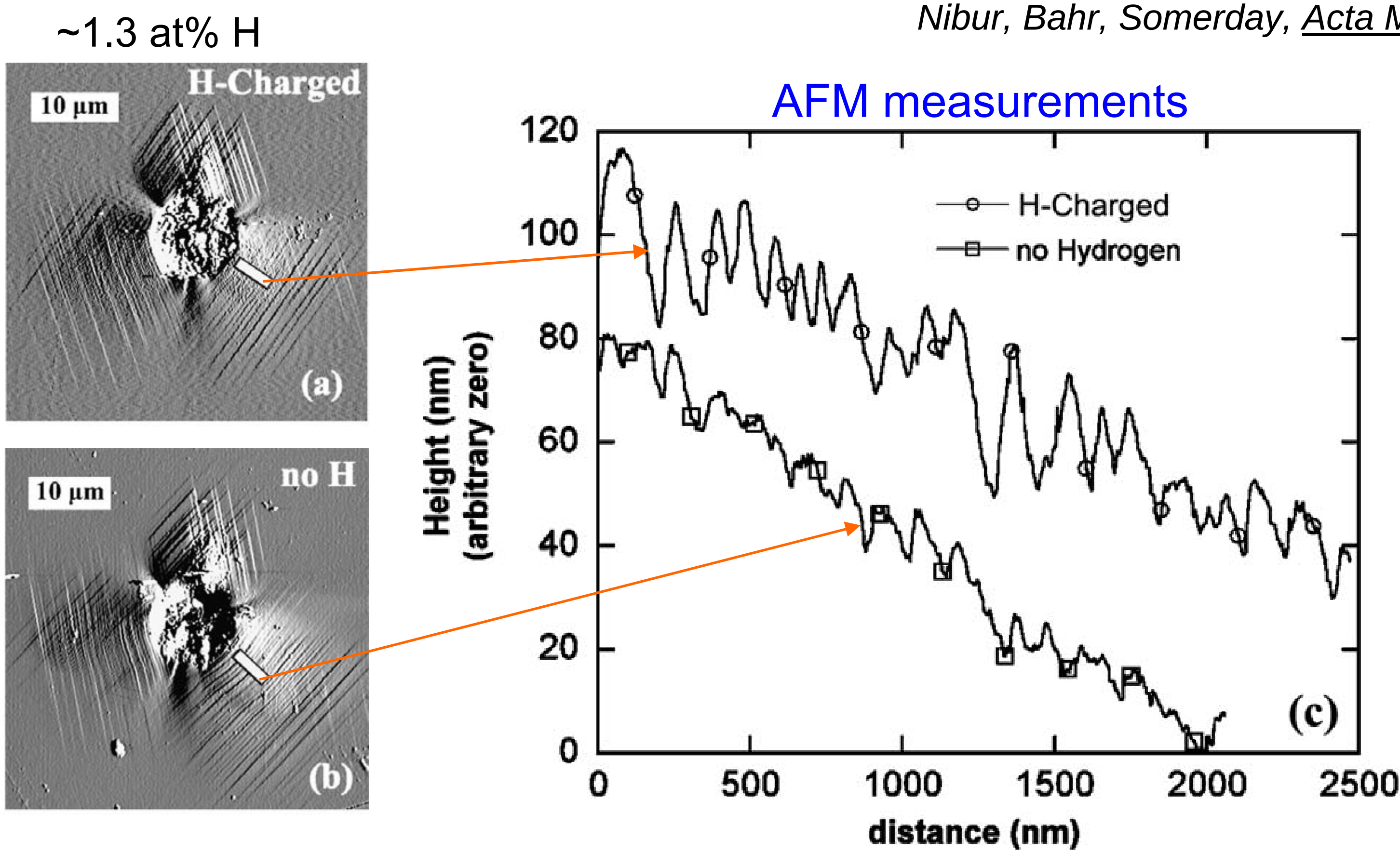
Indentation tests show that hydrogen promotes localized deformation in 21-6-9 stainless steel

Nibur, Bahr, Somerday, Acta Mat, 2006



Pronounced localized deformation in H-charged material reflects H-enhanced dislocation mobility

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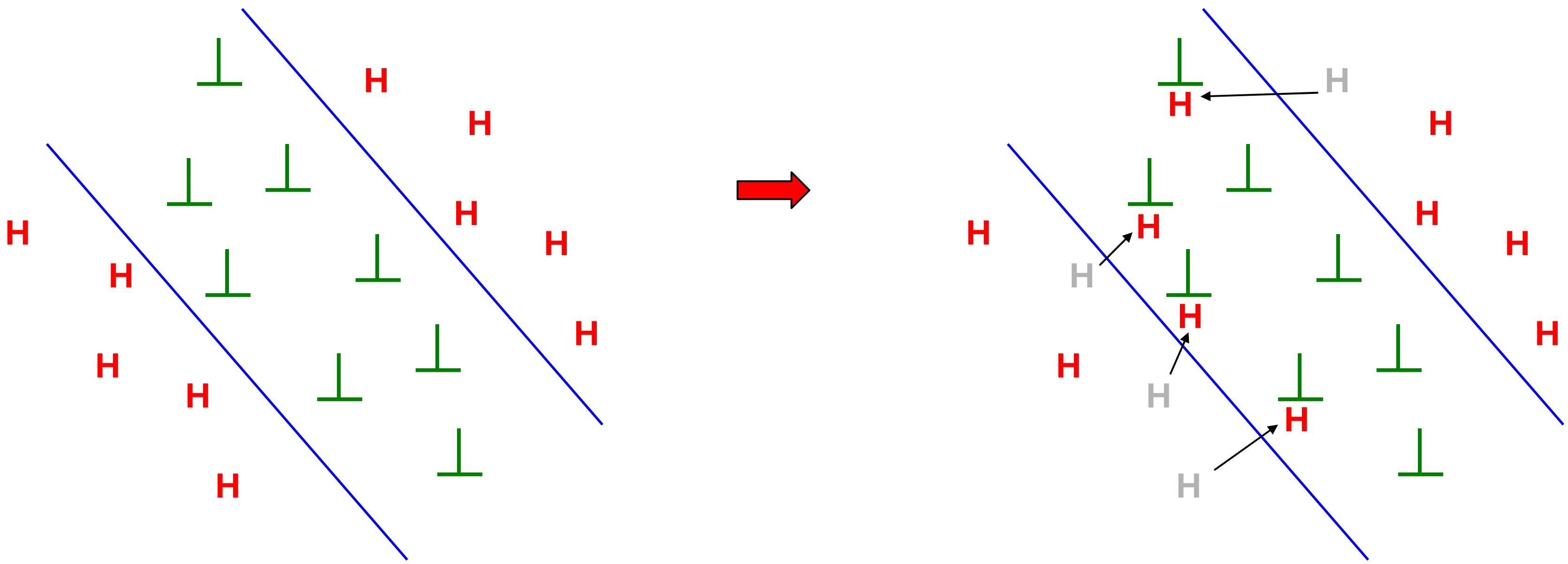
Rationale for link between localized deformation and H-enhanced dislocation mobility

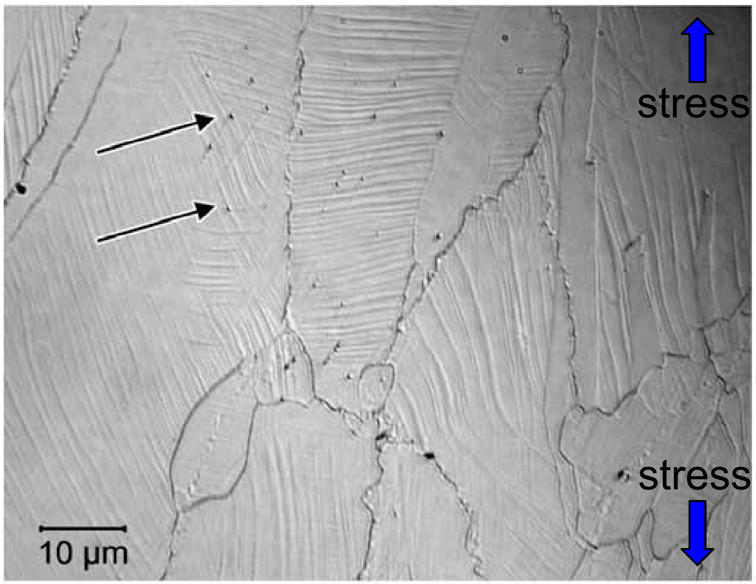
Deformation localizes due to metallurgical features (SFE, SRO, coherent precipitates, etc.)

Hydrogen concentrates in deformation band, enhancing dislocation mobility and further localizing deformation

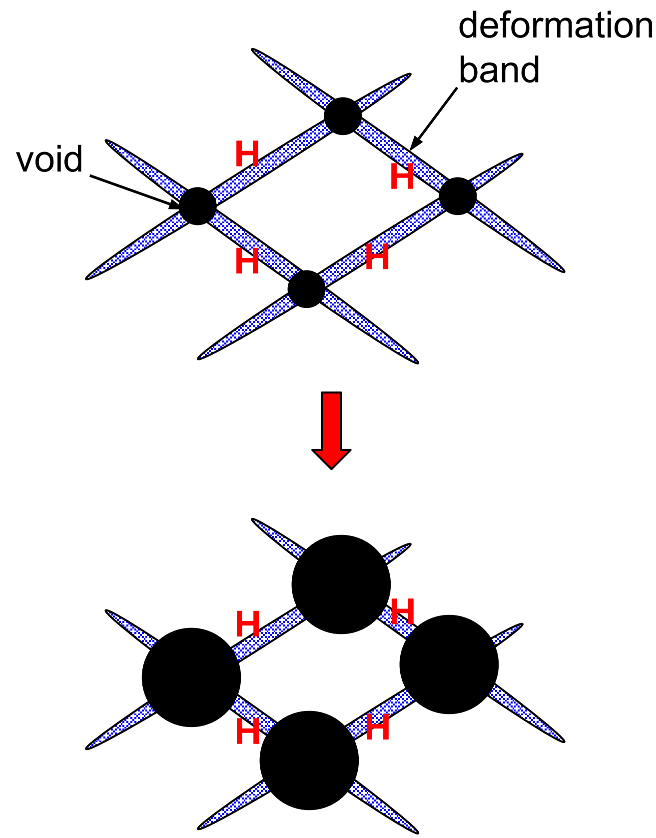


H-induced localized deformation leads to void formation at intersection of deformation bands

Fracture profile from H-precharged 21-6-9 with no ferrite



optical image



Observations provide link between H-enhanced plasticity and fracture in bulk specimens

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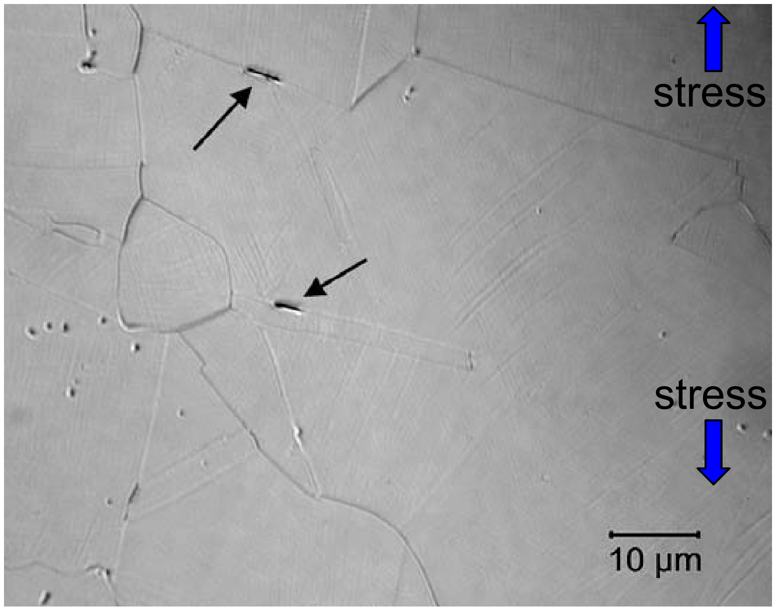
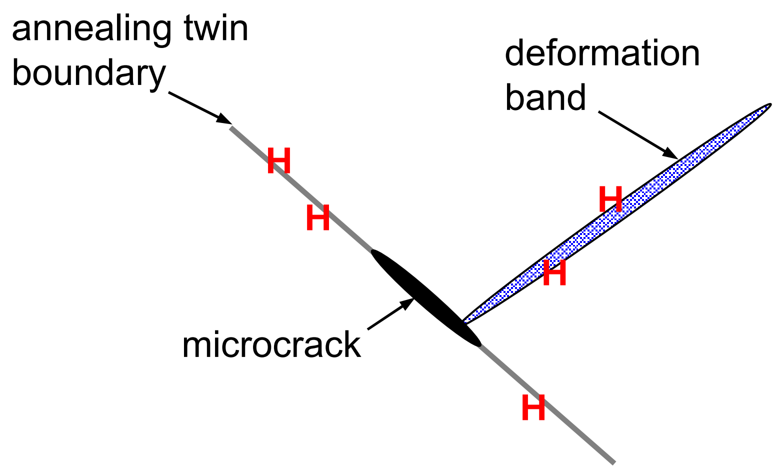
Microcracks at boundaries associated with H-induced localized deformation?

Fracture profile from H-precharged 21-6-9 with no ferrite



optical image



Can deformation-induced stress concentration initiate microcrack without H effect on boundary cohesion?

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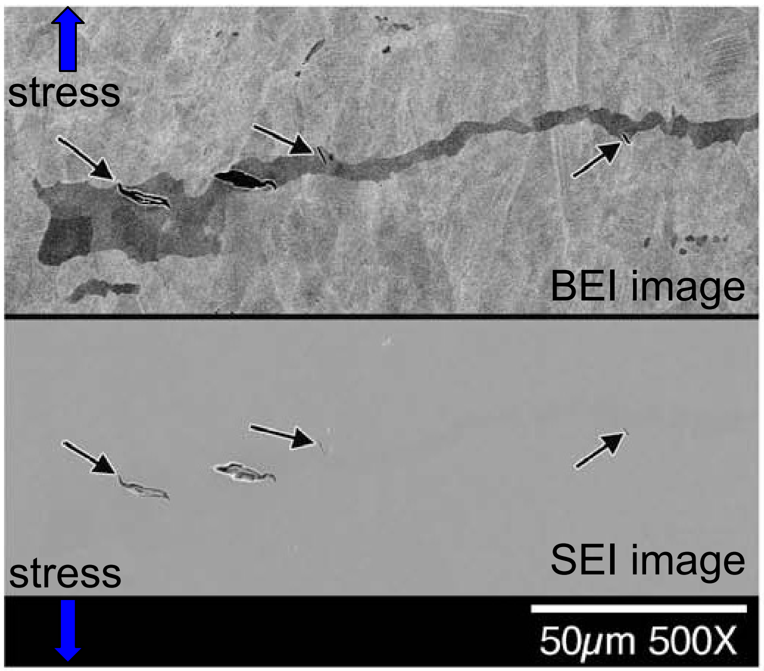
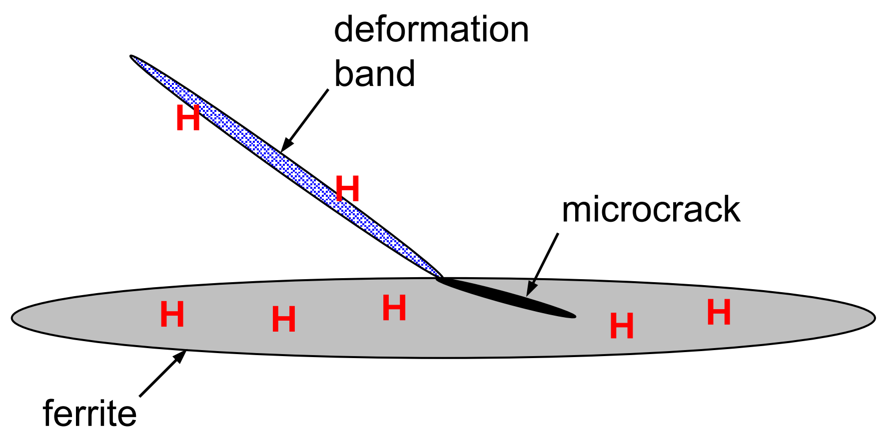
Microcracks in ferrite associated with H-induced localized deformation in austenite?

Fracture profile from H-precharged 21-6-9 with 2 vol% ferrite





Can deformation-induced stress concentration initiate microcrack without H effect on lattice cohesion?

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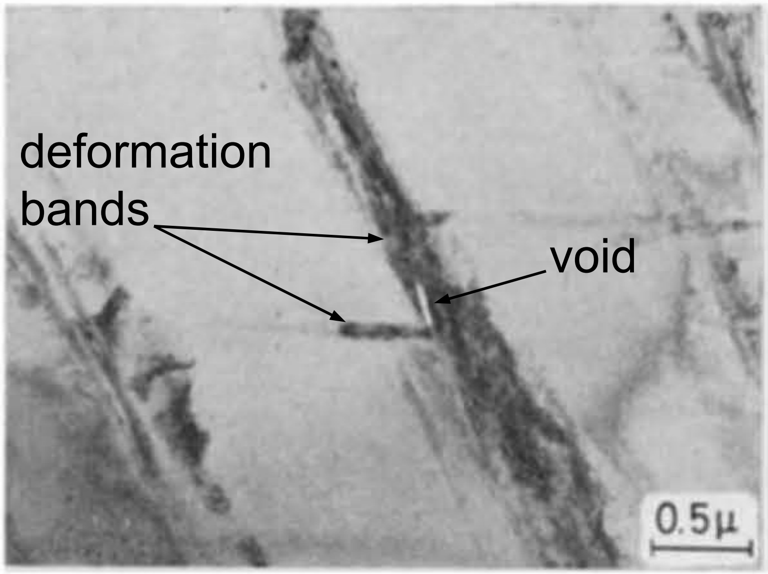
Results from other systems demonstrate that localized deformation alone can govern fracture

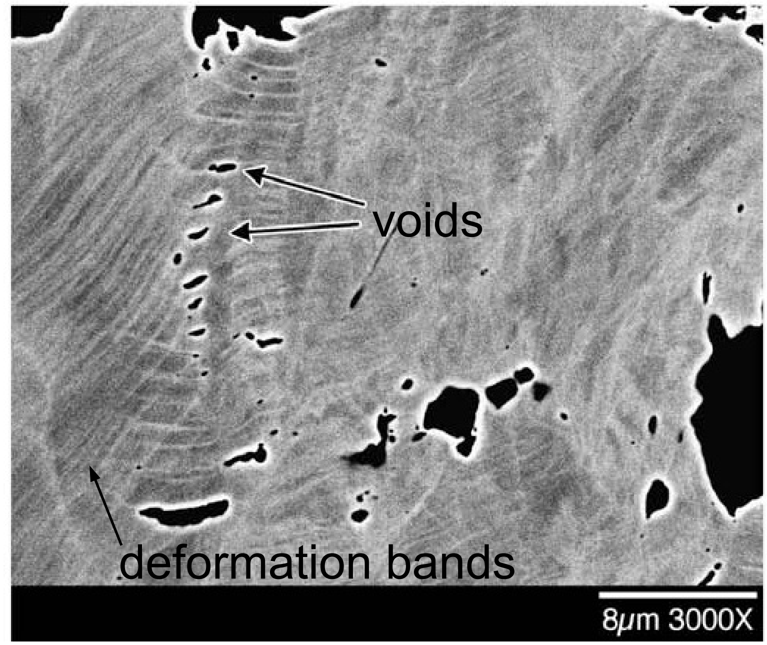
Ti-11 at% Mo (no H)



TEM image

A. Gysler et al., Acta Metall., 1974

H-precharged 21-6-9



BEI image

Nibur, Somerday, San Marchi, Balch, Acta Mat, 2009

- H-assisted fracture in 21-6-9 may be attributed solely to H-enhanced localized deformation
  - Hydrogen need not directly lower fracture resistance

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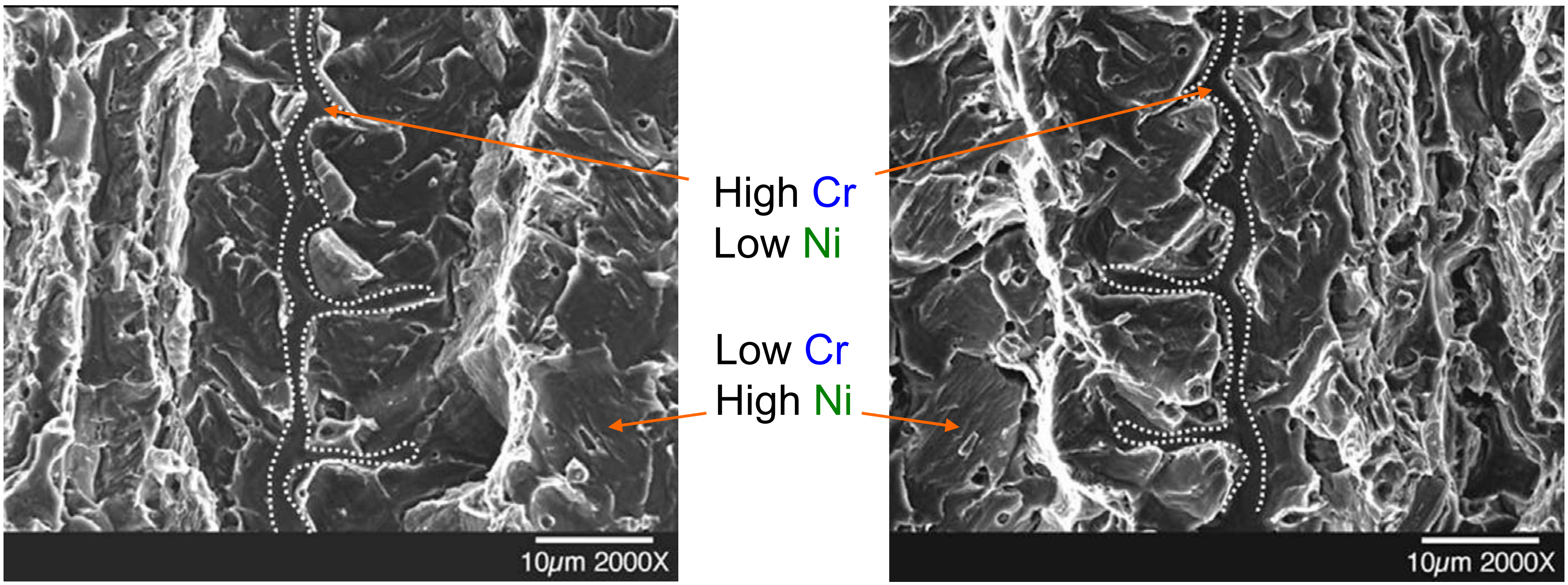
What is role of ferrite in fracture of H_2-charged welds?



EDS analysis on matching fracture surfaces reveals fracture through ferrite phase in H_2-charged welds

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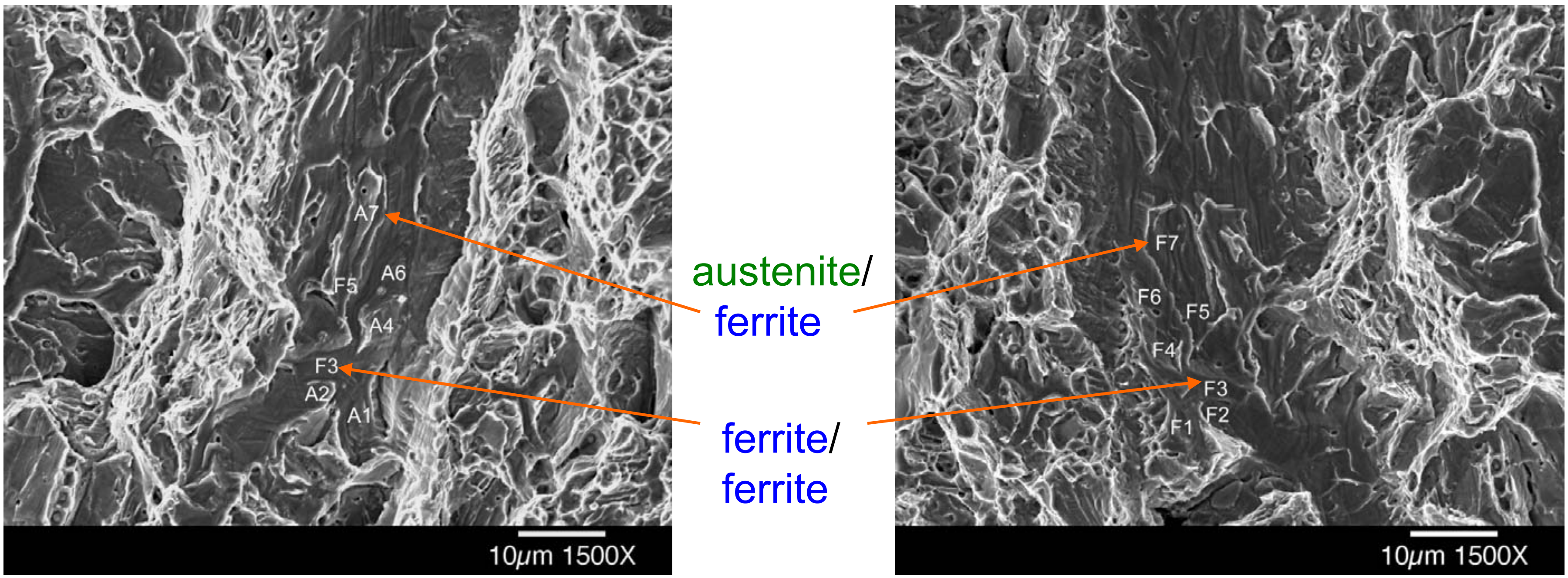
What is role of ferrite in fracture of H_2-charged welds?



Analysis reveals fracture through ferrite phase *and* along ferrite/austenite interfaces in H_2-charged welds

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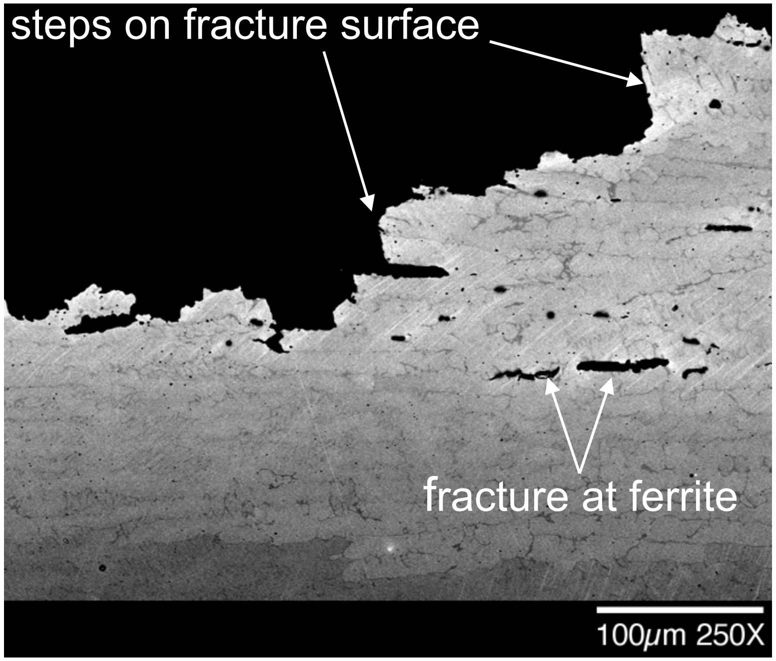
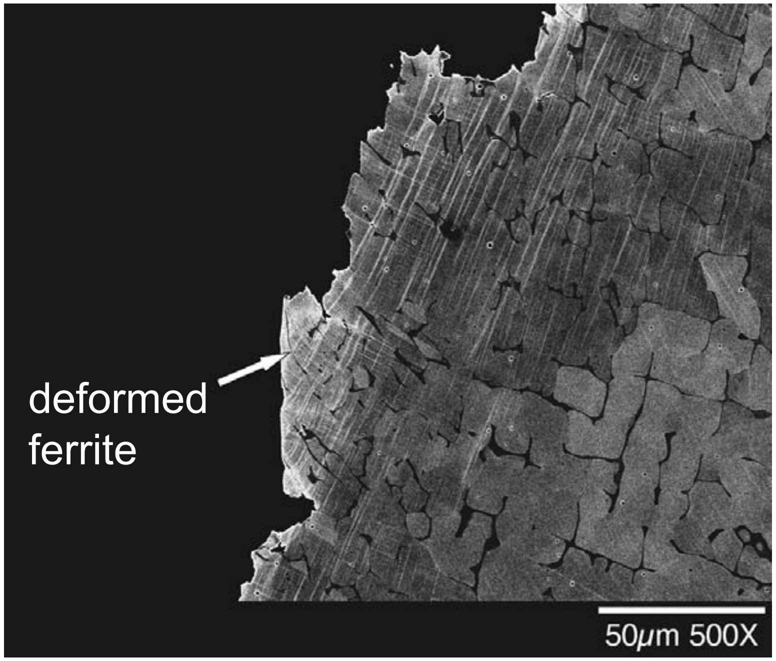
Fracture profiles support crack formation at ferrite and show distinct steps on fracture surface



SEM SEI image



SEM BEI image

Step formation on fracture surfaces of welds is associated with severe deformation

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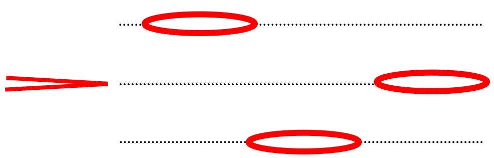
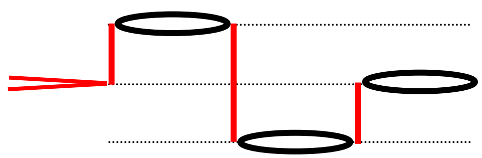
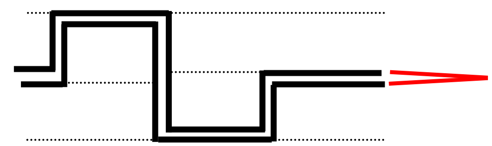
Role of hydrogen in fracture process of welds: microcrack formation at ferrite



microcracks form along dendritic structure away from main crack → fracture of ferrite



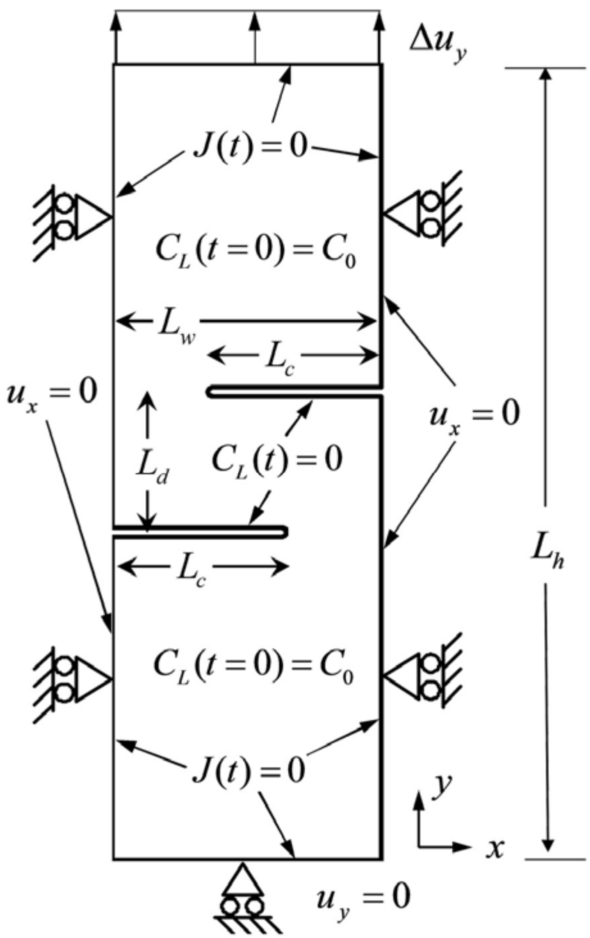
microcracks link *via* localized deformation



crack advances creating "stepped" fracture surface

Does hydrogen have a role in linking microcracks?

Hypothesis that hydrogen intensifies deformation between microcracks explored using FEM



- Physical basis of model
  - Hydrogen trapped at dislocations
  - Trapped hydrogen facilitates dislocation motion
  - Enhanced dislocation motion captured in constitutive relationship:

    $$\sigma_Y(\varepsilon^p, c_T) = \sigma_0[c_T(\xi - 1) + 1]F(\varepsilon^p)$$

  - Determine ξ by assuming hydrogen reduces flow stress by 20% and 40%
- Simulate redistribution of hydrogen into traps and plastic strains

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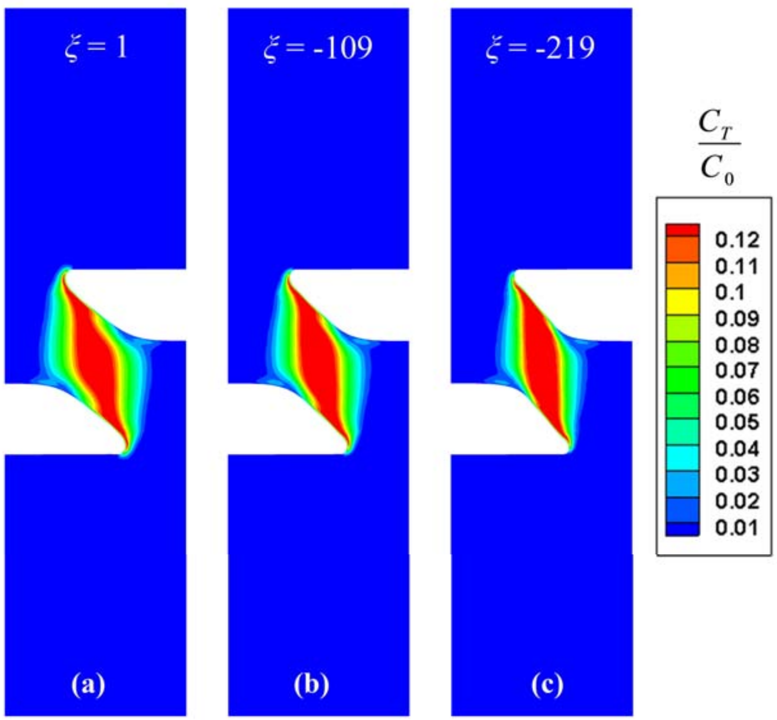
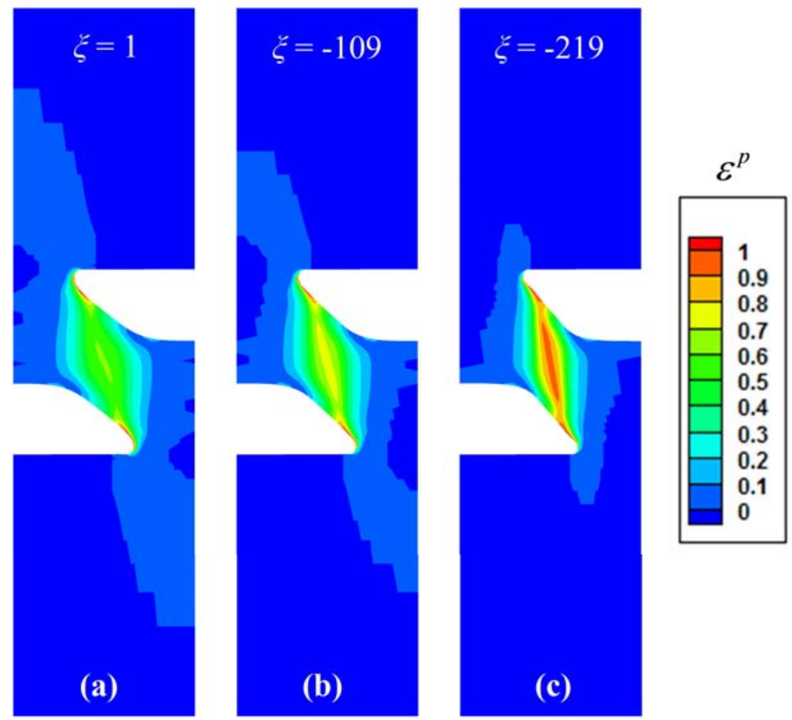
FEM results show intense strain between microcracks from hydrogen-enhanced plasticity

C_o=230 wppm



no softening



Hydrogen causes microcracking at ferrite *and* may facilitate microcrack linking by promoting intense deformation

Conclusions

- Hydrogen reduces fracture toughness of 21-6-9 forgings and 21-6-9/21-6-9 GTA welds
  - Initiation toughness remains high in H_2-charged materials: K_J >200 MPa $m^{1/2}$ in forgings, K_J > 130 MPa $m^{1/2}$ in welds
- Hydrogen-enhanced plasticity governs fracture in H_2-charged 21-6-9 forgings
  - Fracture mechanisms can be interpreted without invoking direct hydrogen effect on fracture resistance
- Hydrogen-enhanced plasticity may also govern fracture in H_2-charged 21-6-9/21-6-9 welds
  - Linking of microcracks due to intense deformation may be facilitated by hydrogen
  - Microcracks at ferrite may result from intersection of deformation bands in austenite

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