Durability & Reliability of SOFC Materials and Components

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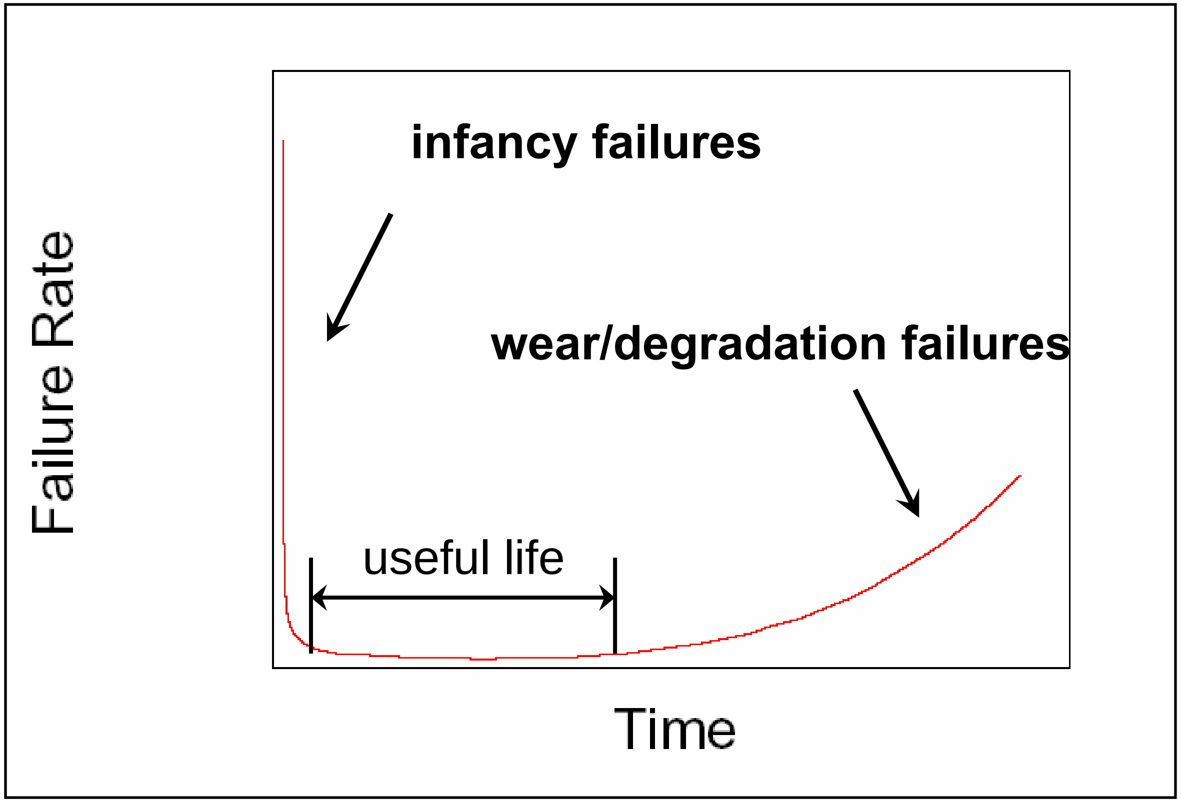
Outline

- Background
- Reduction of NiO-YSZ precursor materials for anodes
  - Kinetics
  - Effect of reduction on mechanical properties of Ni-based anode materials
    - Elastic properties
    - Strength
    - Fracture Toughness
- Effect of cyclic conditions (thermal, oxidation-reduction) on mechanical properties of NiO-YSZ anode materials.
- Stresses during fuel cell assembly
- Summary
- Future work

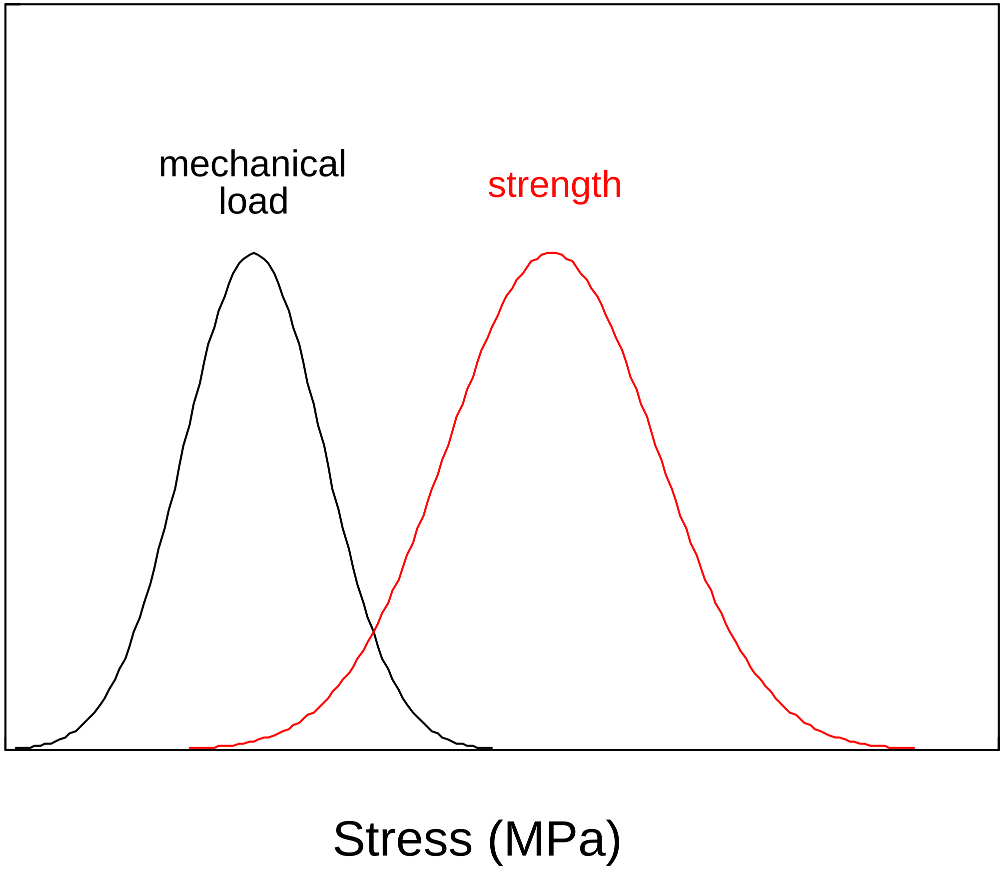
Background

The failure rate of complex systems can be described with a bathtube curve



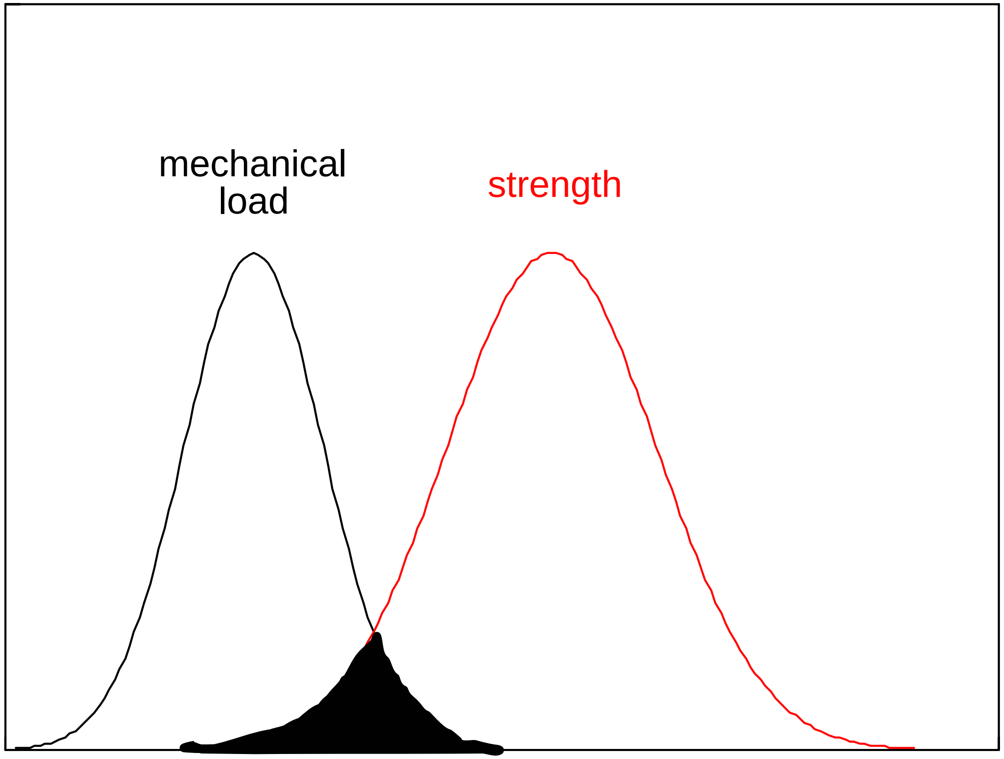
Background

Mechanical failure is determined by the spectrum of mechanical loads and the distribution of strengths for materials that exhibit stochastic strength



Background

The lower tail of the distribution of strengths dictates the reliability of materials that exhibits stochastic strength.



Stress (MPa)

Outline

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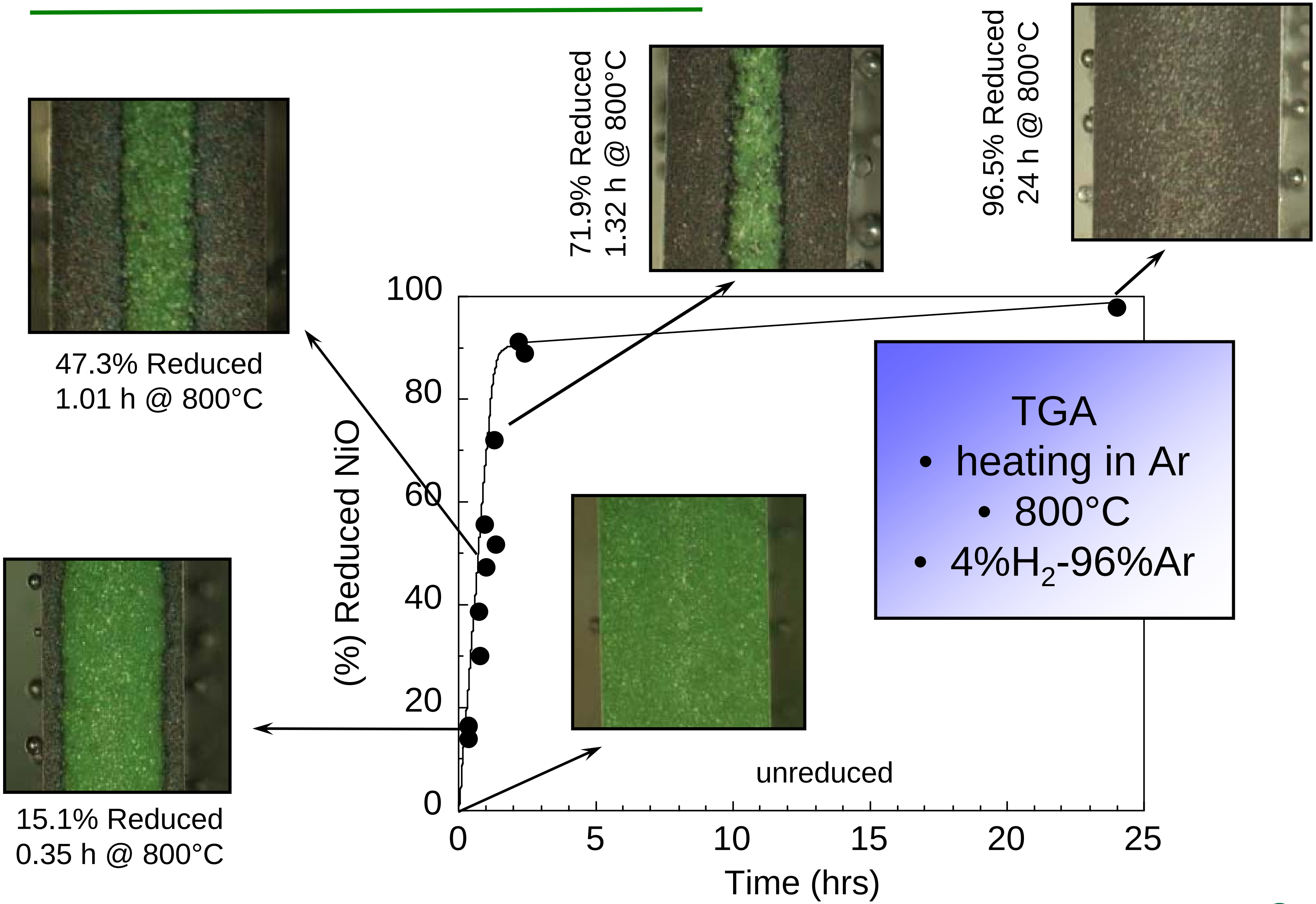
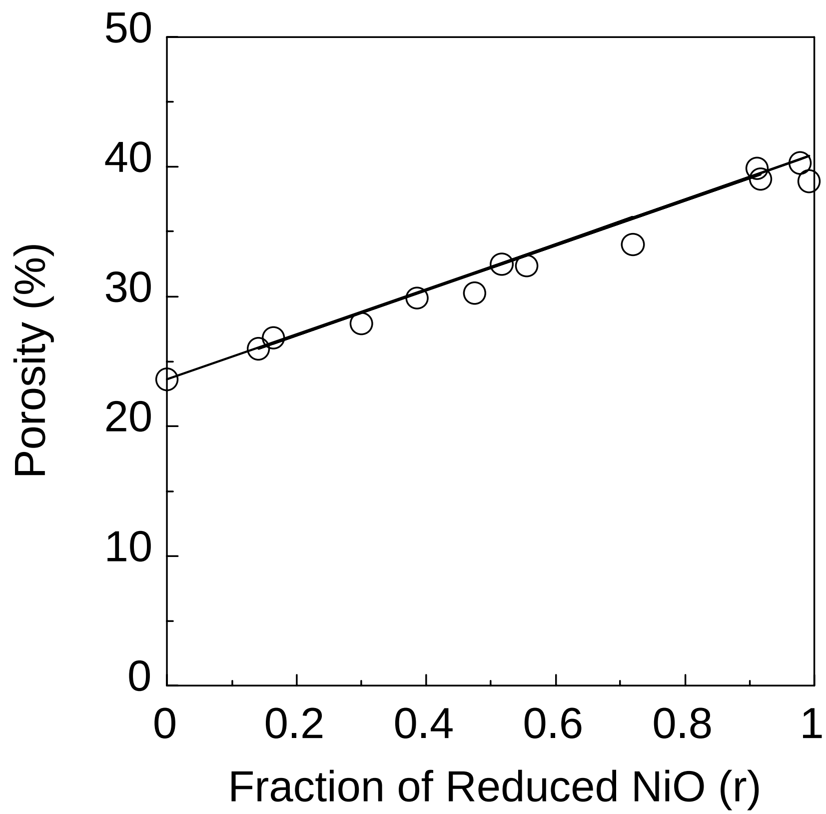
Kinetics of NiO-YSZ Reduction



Kinetics of NiO-YSZ Reduction

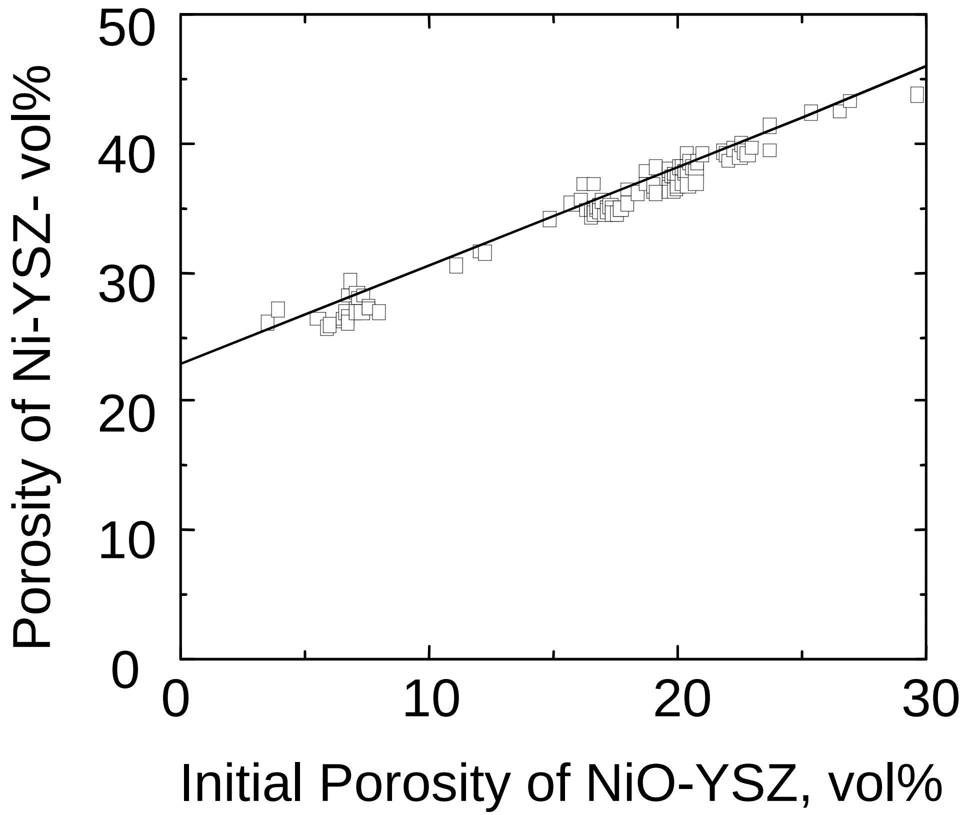
- NiO-YSZ samples were exposed to a gas mixture of 4%H_2-95%Ar at 800°C for different periods of time up to 24 hrs.
- Porosity increases with increasing fraction of reduced NiO

ASTM C20

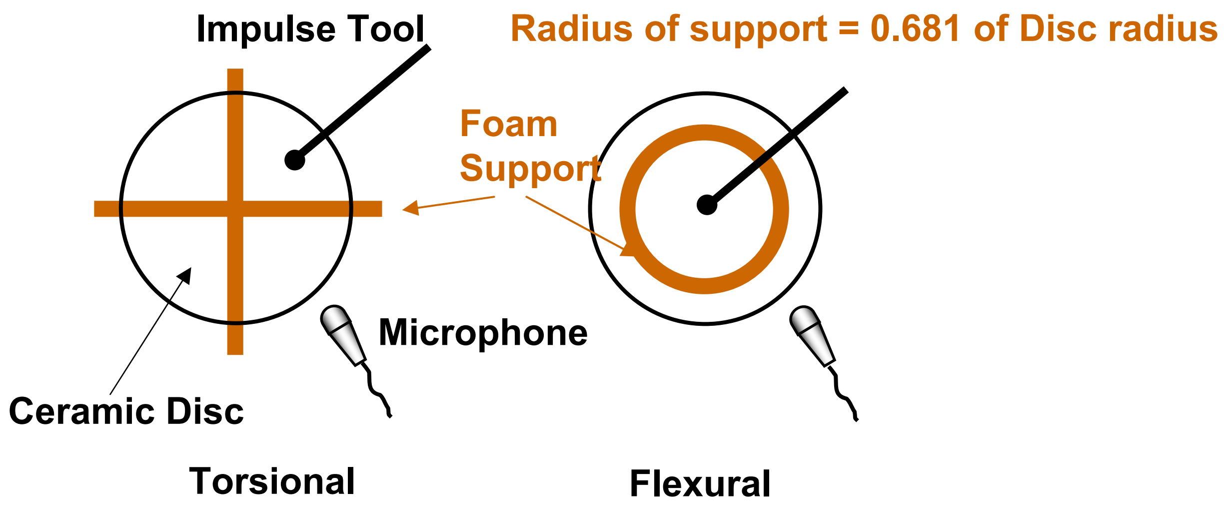


Kinetics of NiO-YSZ Reduction

- NiO-YSZ test specimens were prepared with different amounts of porosity
- On average test specimens had the same thickness.
- NiO-YSZ samples were exposed to a gas mixture of 4%H_2-95%Ar at 800°C for 24 hrs.
- Porosity increases after reduction



Determination of elastic properties

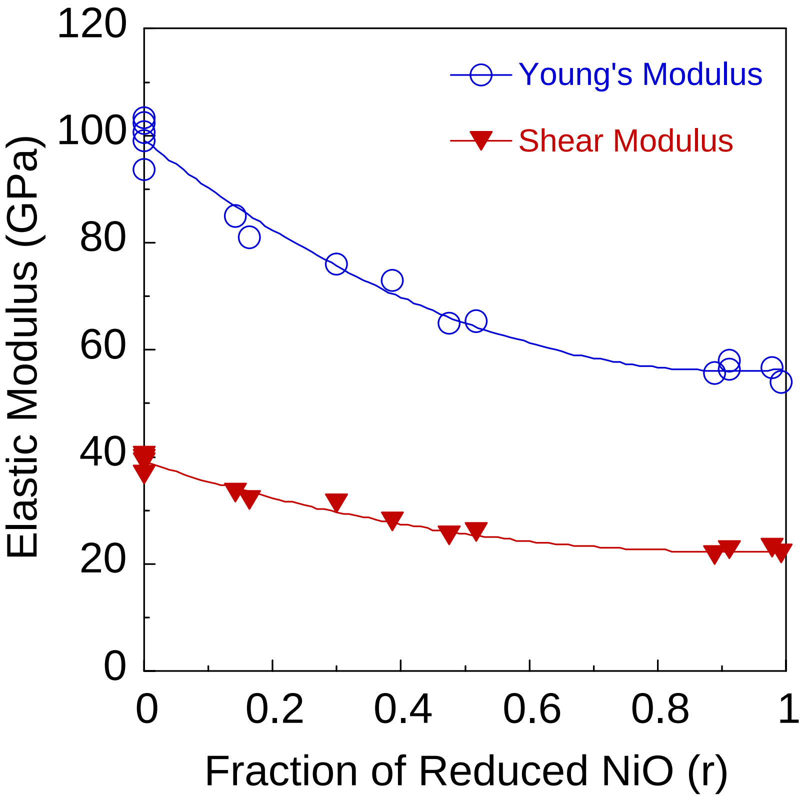


Impulse Excitation
ASTM C1259-98

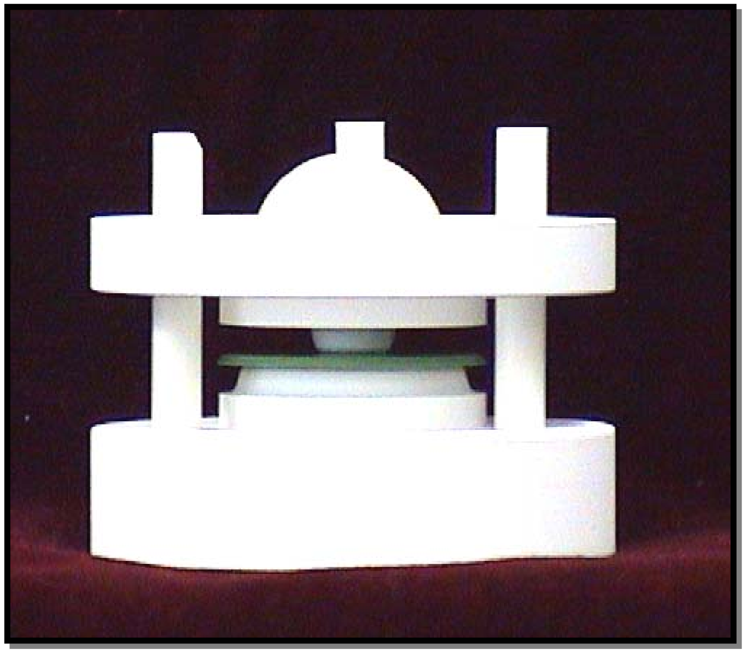
$E_{t,f}$ = Young's modulus as measured by torsional/flexural resonance
m = mass of the disc
t = height of the disc
D = diameter of the disc
$F_{t,f}$ = fundamental torsional/flexural resonant frequency of the disc
K_t = a correction factor (ASTM C1259-98)
μ = Poisson's ratio

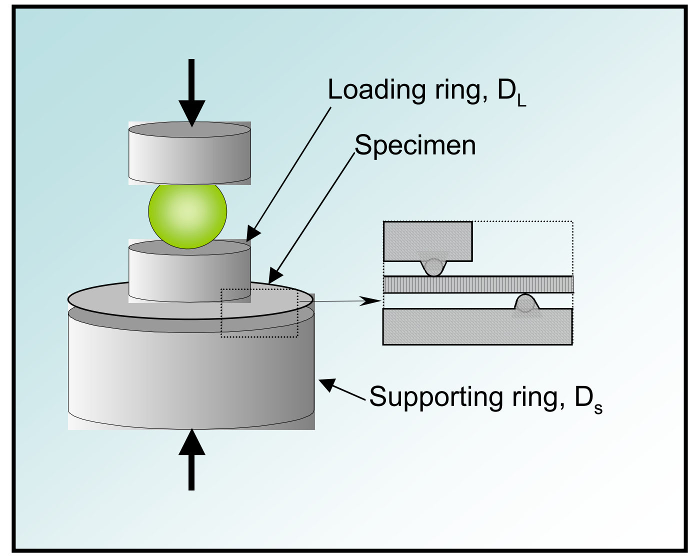
Effect of reduction on Elastic properties of NiO-YSZ

- NiO-YSZ samples were exposed to a gas mixture of 4%H_2-95%Ar at 800°C for different periods of time up to 24 hrs.
- Young's and shear moduli were obtained at 20°C after reduction using impulse excitation and resonant ultrasound spectroscopy.
- Elastic moduli decreases with fraction of reduced NiO.
- Changes are mostly due to increase in porosity as a result of reduction.



Biaxial Strength Ring-on-Ring ASTM C1499



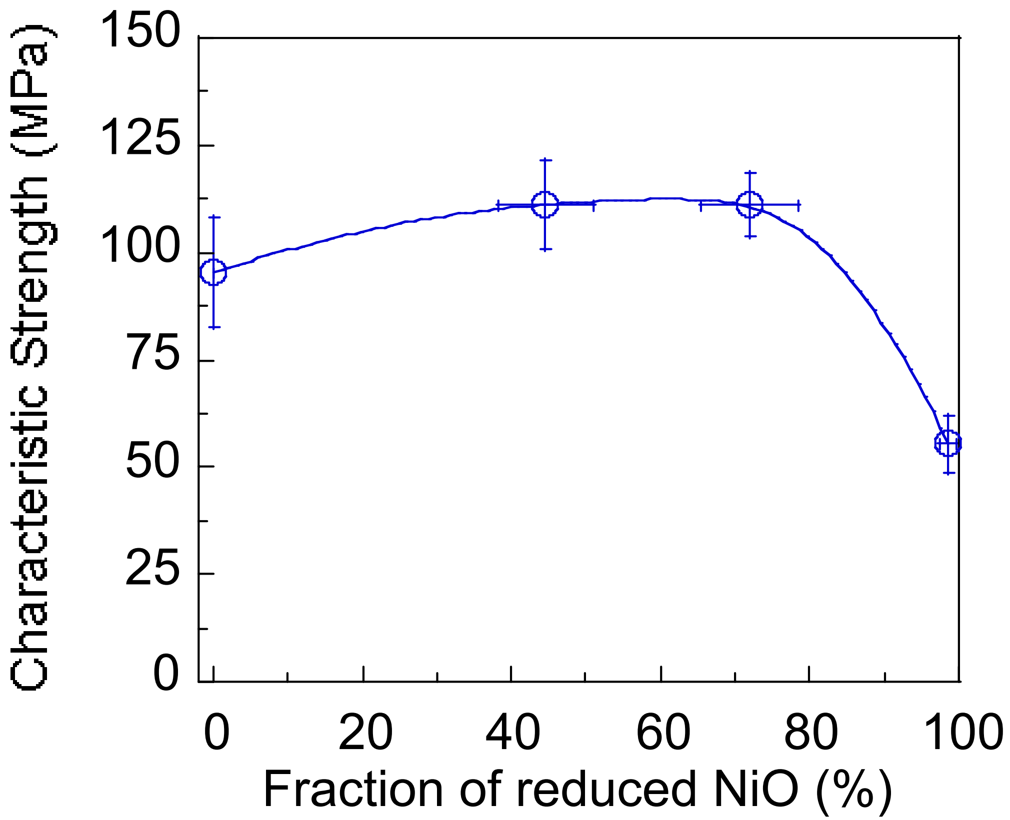


$$\sigma_f = \frac{3F}{2\pi h^2}\left[(1-\nu)\frac{D_s^{\,2} - D_l^{\,2}}{2D^2} + (1+\nu)\ln\frac{D_s}{D_l}\right]$$

where F is breaking load, h sample thickness, ν is Poisson's ratio and D, D_s and D_l are diameter of sample, supporting ring and loading ring, respectively

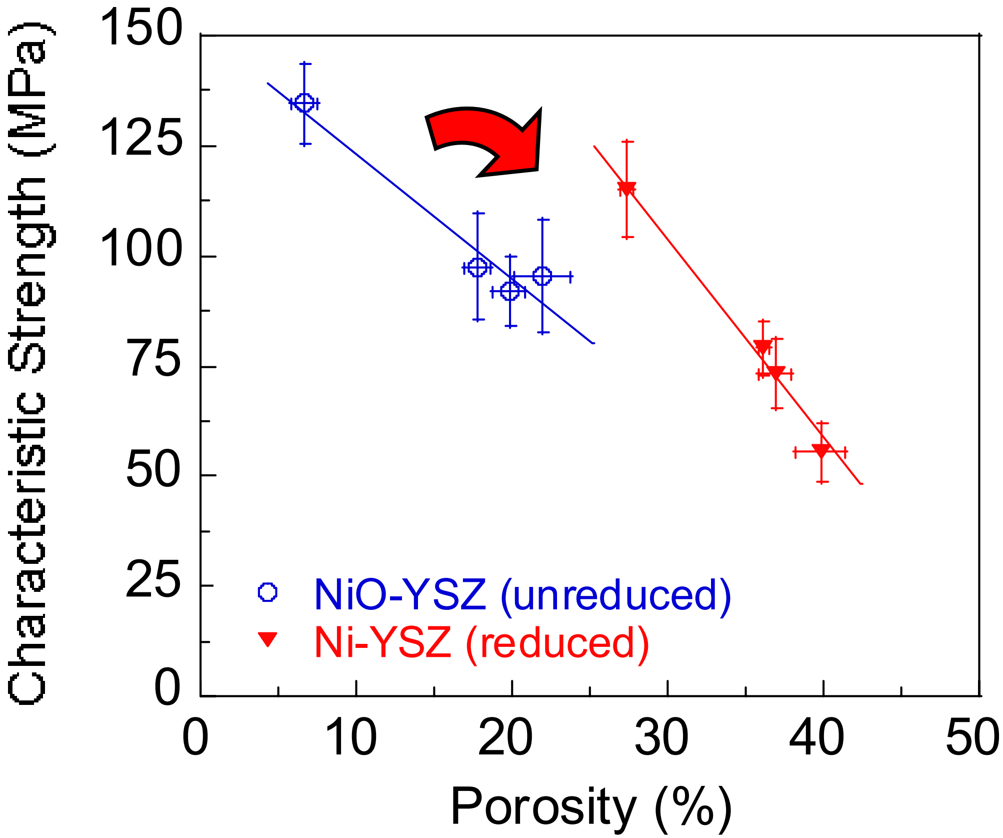
Biaxial Strength of NiO-YSZ and Ni-YSZ materials

- NiO-YSZ samples were exposed to a gas mixture of 4%H_2-95%Ar at 800°C for various periods of time up to 24 hrs.
- On average the samples had the same thickness and initial porosity (~20%).
- The biaxial strength of fully-reduced NiO-YSZ (Ni-YSZ) materials is lower than that of its precursor.



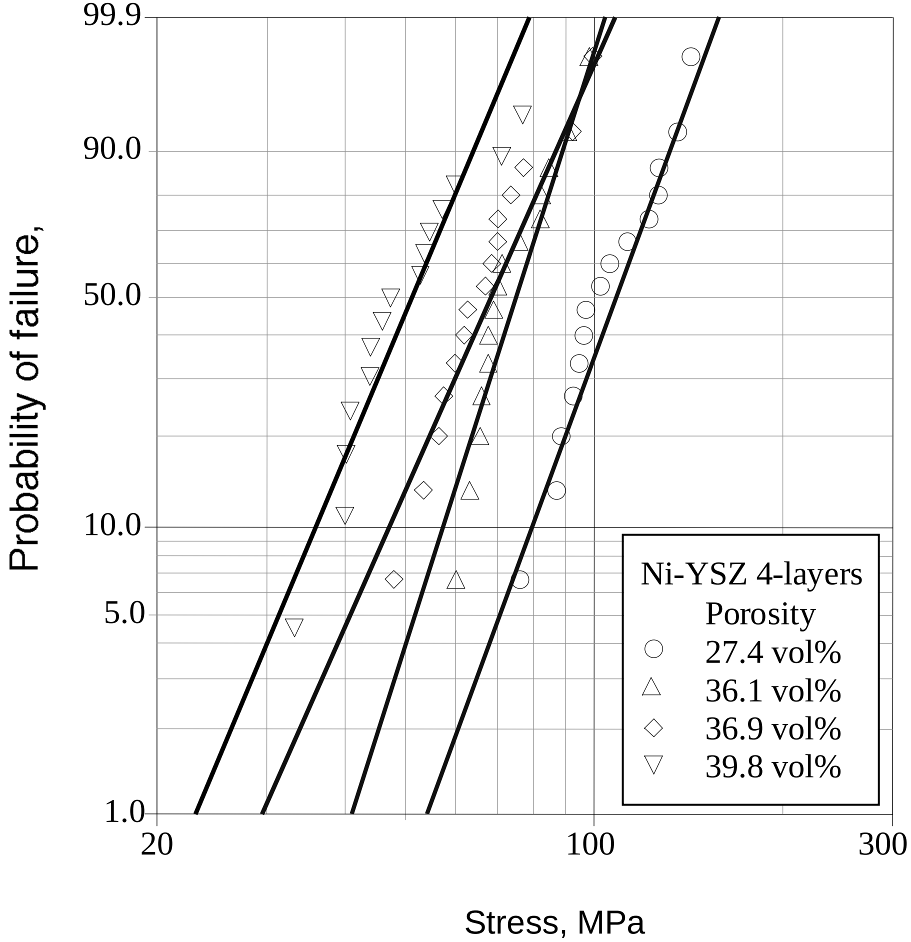
Biaxial Strength of NiO-YSZ and Ni-YSZ materials

- The porosity of NiO-YSZ samples increases after reduction in a gas mixture of 4%H_2-95%Ar at 800°C for 24 hrs.
- On average the samples had the same thickness.
- The biaxial strength of NiO-YSZ decreases after reduction into Ni-YSZ.
- Biaxial strength of both materials decreases with increasing porosity.



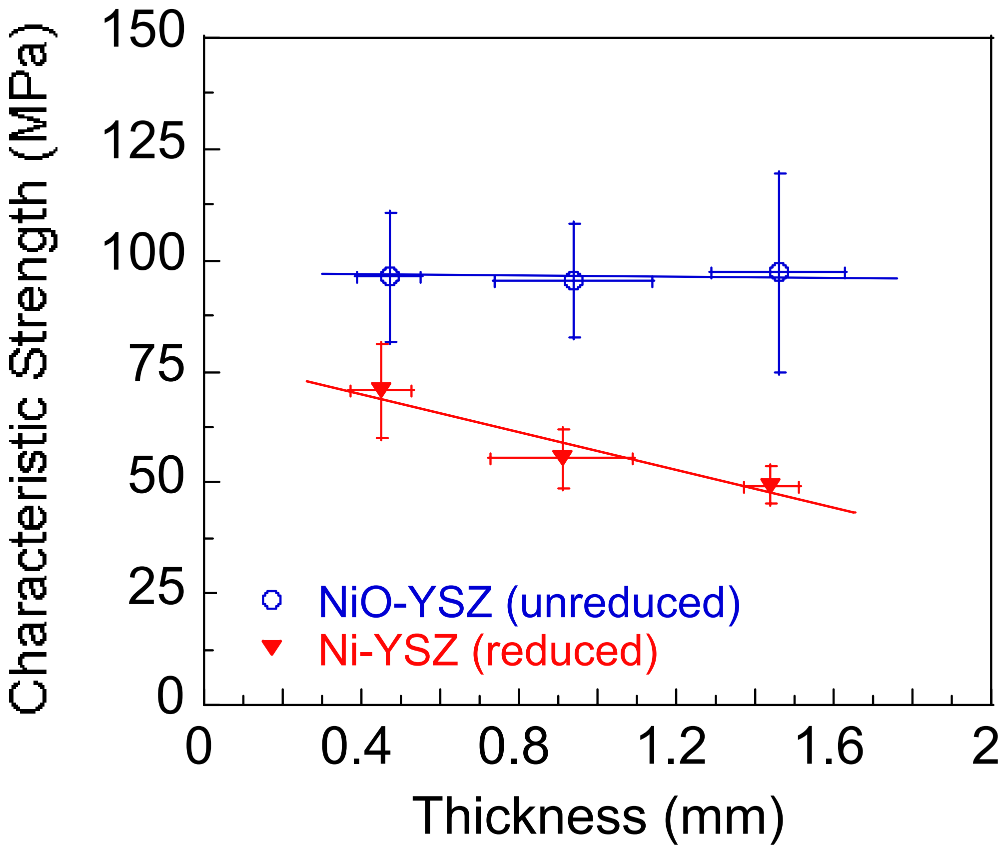
Biaxial Strength of Ni-YSZ materials as a function of porosity

- NiO-YSZ precursors with different porosities were reduced in a gas mixture of 4%H_2-95%Ar at 800°C for 24 hrs.
- All samples had on average the same thickness.
- The biaxial strength of Ni-YSZ materials decreases with increasing porosity.

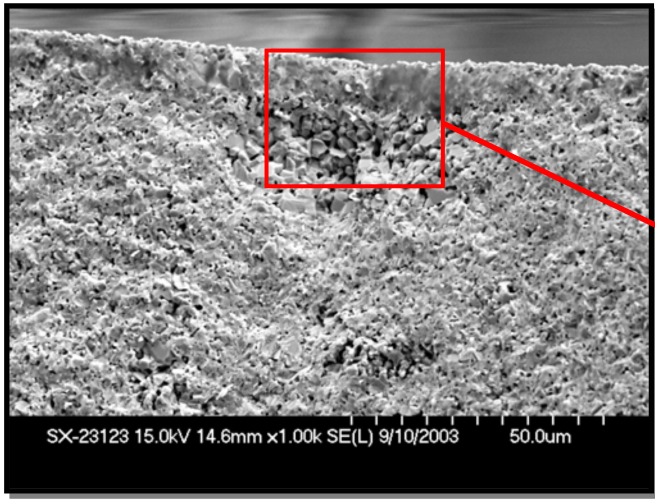


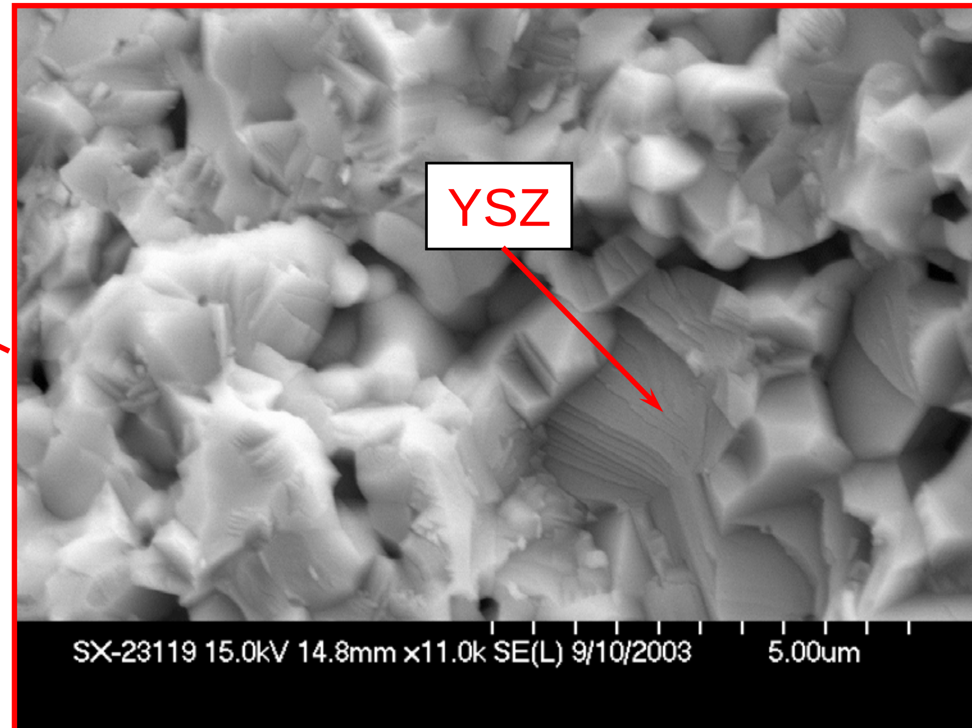
Effect of sample thickness on Strength of NiO-YSZ and Ni-YSZ

- While the characteristic strength of NiO-YSZ is insensitive to the thickness of the test specimen, the characteristic strength of Ni-YSZ samples <u>decreases</u> with increasing thickness.
- Ni-YSZ was obtained after reducing NiO-YSZ in a gas mixture of 4%H_2-95%Ar at 800°C for 24 hrs.
- On average the porosity of the initial NiO-YSZ samples was the same (~ 20%).



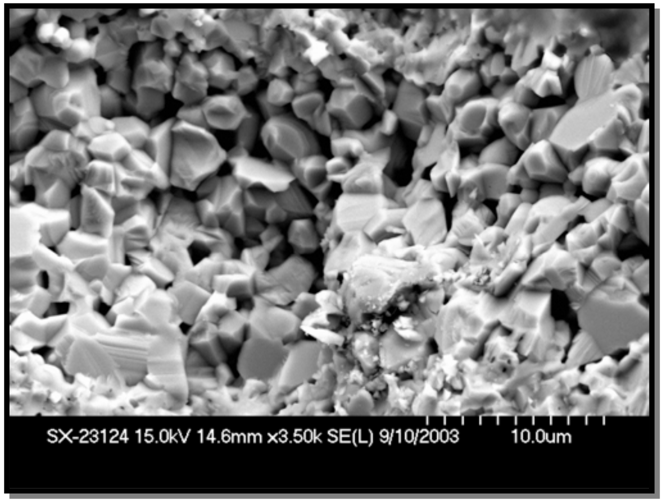
Biaxial Strength of NiO-YSZ materials

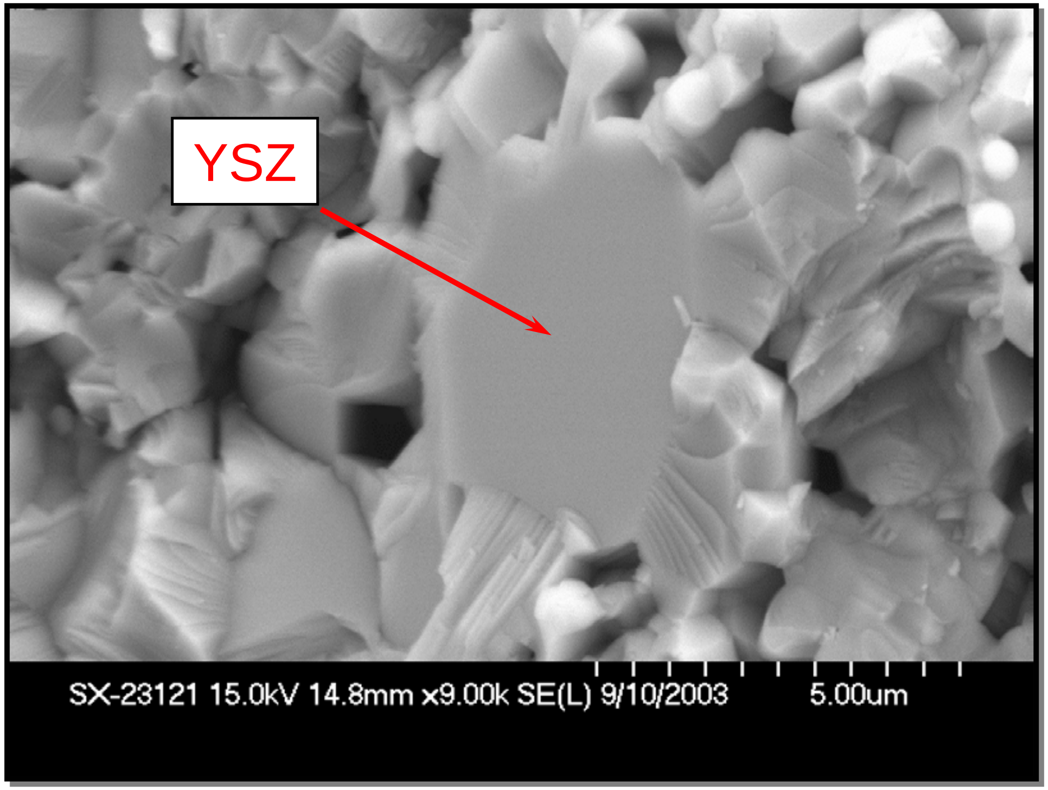




Fracture surface of unreduced NiO-YSZ sample.
Initial porosity 6%

Biaxial Strength of NiO-YSZ materials





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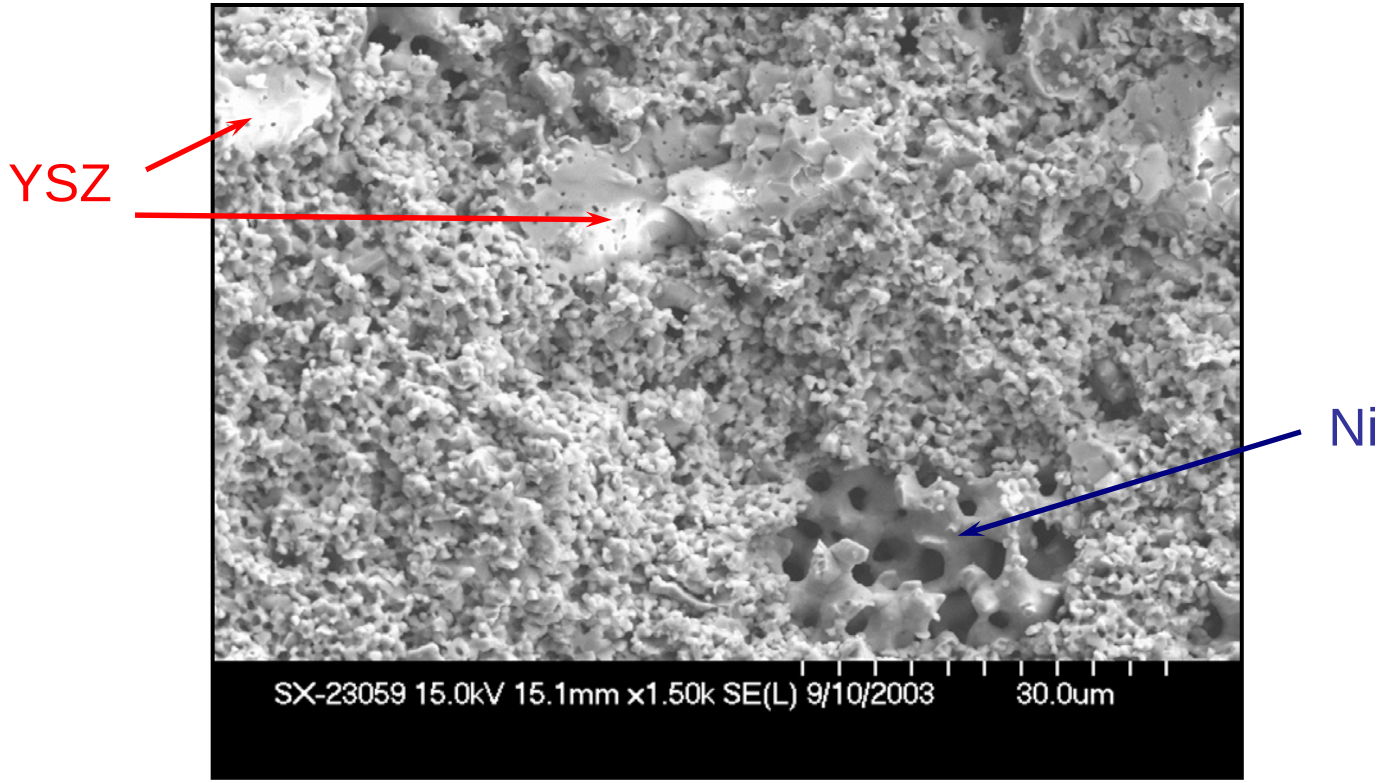
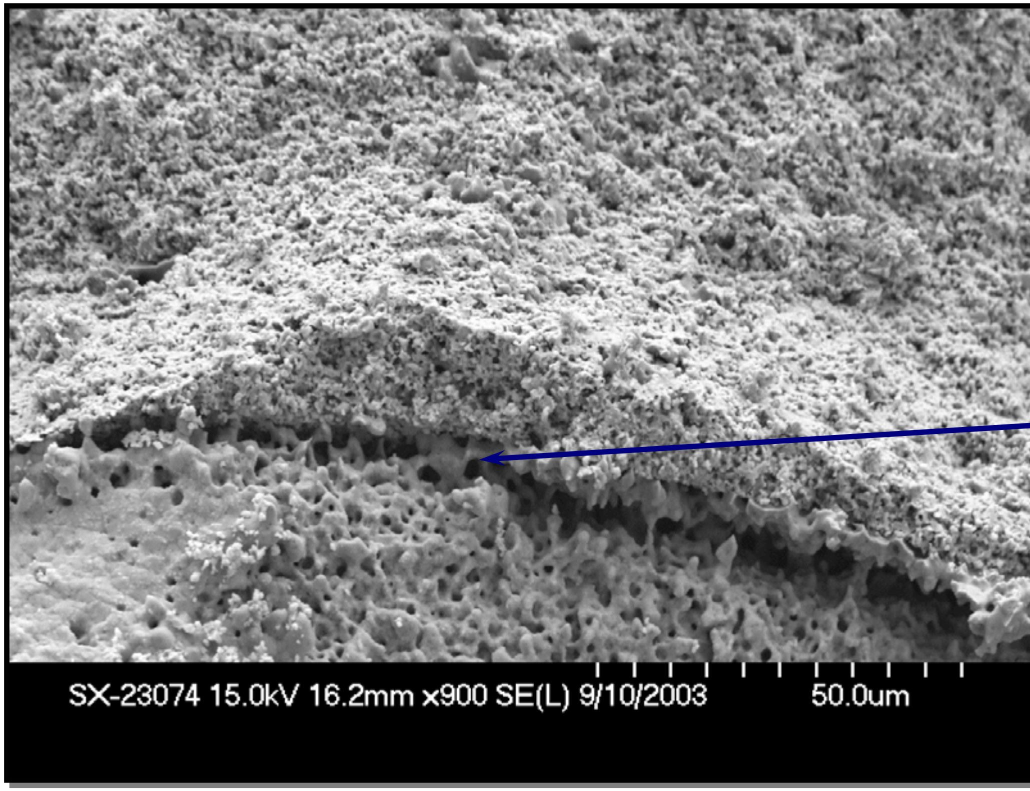
Biaxial Strength of Ni-YSZ materials



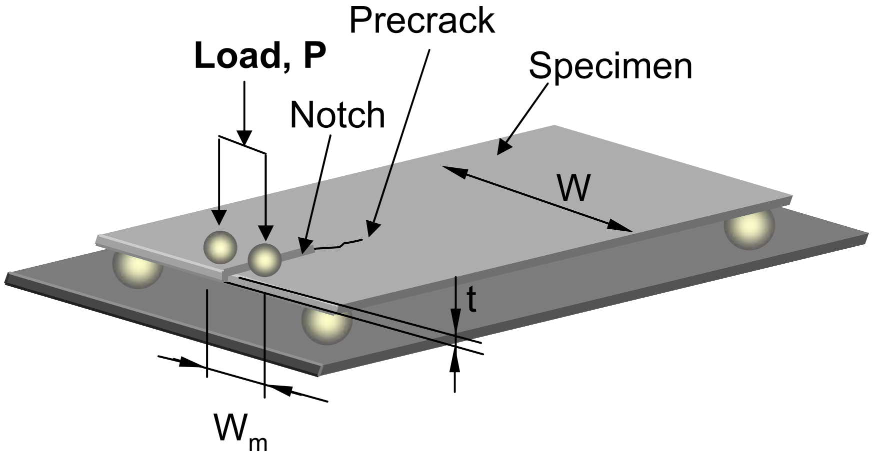
Fracture surface Ni-YSZ sample after complete reduction.
Initial porosity 6%

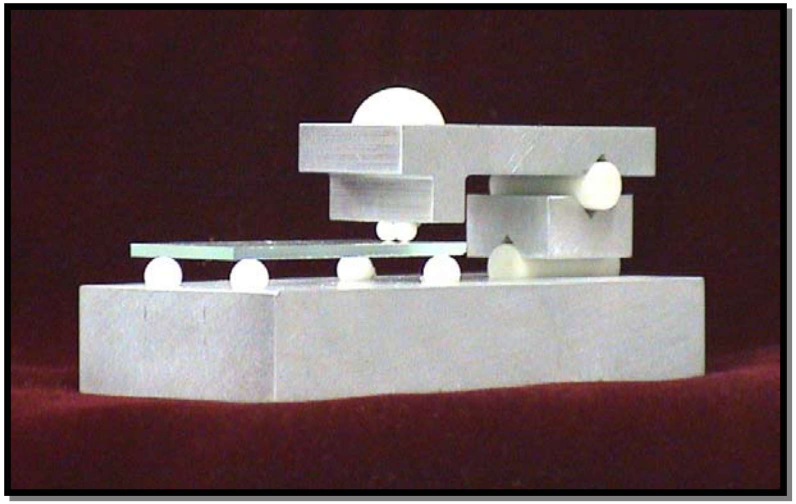
Biaxial Strength of Ni-YSZ materials



Fracture surface Ni-YSZ sample after complete reduction.
Initial porosity 6%

Fracture Toughness
Double-torsion testing



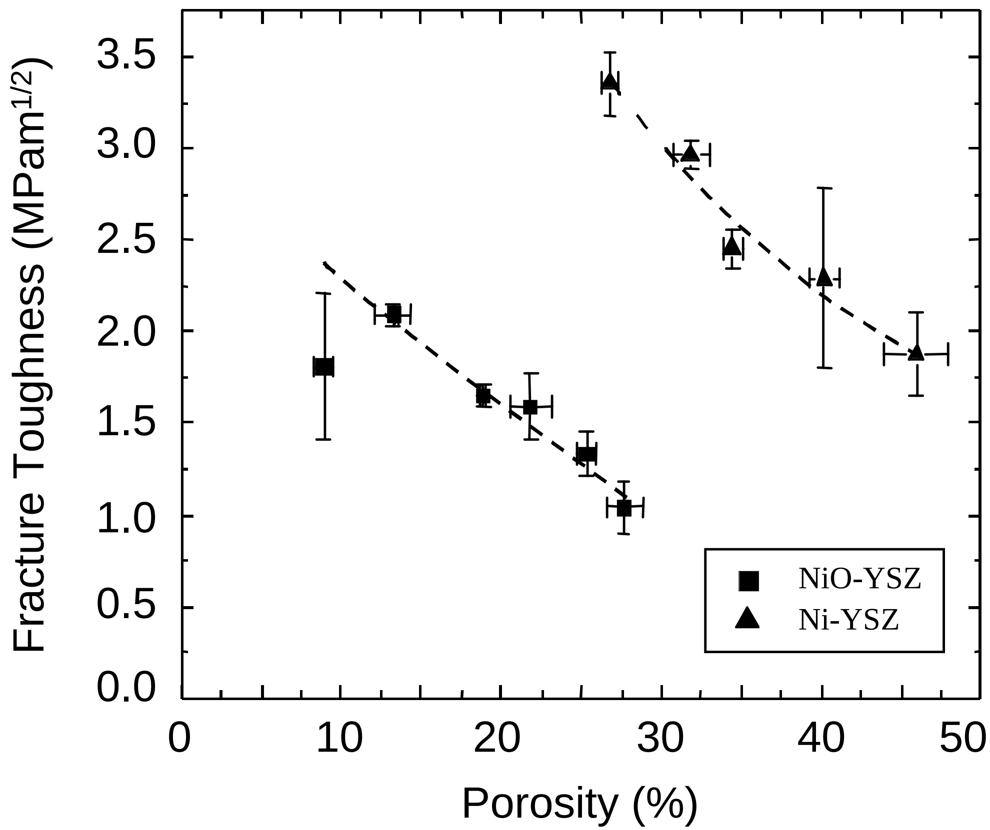


$$K_I = PW_m\left[\frac{3(1+\nu)}{Wt^4\xi}\right]^{1/2}, \xi = 1 - 1.26(t/W) + 2.4(t/W)\exp[-\pi W/(2t)]$$

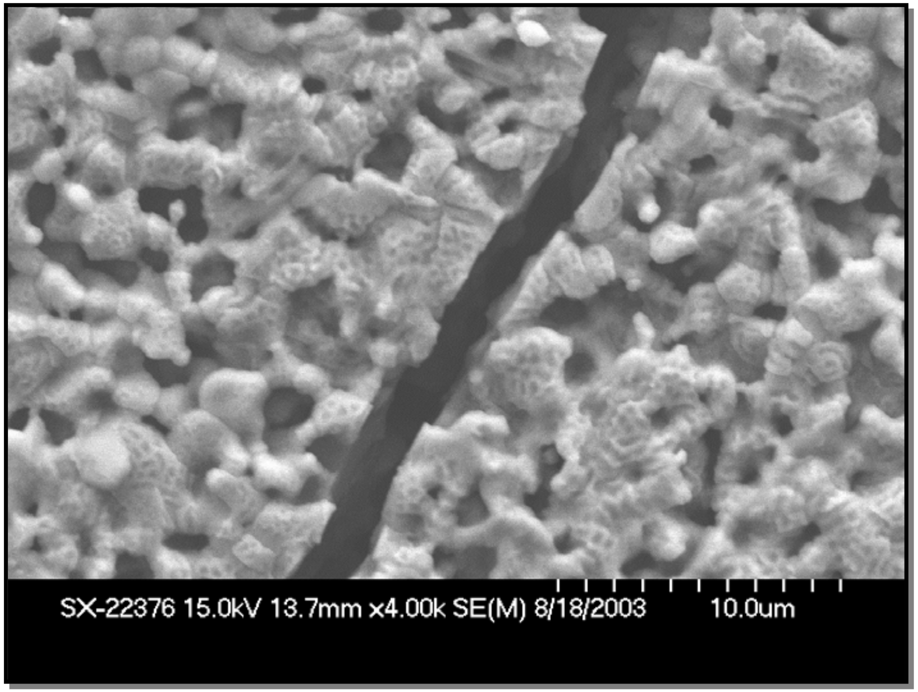
Precracked @ 0.02 mm/min and tested @ 1 mm/min

Fracture Toughness of NiO-YSZ and Ni-YSZ materials

- The porosity of NiO-YSZ samples increases after reduction in a gas mixture of 4%H_2-95%Ar at 800°C for 24 hrs.
- All samples had on average the same thickness.
- The fracture toughness of NiO-YSZ and Ni-YSZ materials <u>decreases</u> with increasing porosity.
- Ni-YSZ materials are <u>tougher</u> than their NiO-YSZ precursors

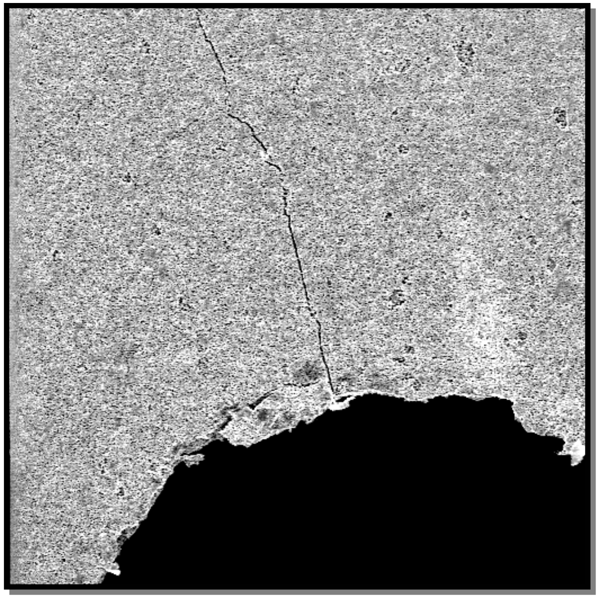


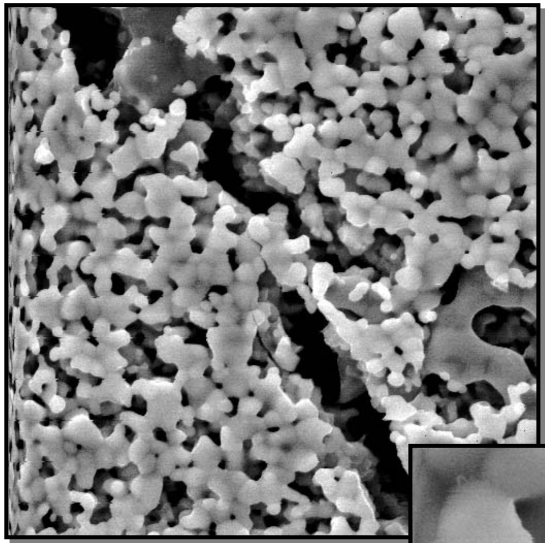
Fracture Toughness of NiO-YSZ materials

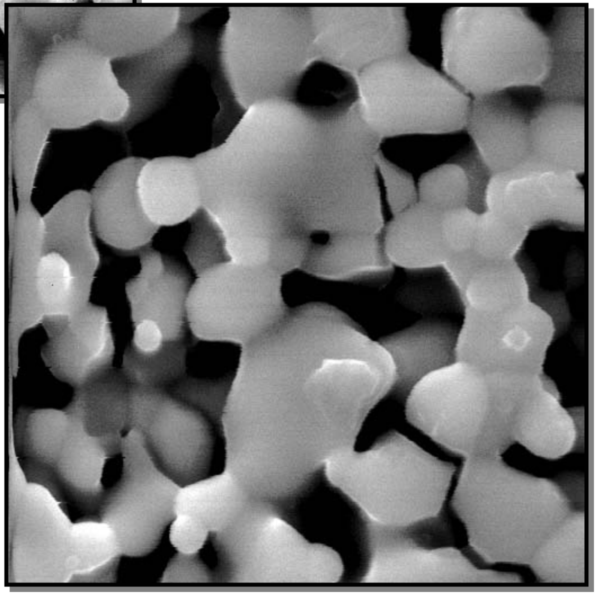


Pre-cracked NiO-YSZ specimen

Fracture Toughness of Ni-YSZ materials







Pre-cracked Ni-YSZ specimen

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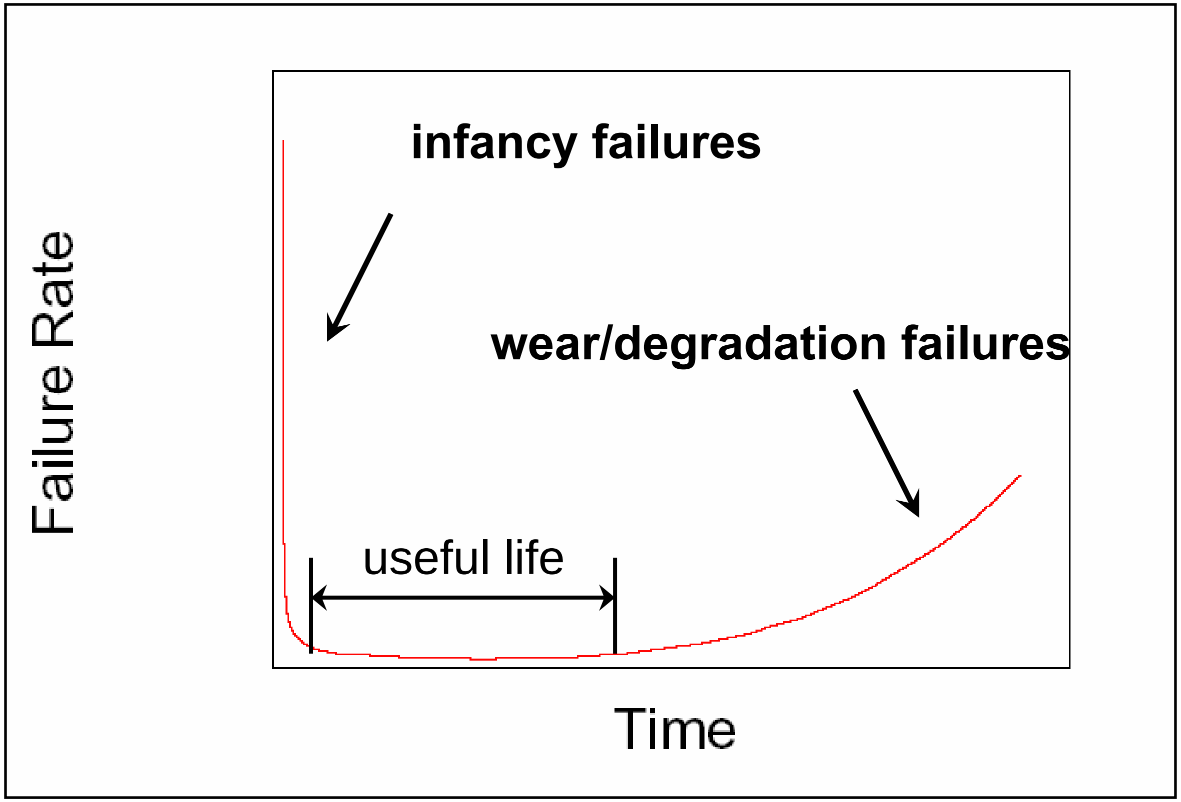
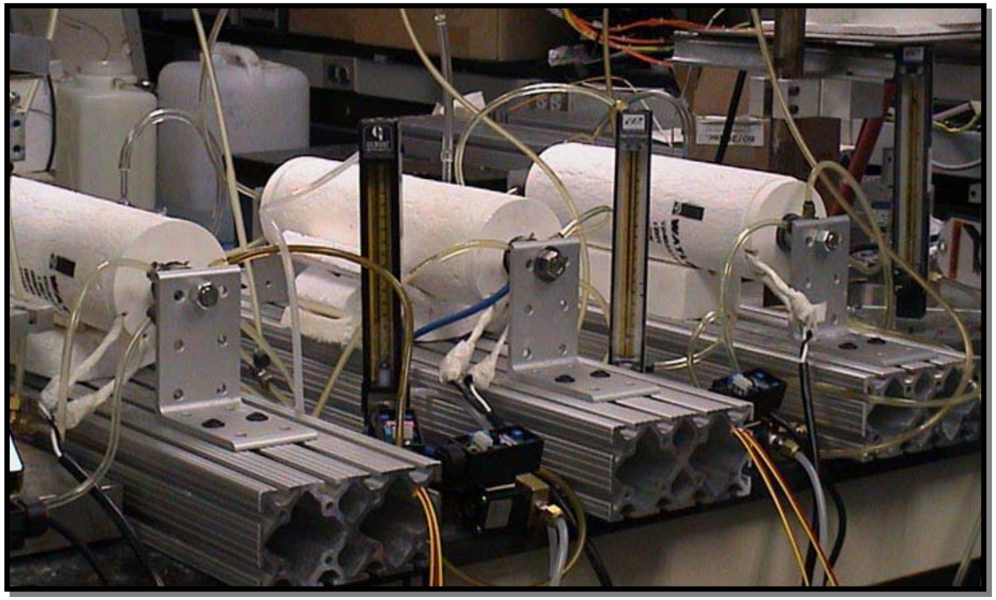
- Effect of cyclic conditions (temperature, oxidation, reduction) on mechanical properties

Background

The failure rate of complex systems can be described with a bathtube curve



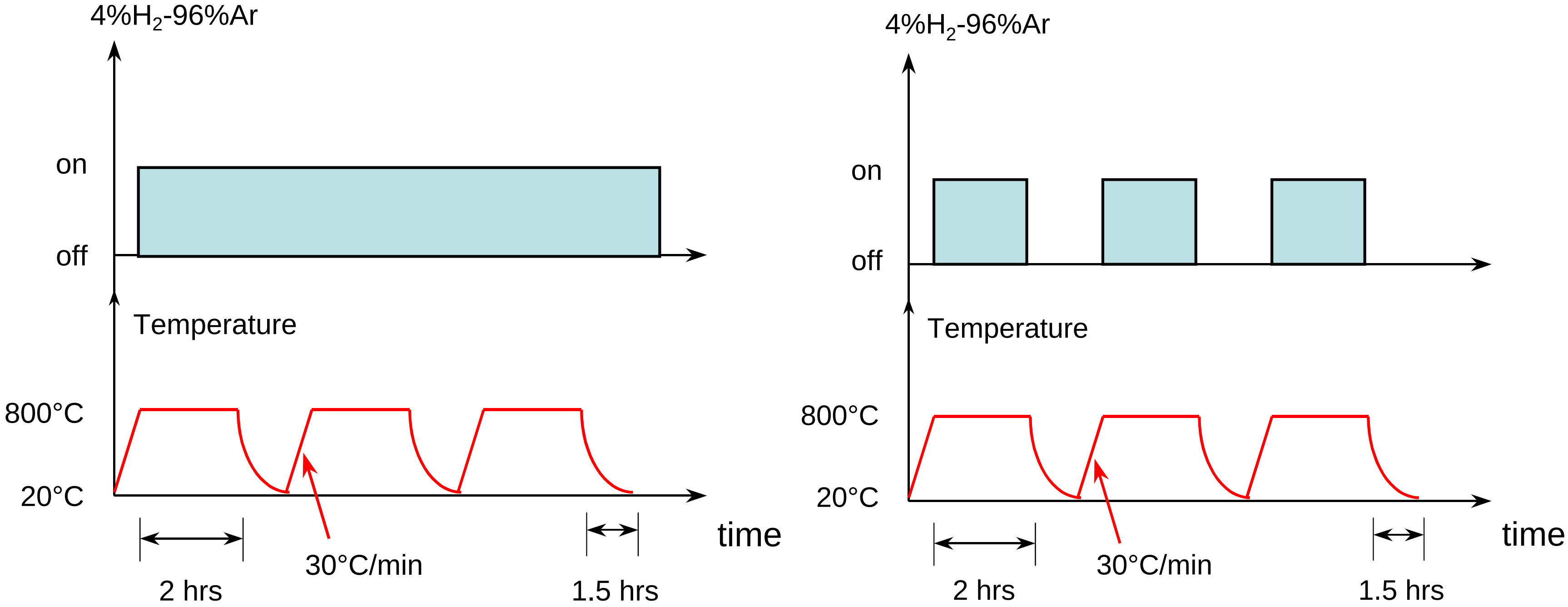
Effect of thermal cycling on strength



Cyclic Testing Experimental Stations

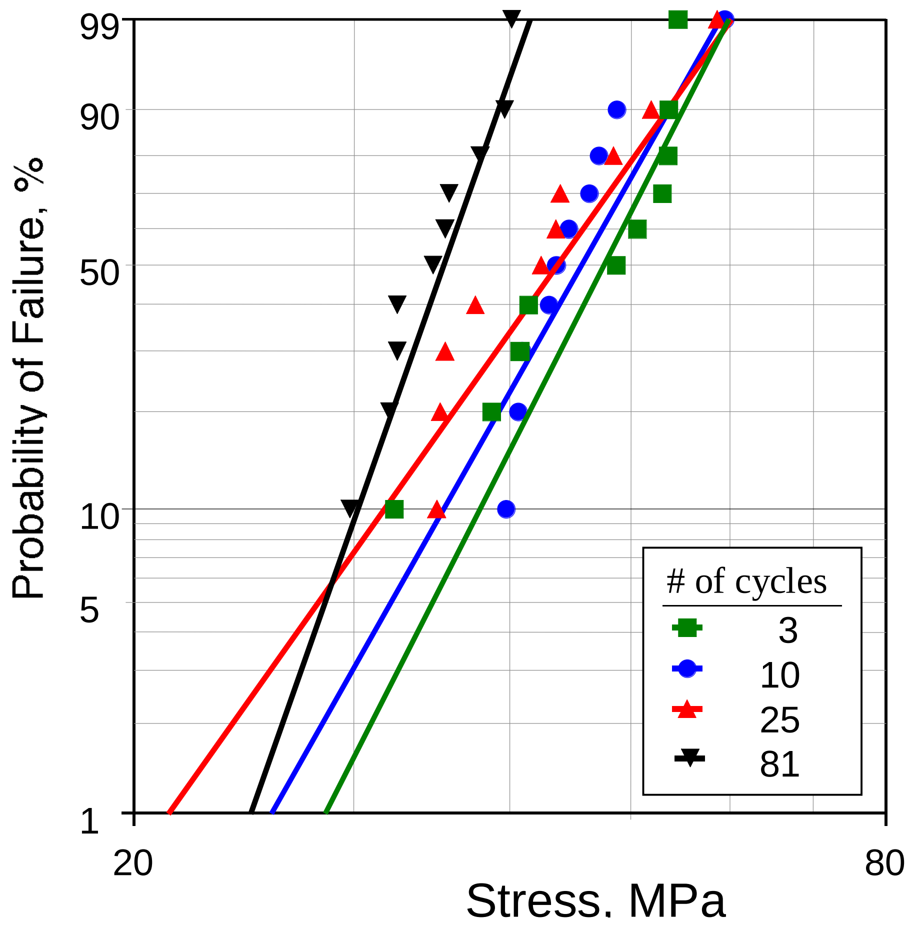
- Tubular furnaces
- Thermal cycling under constant environment.
- Thermal cyclic coupled with cyclic oxidation/reduction

Effect of thermal cycling on strength

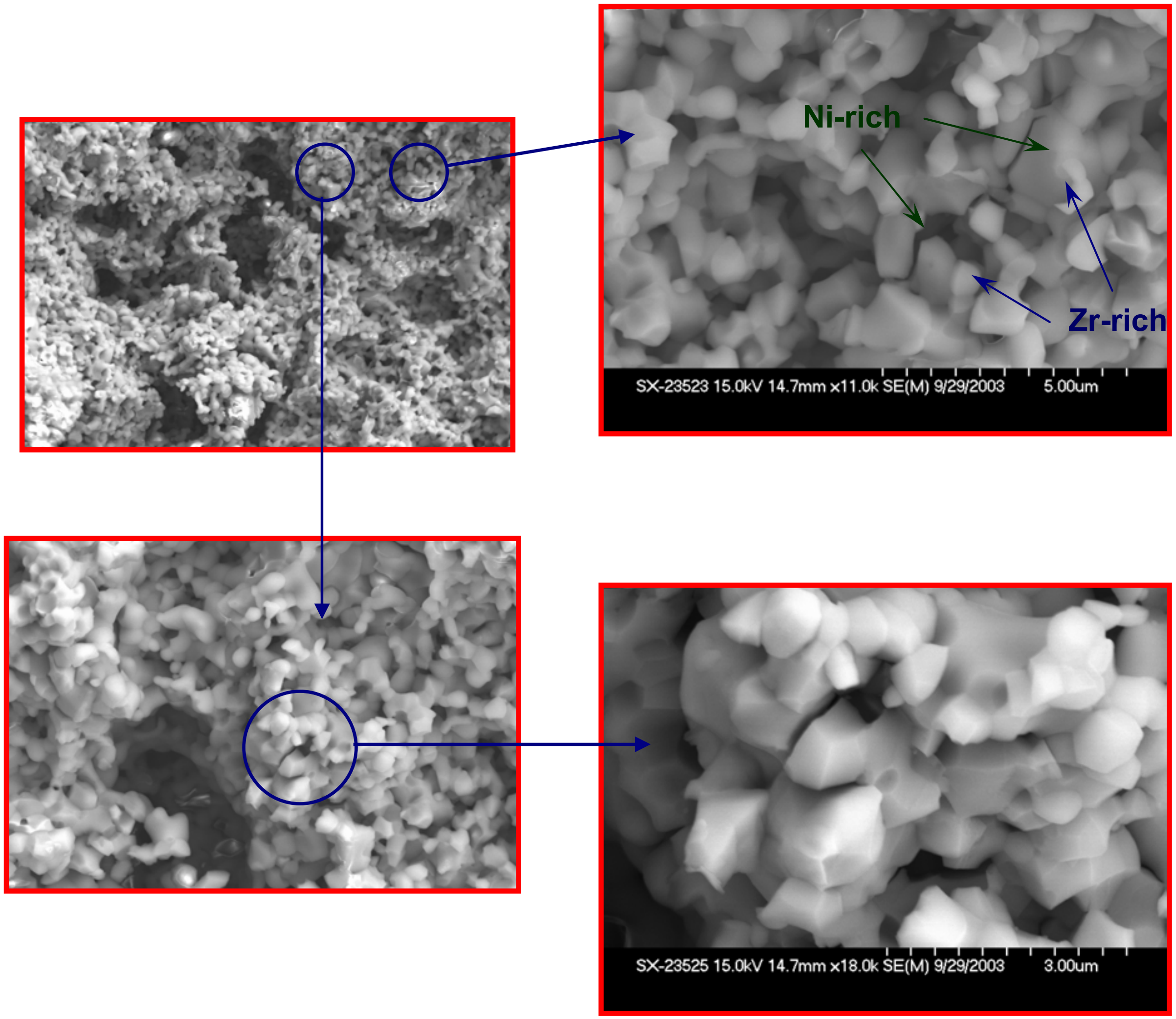


Effect of thermal cycling on strength

- Thermal cycling of NiO-YSZ anode materials between 20°C and 800°C.
  - Constant heating rate: 30°C/min.
  - 2-hr dwell at 800°C
  - Cooling at natural cooling rate of system. Repeat cycle after 1.5 hrs.
  - Gas mixture of 4%H_2-96%Ar
- Strength decrease with number of thermal cycles



Effect of thermal cycling on strength



- Ni-YSZ
- 81 cycles
- 20-800°C
- 4%H2-96%Ar

Effect of thermal cycling coupled with cyclic oxidation-reduction

- Thermal cycling of NiO-YSZ anode materials between 20°C and 800°C.
  - Heating in air at a constant rate of 30°C/min.
  - 2-hr dwell at 800°C in a gas mixture of 4%H_2-96%Ar
  - Cooling at natural cooling rate of system. Repeat cycle after 1.5 hrs.
- Significant damage after 81 cycles.

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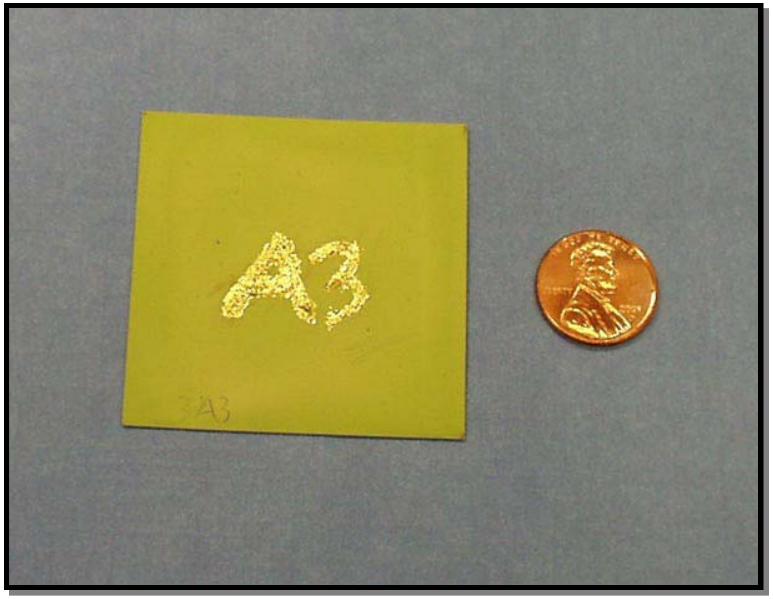
- Effect of cyclic conditions (temperature, oxidation, reduction) on mechanical properties
- Stresses during fuel cell assembly

Reliability of structures

- Delphi has synthesized bi-layers (NiO-YSZ/YSZ)
- OSU has determined the geometry of the bi-layers



Curvature of NiO-YSZ/YSZ bi-layers

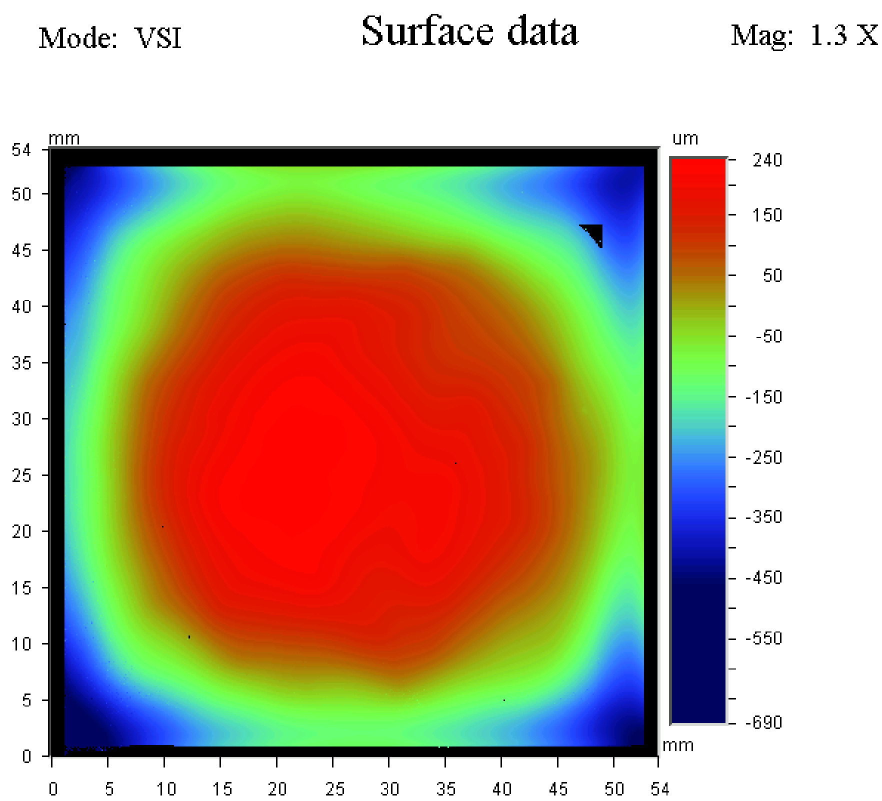
Ra: 141.74 um

Rz: 887.53 um

Rt: 929.95 um

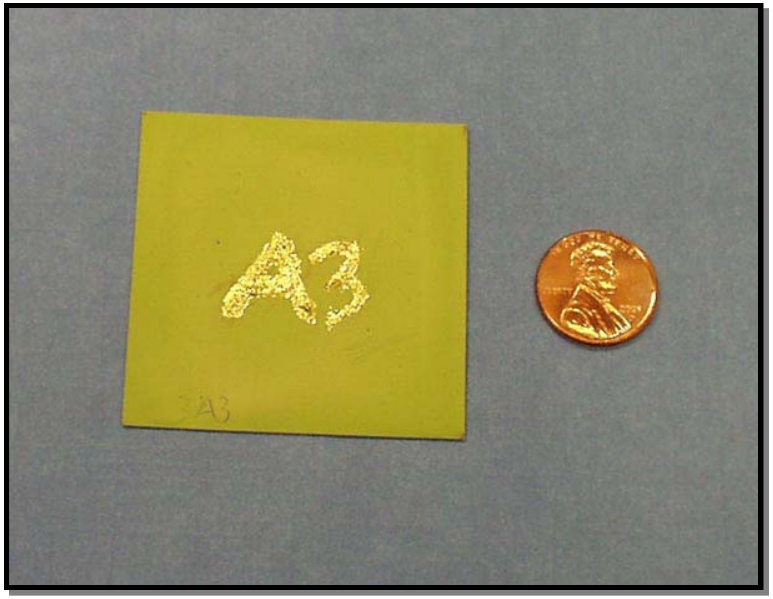
Title: A9

Note:

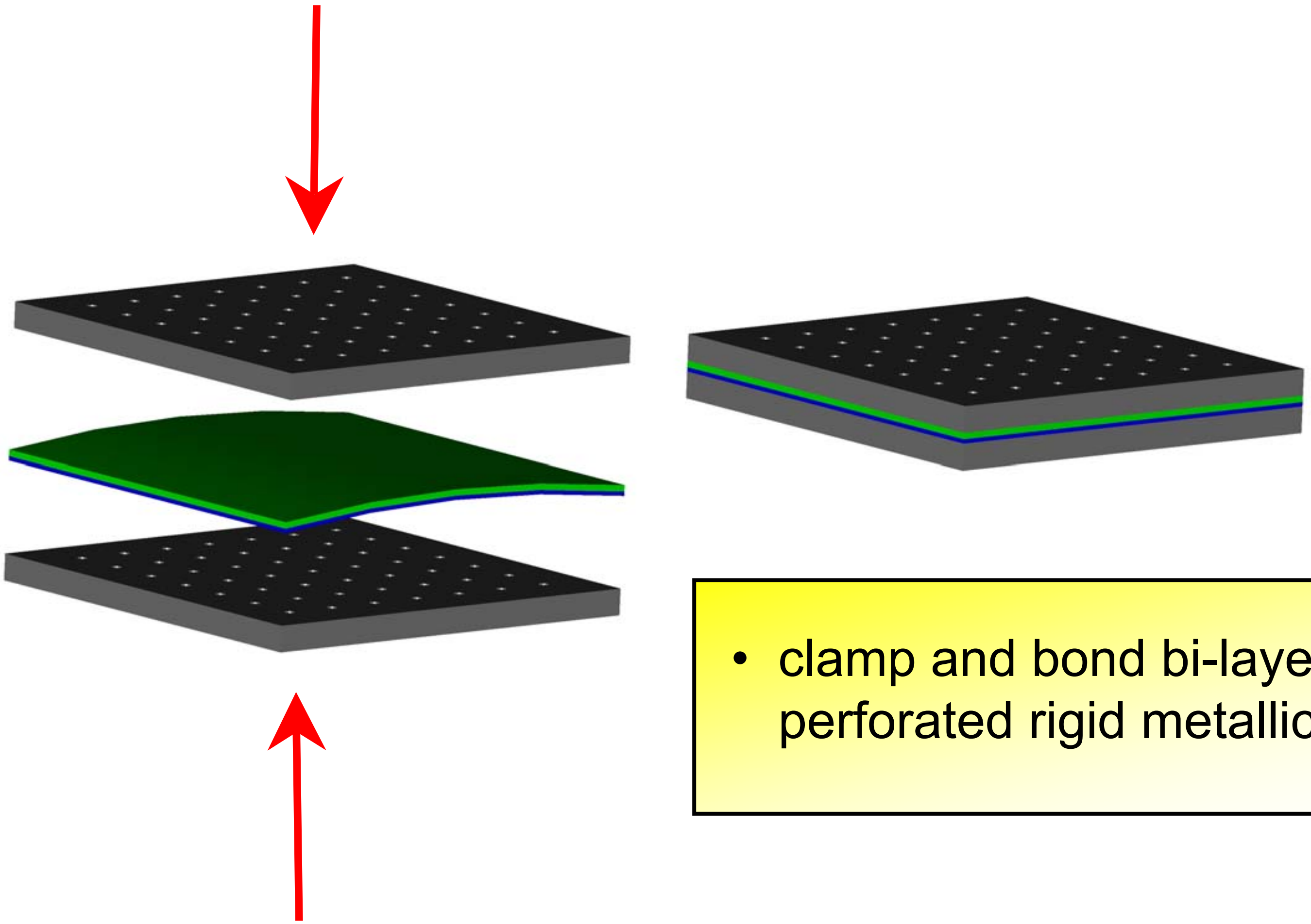


Reliability of structures

- Delphi has synthesized bi-layers (NiO-YSZ/YSZ)
- OSU has determined the geometry of the bi-layers
- ORNL will estimate stresses associated with “sandwiching” and bonding bi-layers between two rigid metallic plates.



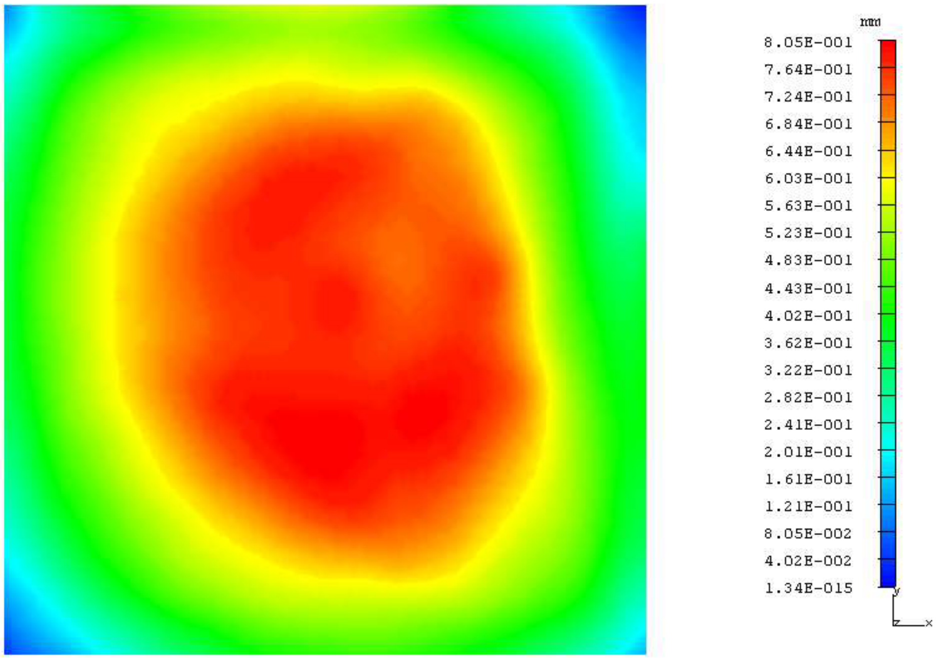
Reliability of structures



- clamp and bond bi-layer using perforated rigid metallic plates.

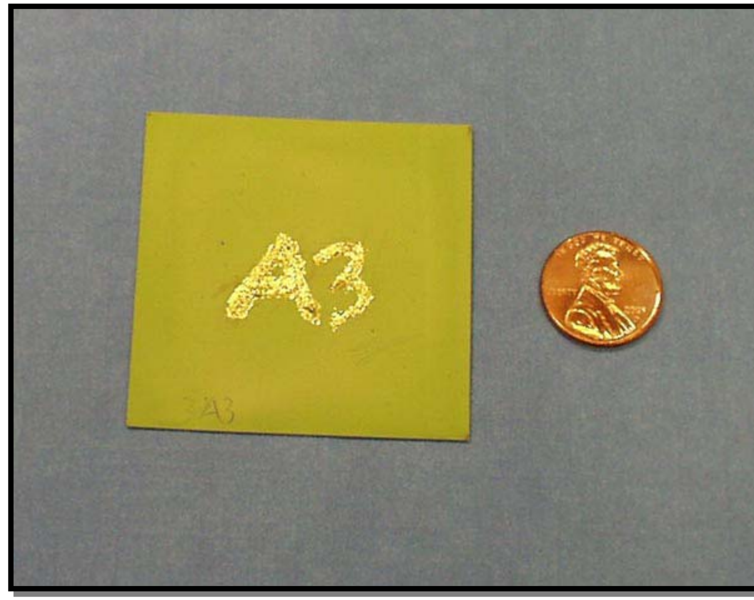
Reliability of structures

- Displacements associated with clamping bi-layer between two rigid plates

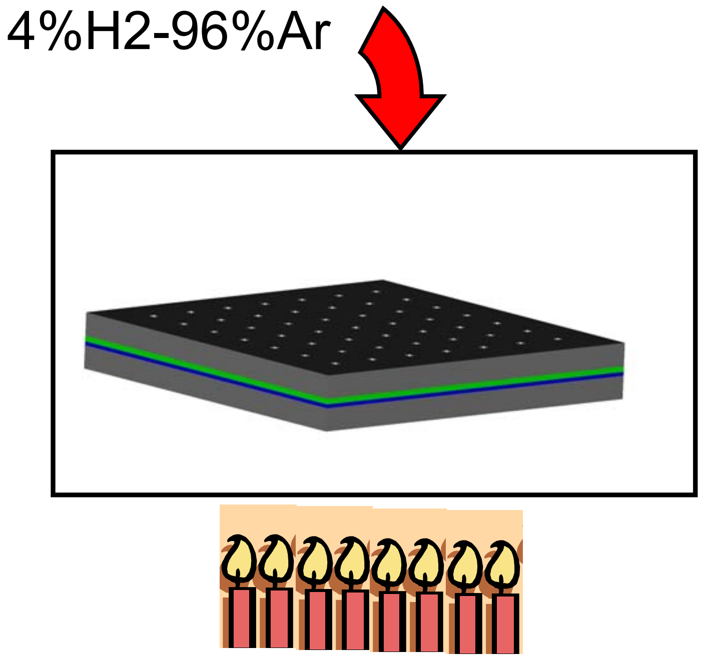


Reliability of structures

- Delphi has synthesized bi-layers (NiO-YSZ/YSZ)
- OSU has determined the geometry of the bi-layers
- ORNL will estimate stresses associated with “sandwiching” and bonding bi-layers between two rigid metallic plates.
- ORNL will heat the assembly up to 800°C followed by reduction in 4%H2-96%Ar. ORNL will predict the failure rate and compare predictions with experimental values.



Reliability of structures



- heat-up assembly in air up to 800°C.
- change atmosphere to 4%H_2-96%Ar
- Detect cracking using AE sensors

- select thickness and material of rigid metallic plate based on strength predictions at 800°C.
- Compare predicted and actual failure rates.

Summary

- The kinetics of NiO-YSZ were investigated at 800°C using a gas mixture of 4%H2-96%Ar.
  - Paralinear kinetics
  - The porosity of reduced samples increases after reduction
  - Elastic properties decrease after reduction
  - Biaxial strength decreases after reduction
  - Fracture toughness increases after reduction
- Experimental facilities are now operational to investigate the effect of thermal cycling and cyclic oxidation-reduction on the physical and mechanical properties of SOFC materials.
  - The strength of Ni-YSZ decreases significantly after thermal cycling between 20°C and 800°C in 4%H2-96%Ar.
  - Significant destructive damage (cracking, warping) resulting from thermal cycling coupled with cyclic reduction-oxidation.
- Work has been initiated to validate reliability predictions in model (NiO-YSZ/YSZ bi-layer) system

Future Work

- Evaluate model bi-layer system and compare predicted and actual failure rates.
- Continue evaluating effect of thermal cycling and cyclic oxidation-reduction on properties, durability and reliability of SOFC materials.
- Continue interacting with industrial teams to address specific problems.
- Integrate results with modeling task.