Reduction, Creep Deformation and the Evolution of Residual Stresses in SOFC Anodes

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2018 SOFC Program Review

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Acknowledgments

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Program managers Rin N. Burke and Shailesh D. Vora.

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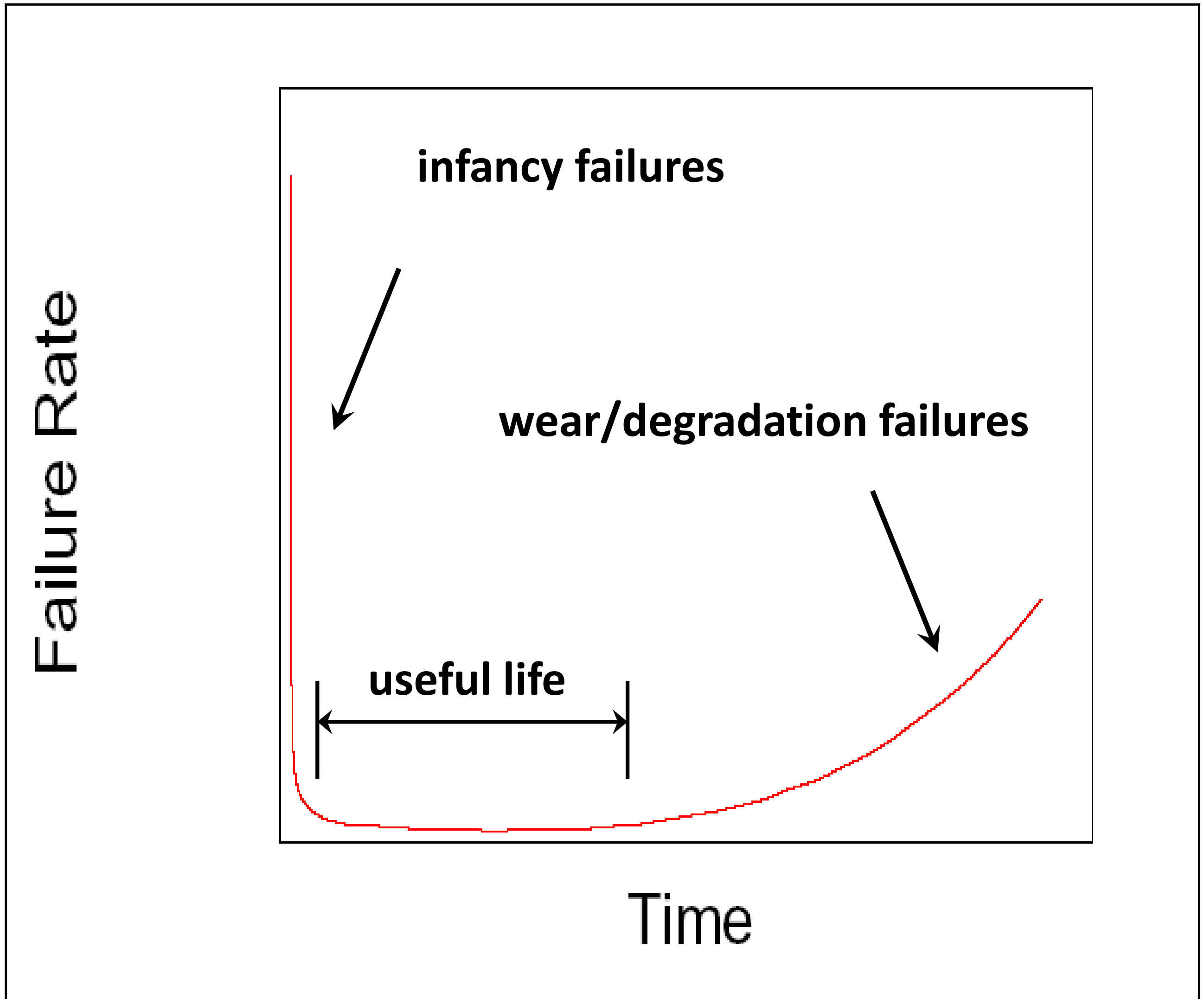
Failure, Reliability and Durability of Systems

The failure rate of complex systems can be described by the bathtub curve



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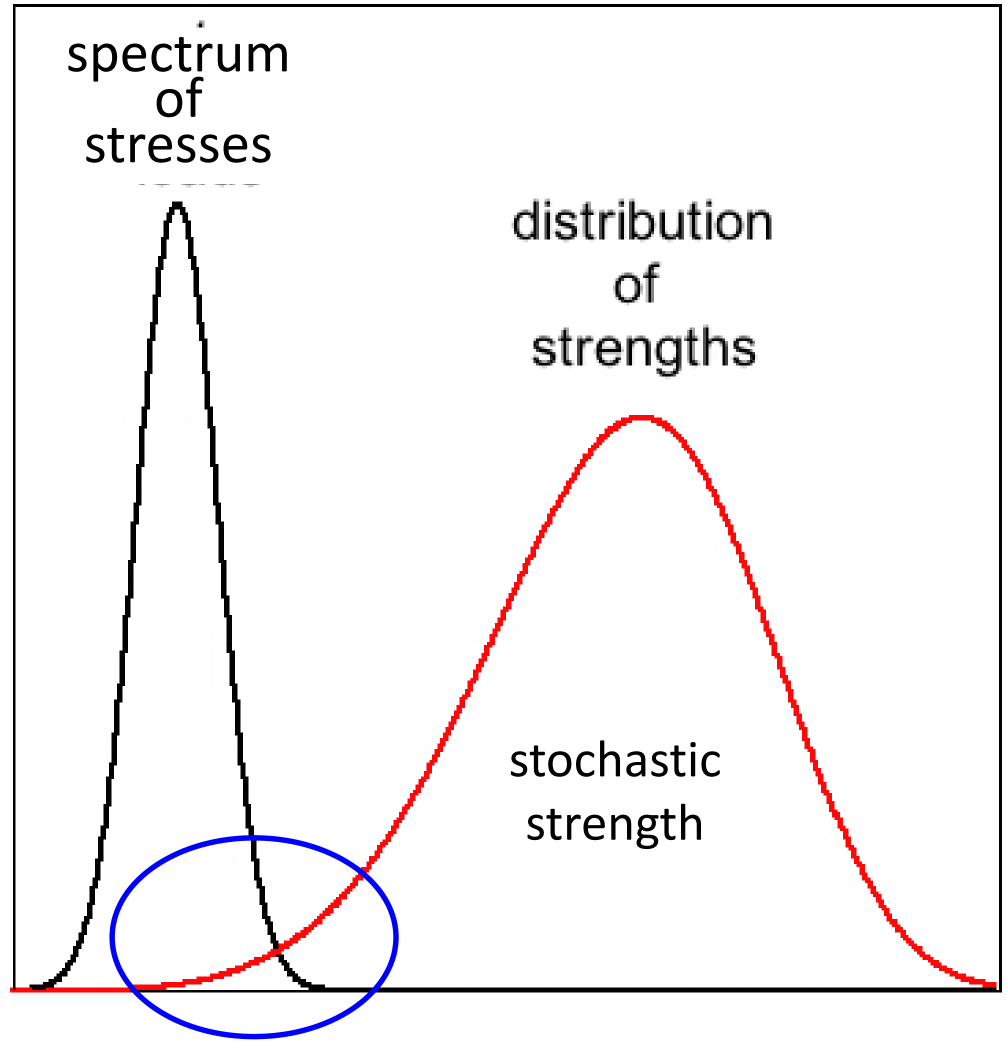
Failure, Reliability and Durability of Systems

- Failure is determined by the intersection of the distributions of loads and strengths.
- The weakest elements of the population determine the reliability of the system.



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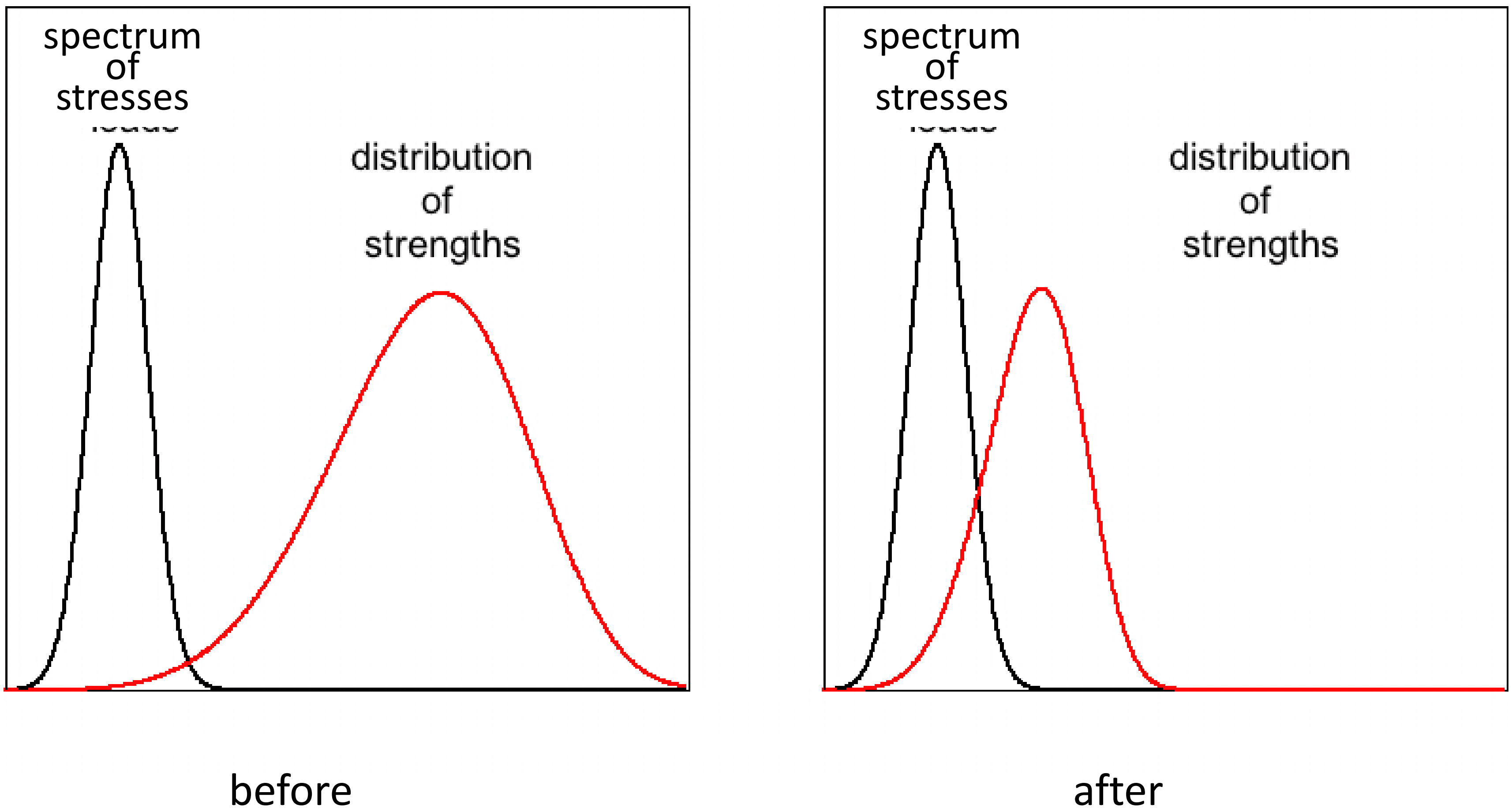
Failure, Reliability and Durability of Systems



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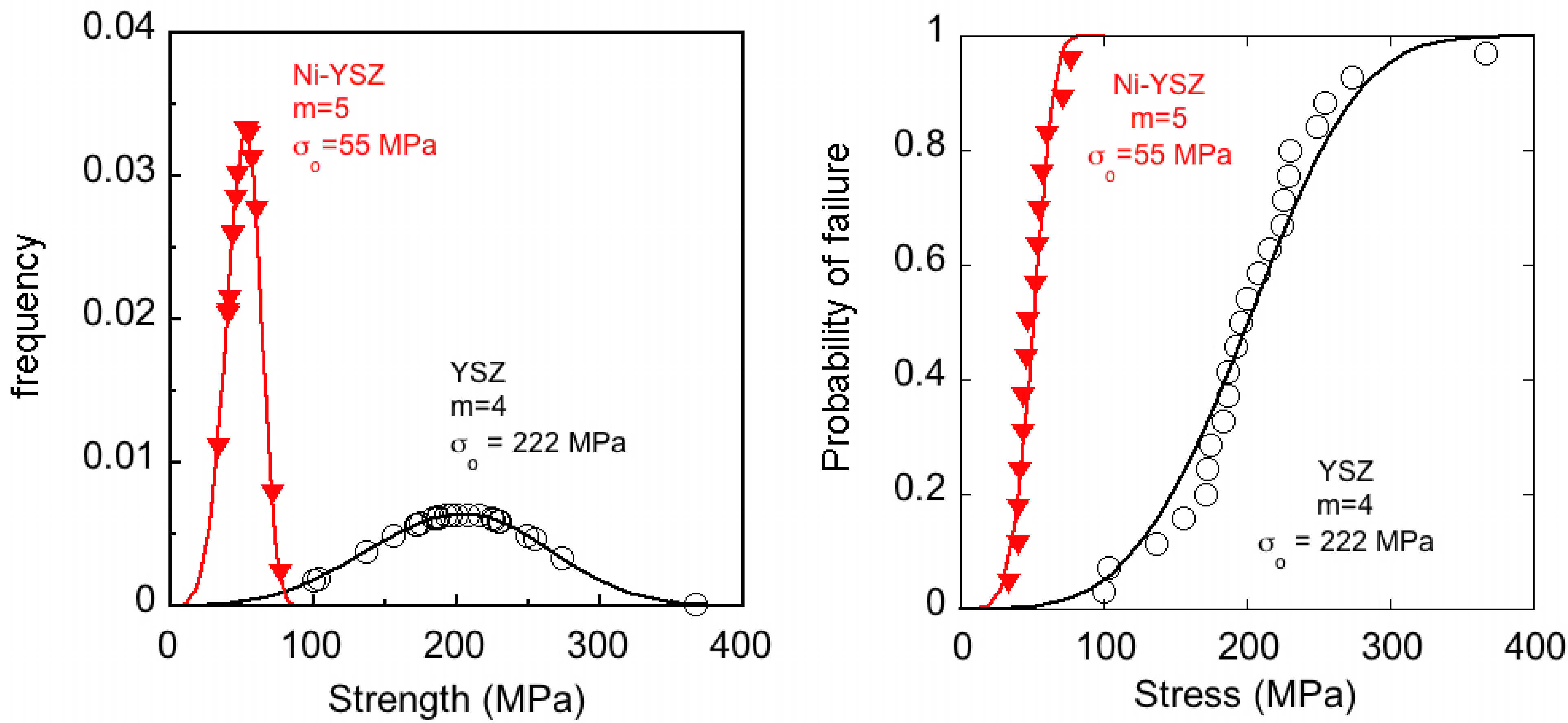
Strength of SOFC materials



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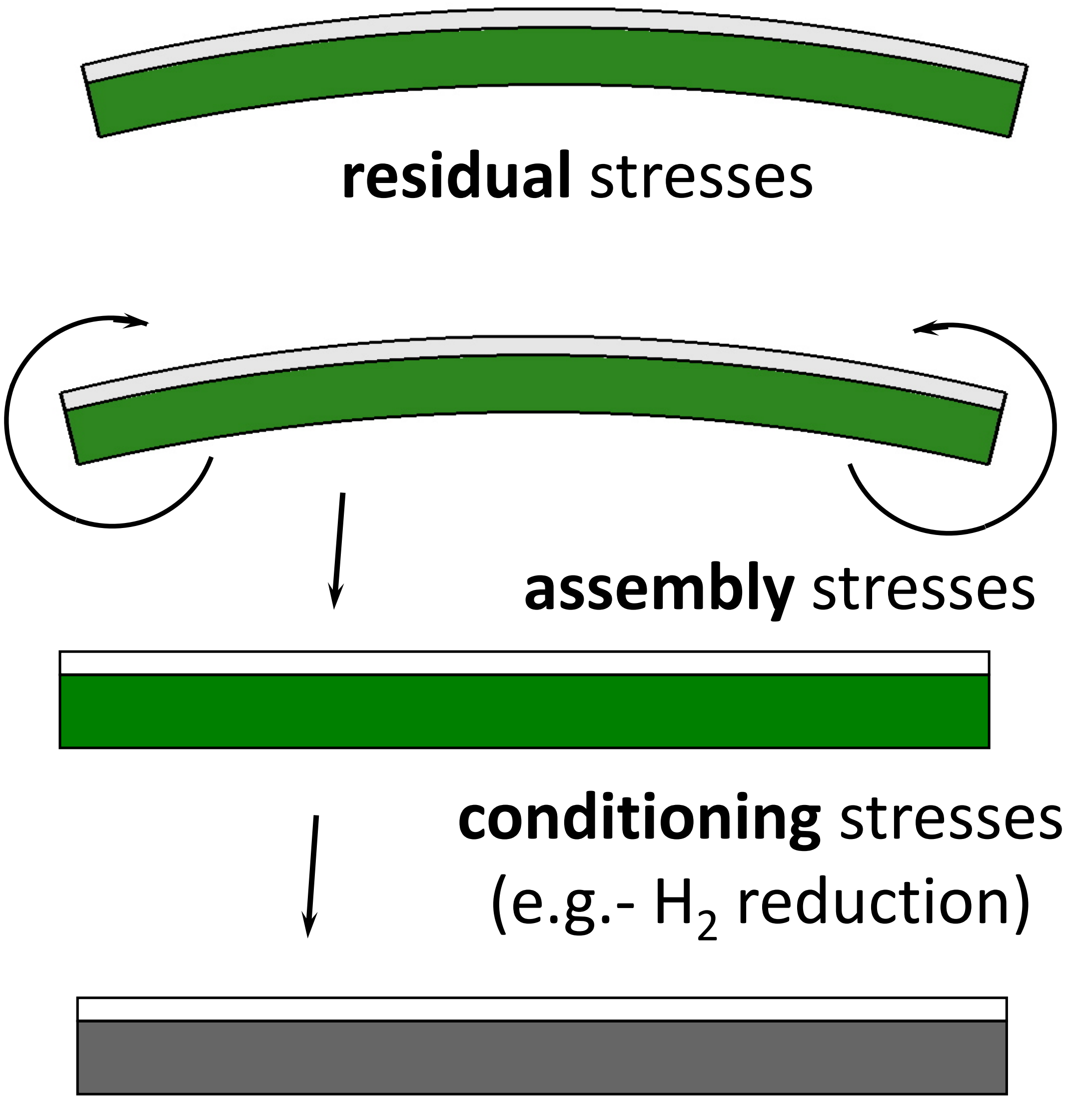
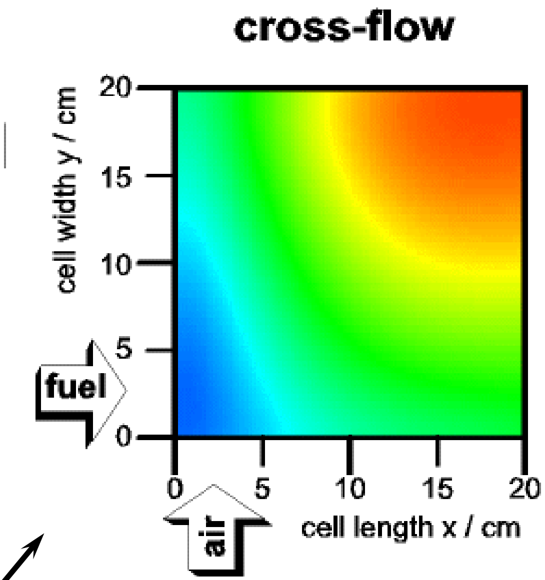
Objectives

- To understand the effect of **reduction temperature** on the state of stress of solid-oxide fuel cells
- To understand the effect of **creep deformation** of anode materials on its microstructure and on the redistribution of stresses in solid-oxide fuel cells

Background





temperature gradients and gas pressure induce **operational** stresses

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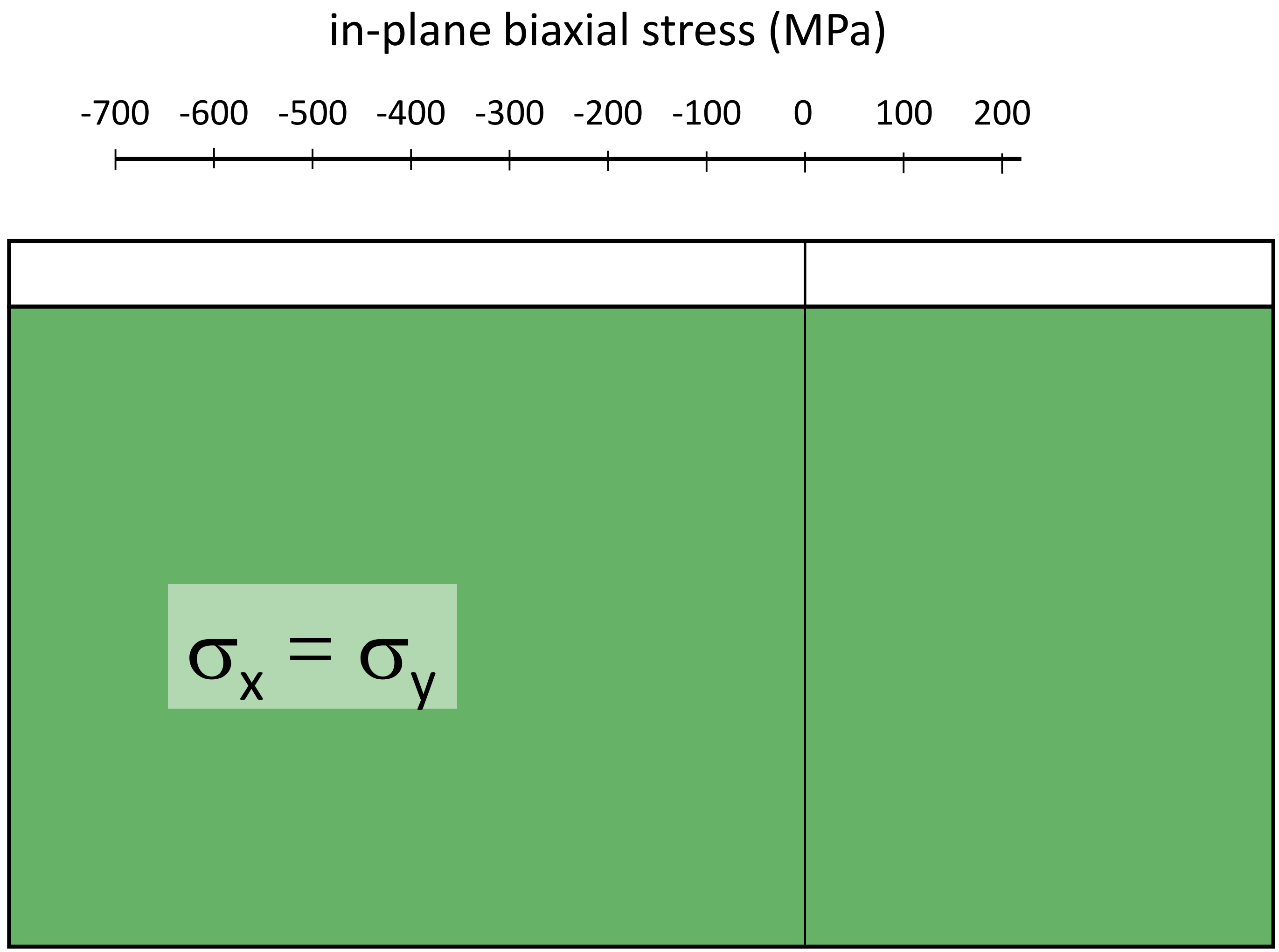
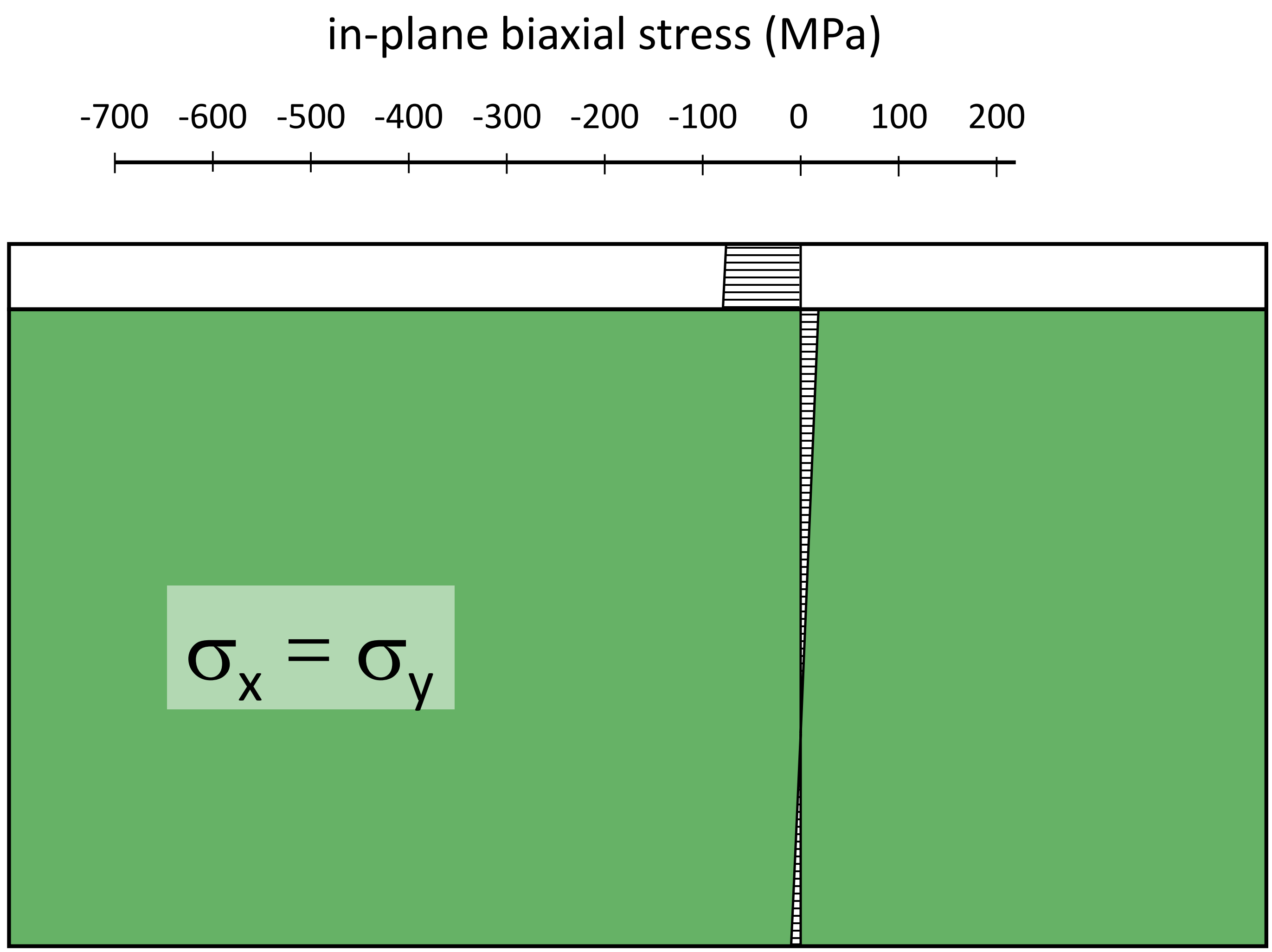
Residual Stresses in YSZ-NiO-YSZ bilayer



~1,000° C

Residual Stresses in YSZ-NiO-YSZ bilayer



800° C

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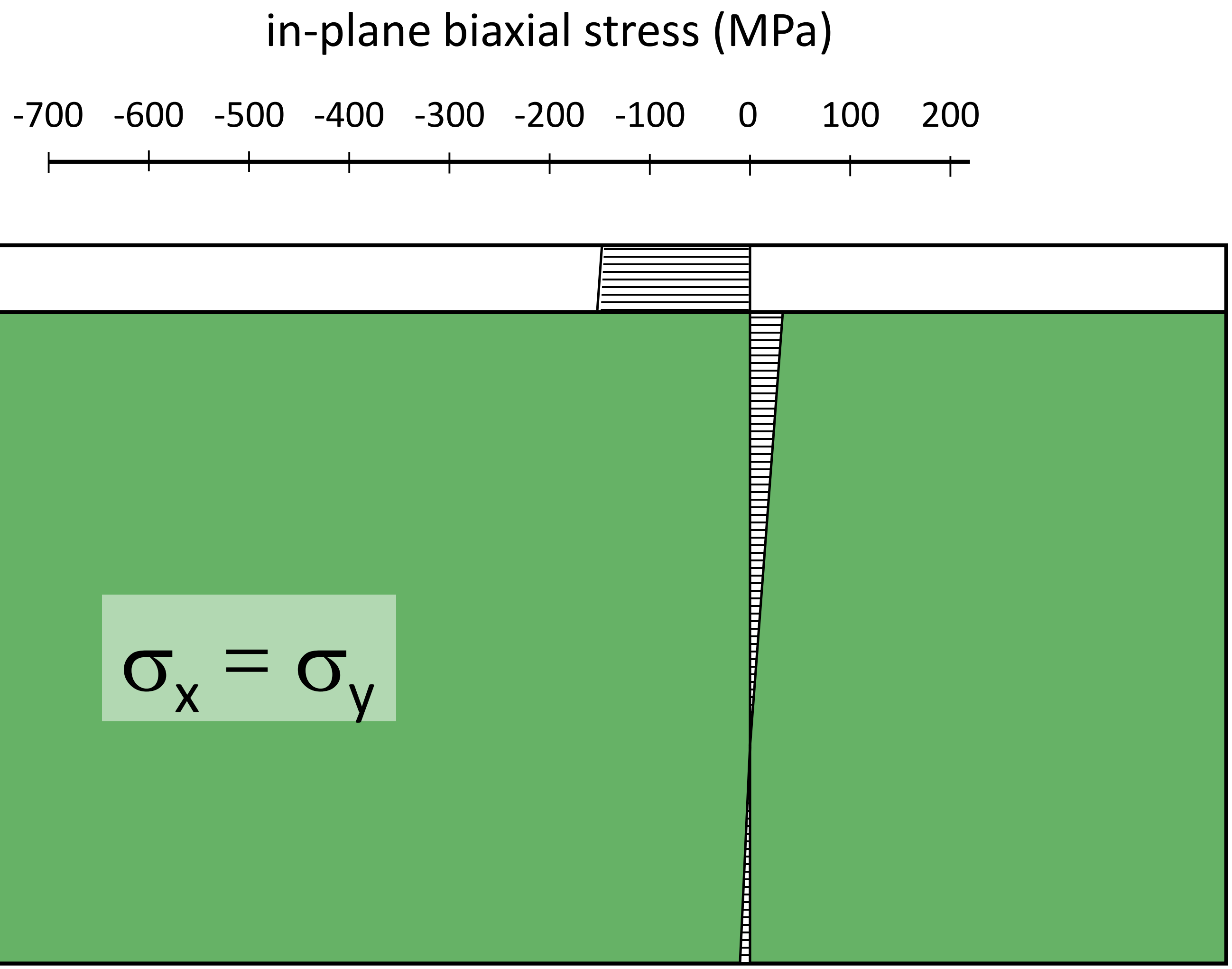
Residual Stresses in YSZ-NiO-YSZ bilayer



600° C

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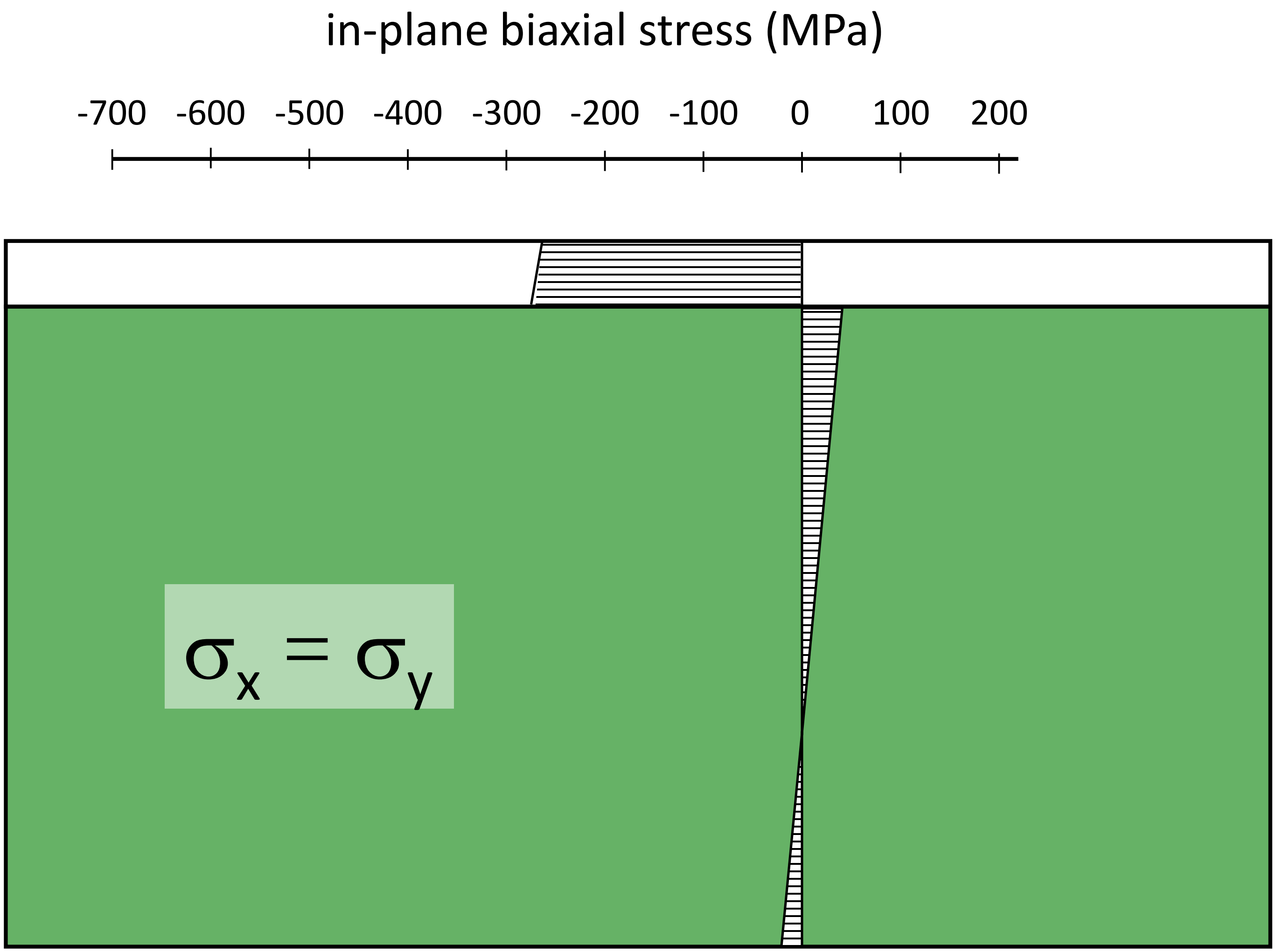
Residual Stresses in YSZ-NiO-YSZ bilayer



400° C

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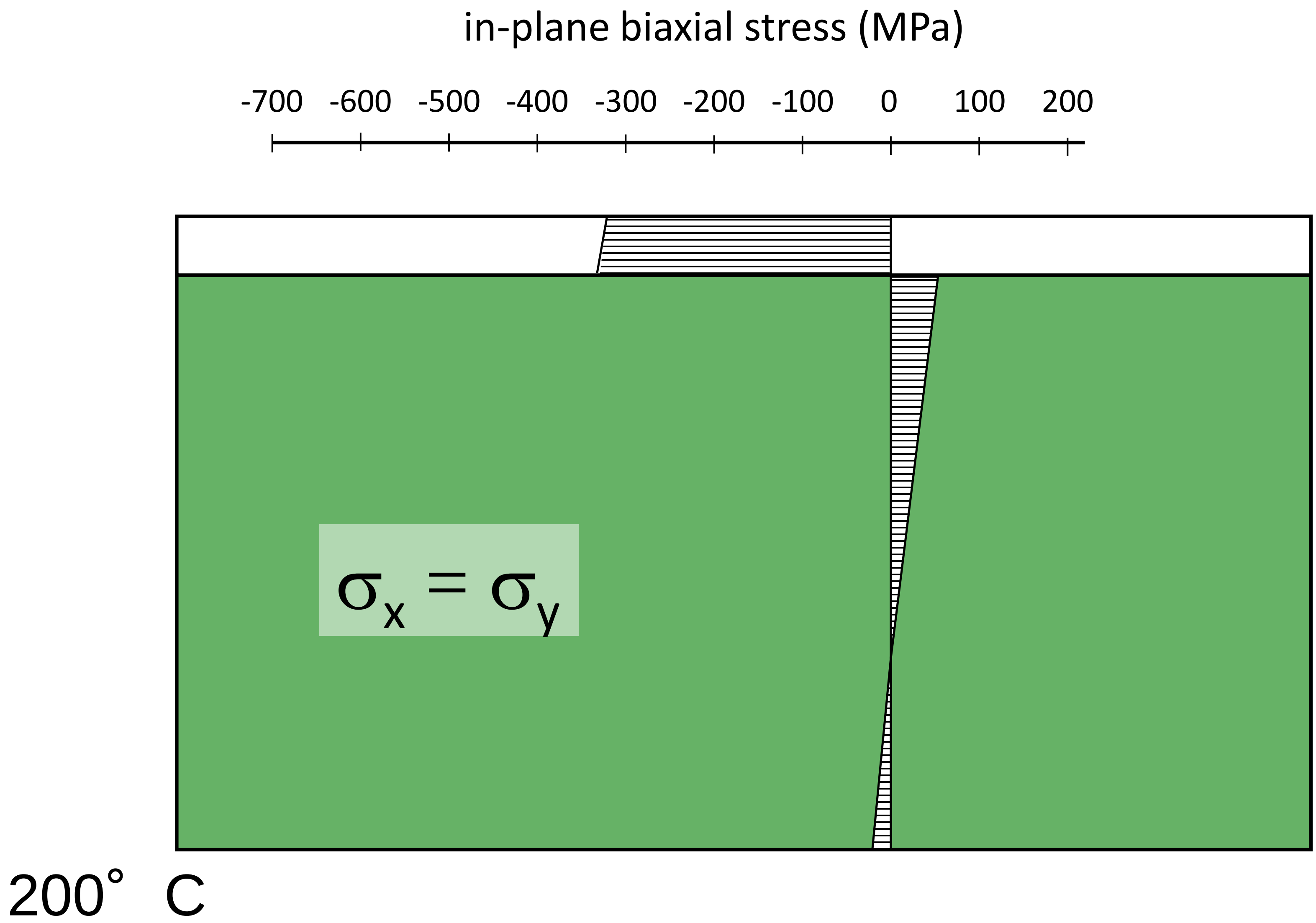
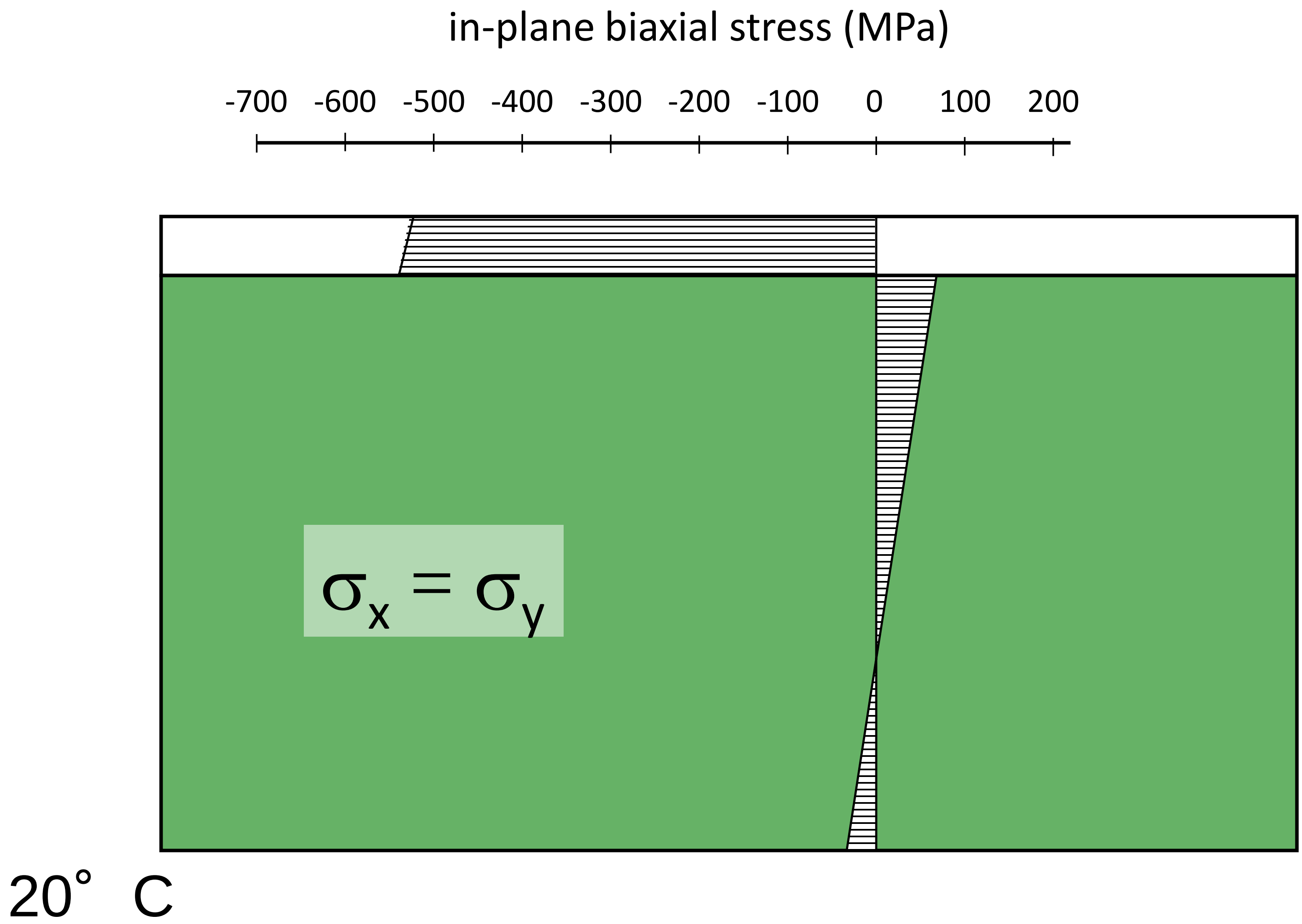
Residual Stresses in YSZ-NiO-YSZ bilayer



Residual Stresses in YSZ-NiO-YSZ bilayer



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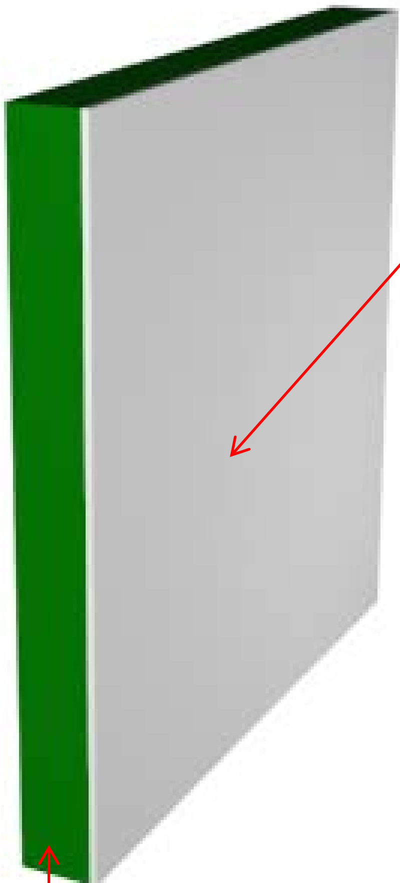
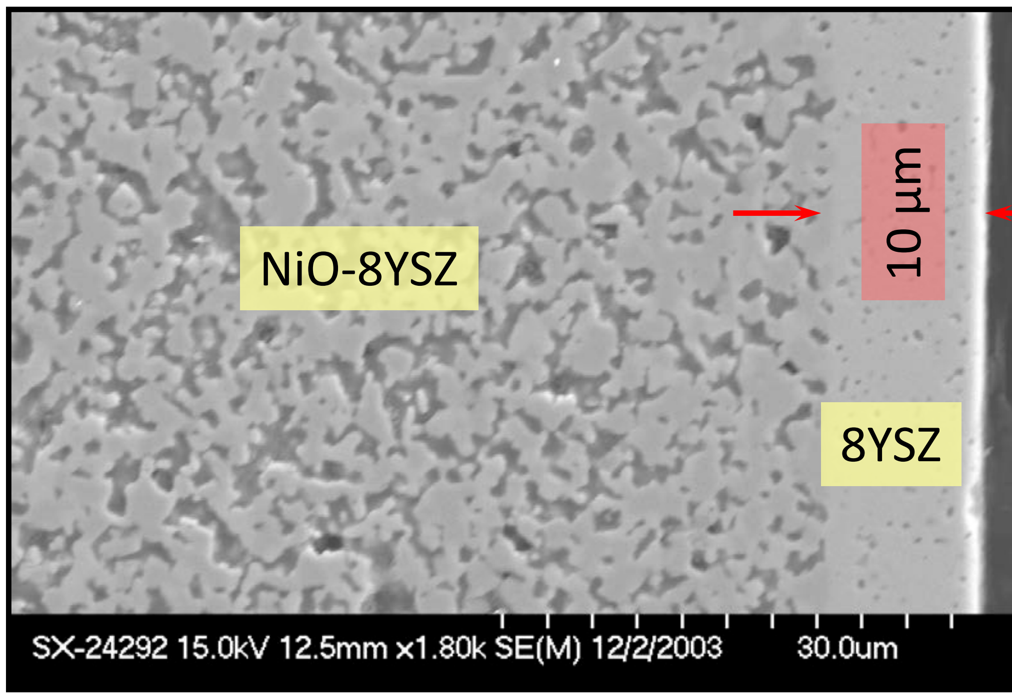
NiO-YSZ/YSZ bilayer



10–µm thick 8YSZ coating

500–µm thick
NiO-8YSZ substrate



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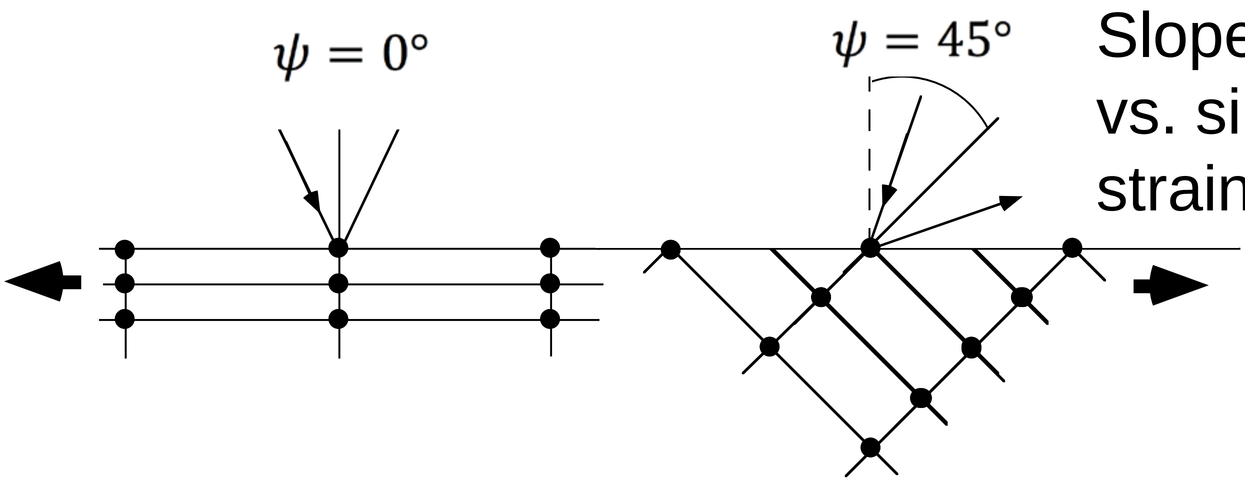
Measurement of Residual Stresses

- PANalyitcal X'pert PRO diffractometer
- CuKα radiation (λ=1.540598 Å)
- YSZ phase (6 2 0) Reflection
- 2θ=141°-144.5° - using the $\sin^2\psi$ method. A maximum ψ=55° was used with equal steps of $\sin^2\psi$ with 7 steps (positive and negative tilts)

High-temperature Diffractometer



Slope of d (interplanar spacing) vs. $\sin^2\psi$ is used to calculate strain.

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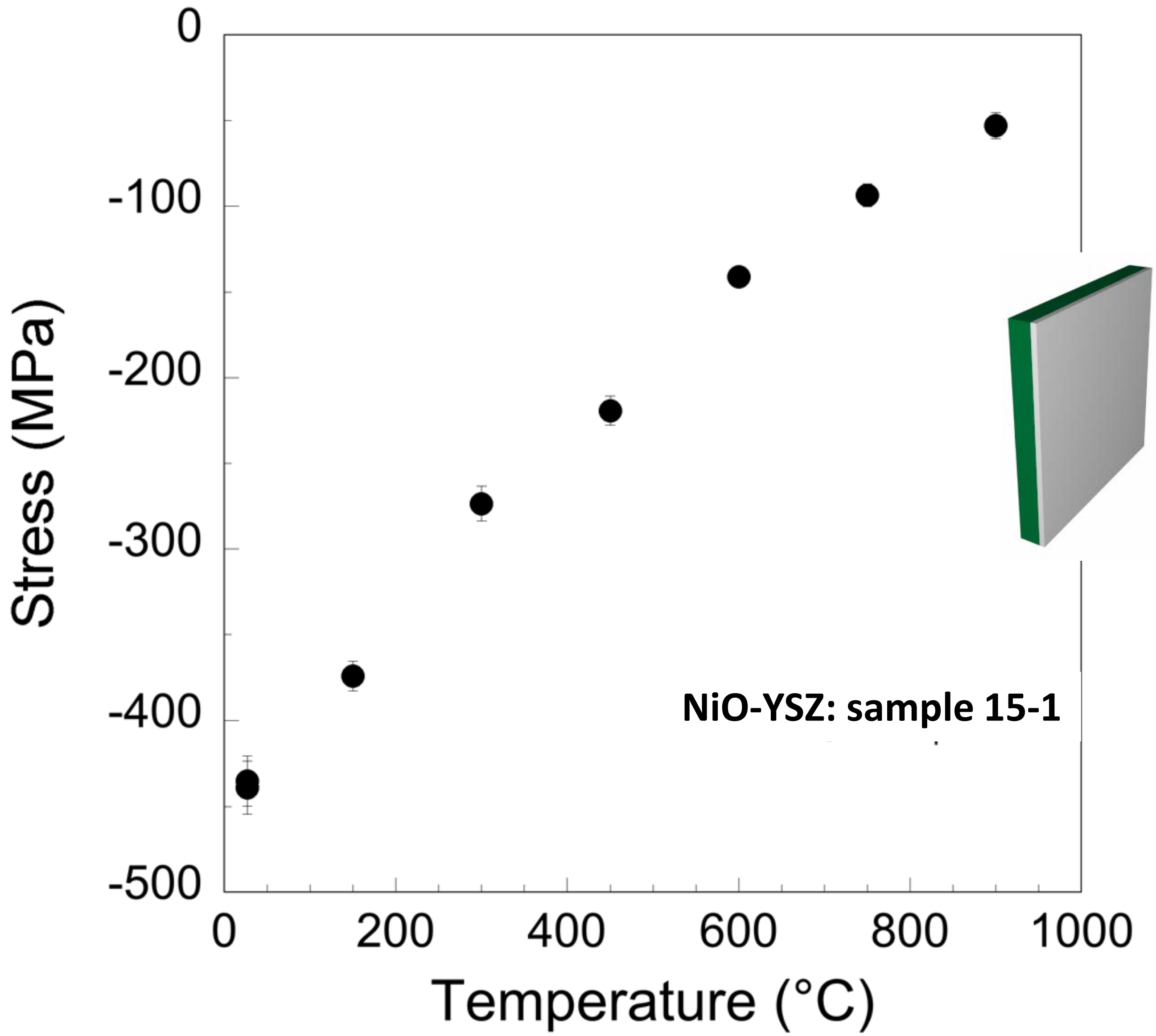
Residual Stresses in YSZ-NiO-YSZ bilayer



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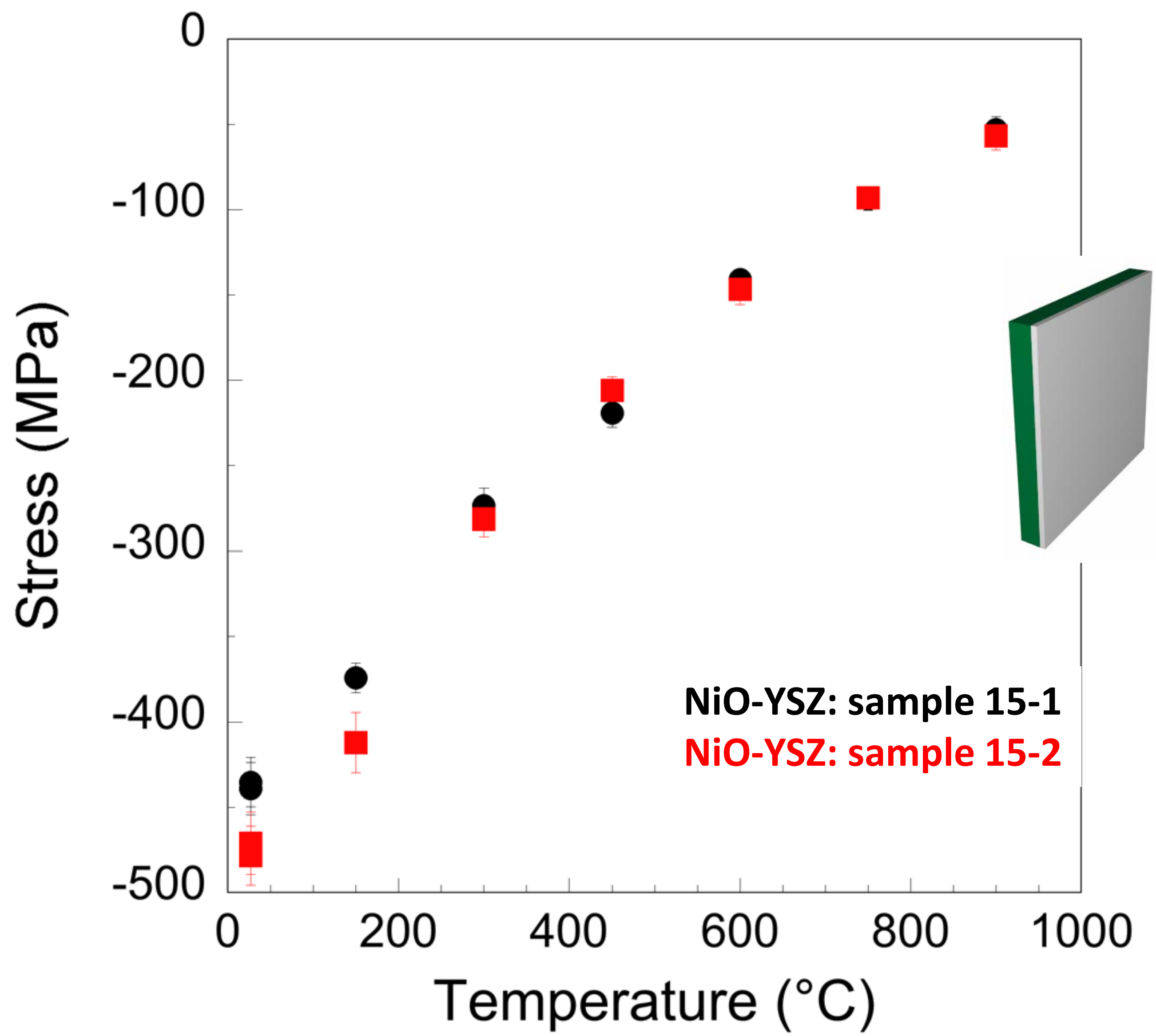
Residual Stresses in YSZ-NiO-YSZ bilayer



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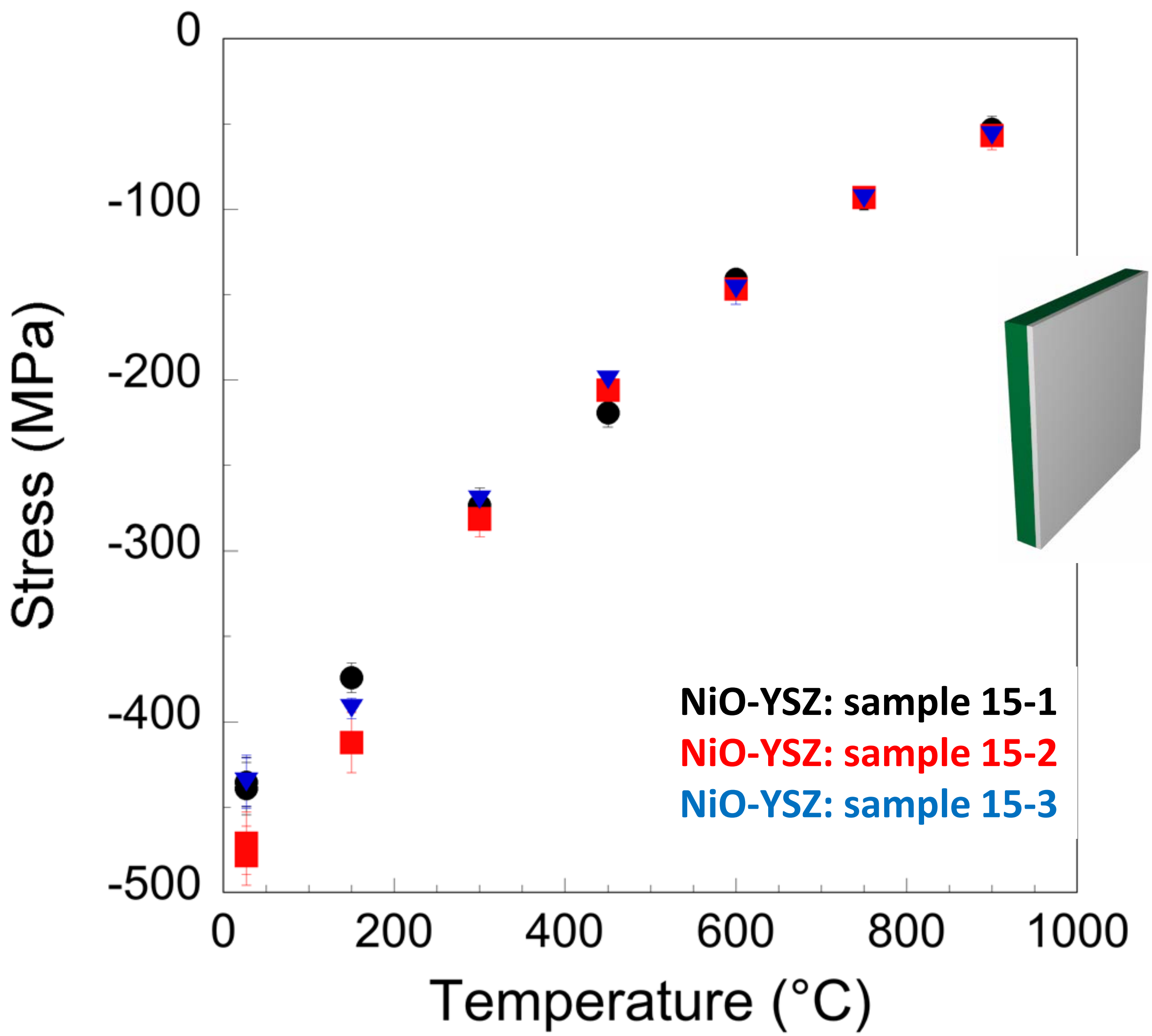
Residual Stresses in YSZ-NiO-YSZ bilayer



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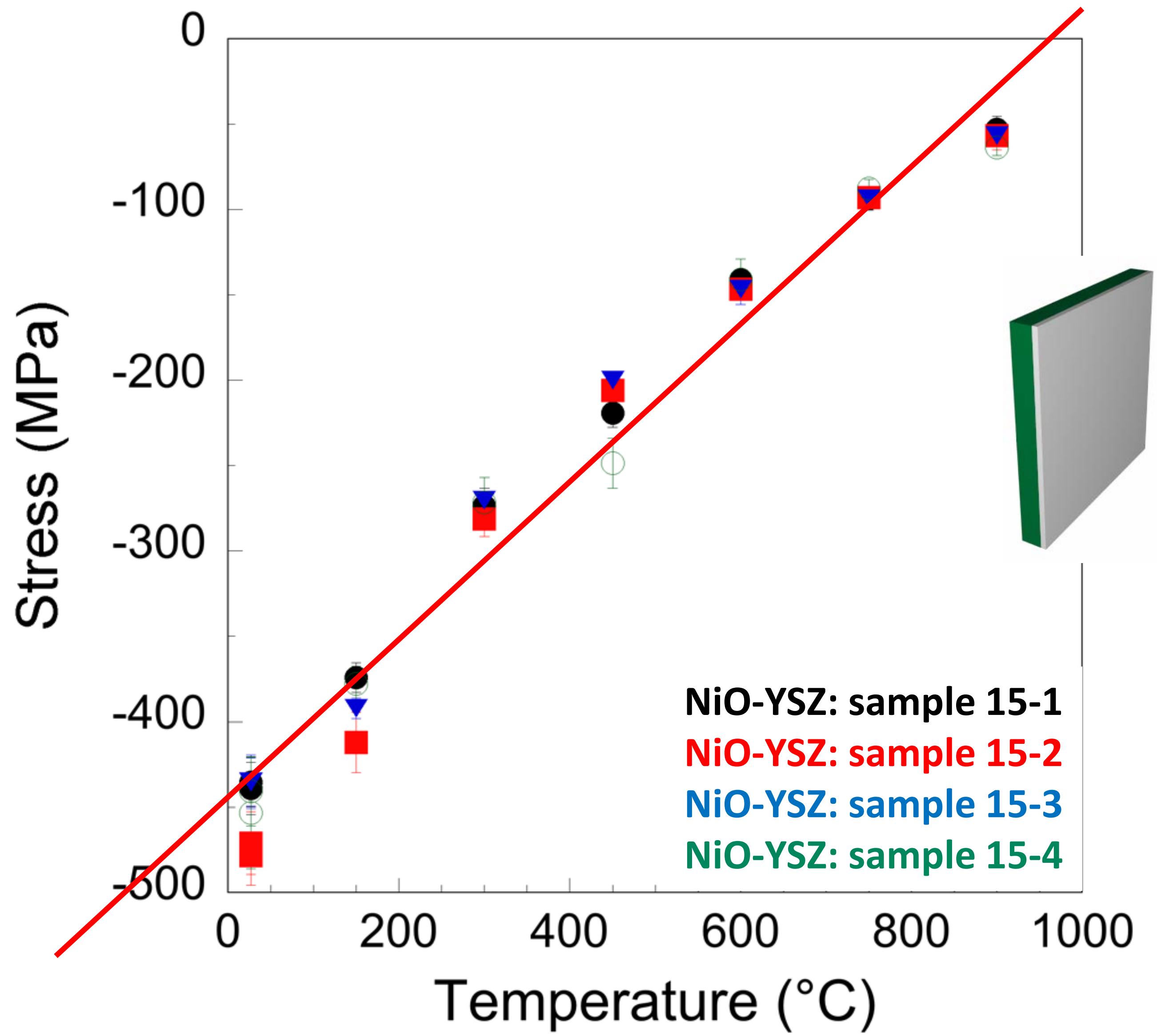
Residual Stresses in YSZ-NiO-YSZ bilayer



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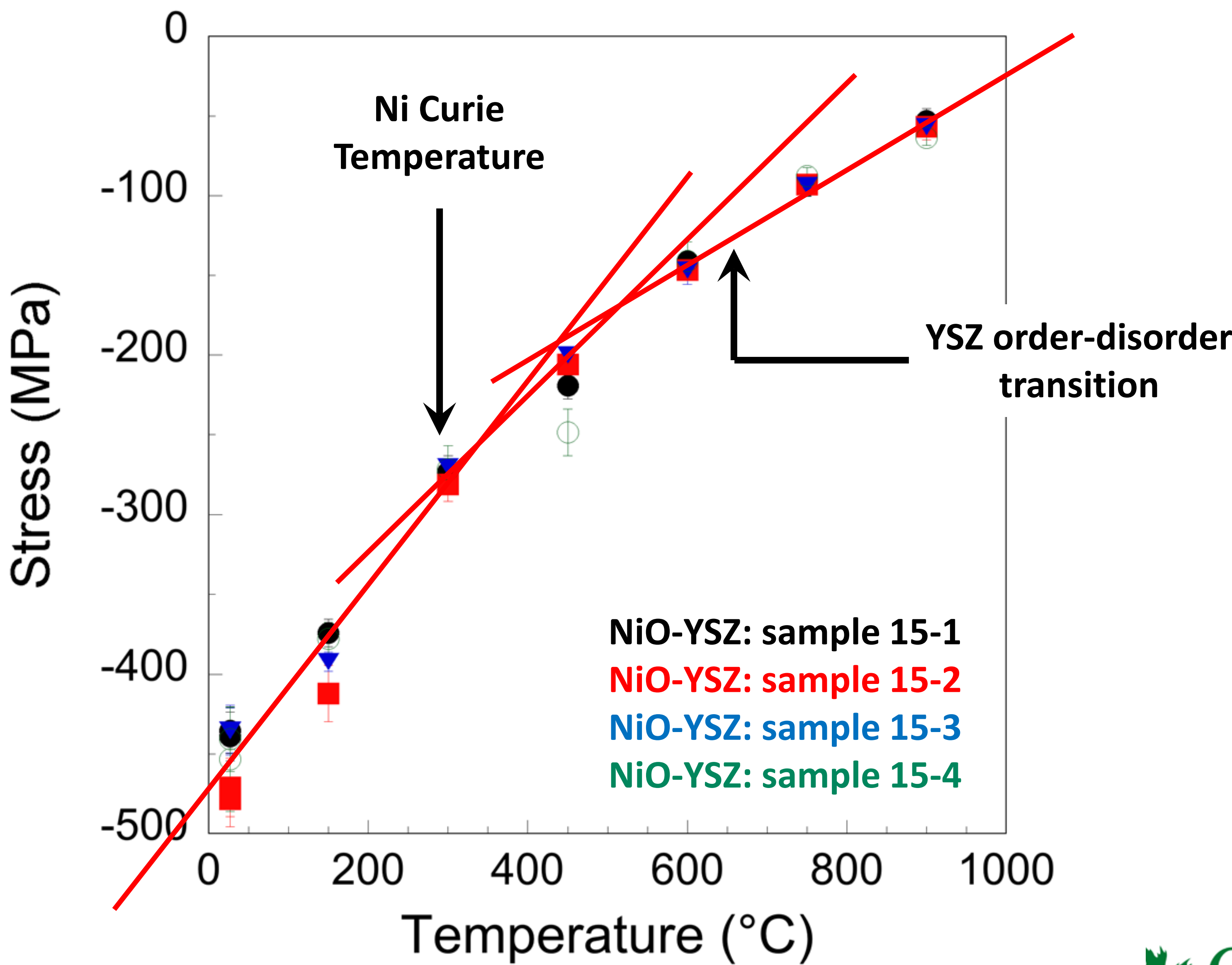
Residual Stresses in YSZ-NiO-YSZ bilayer



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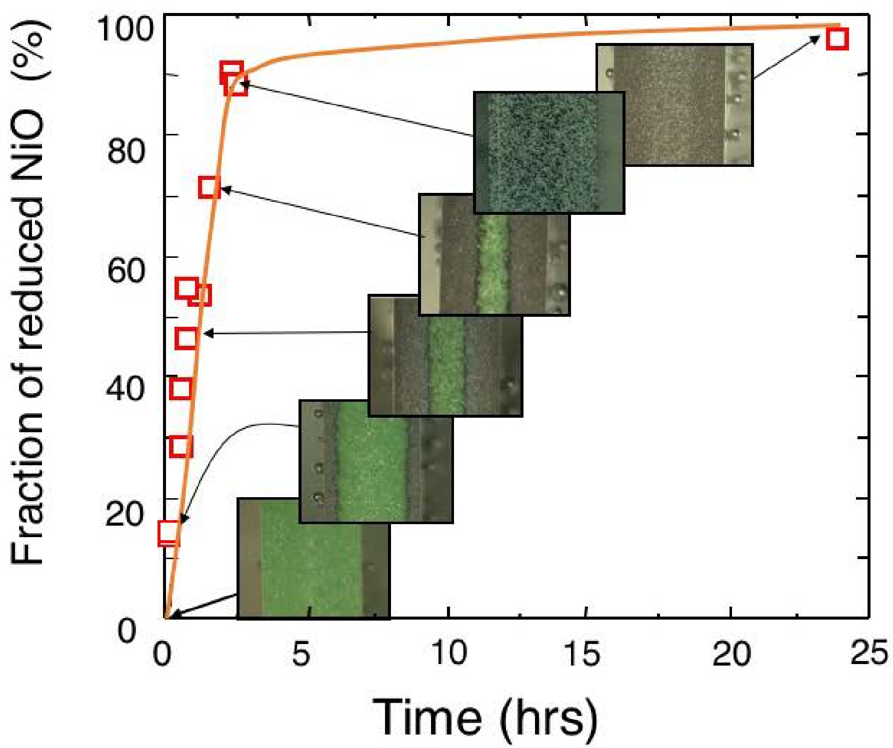
NiO Reduction

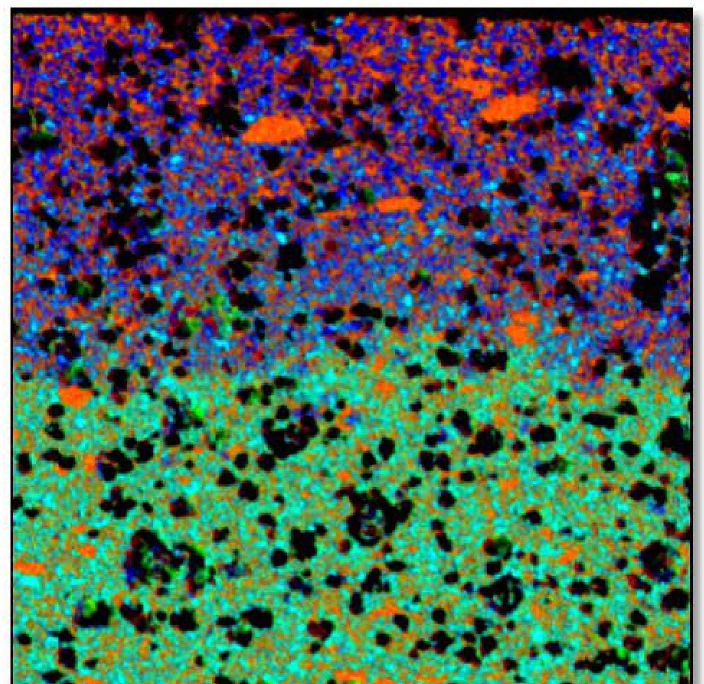
journal
J. Am. Ceram. Soc., 87 [12] 2242–2246 (2004)

Elastic Properties of Nickel-Based Anodes for Solid Oxide Fuel Cells as a Function of the Fraction of Reduced NiO

Miladin Radovic* and Edgar Lara-Curzio*

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6069





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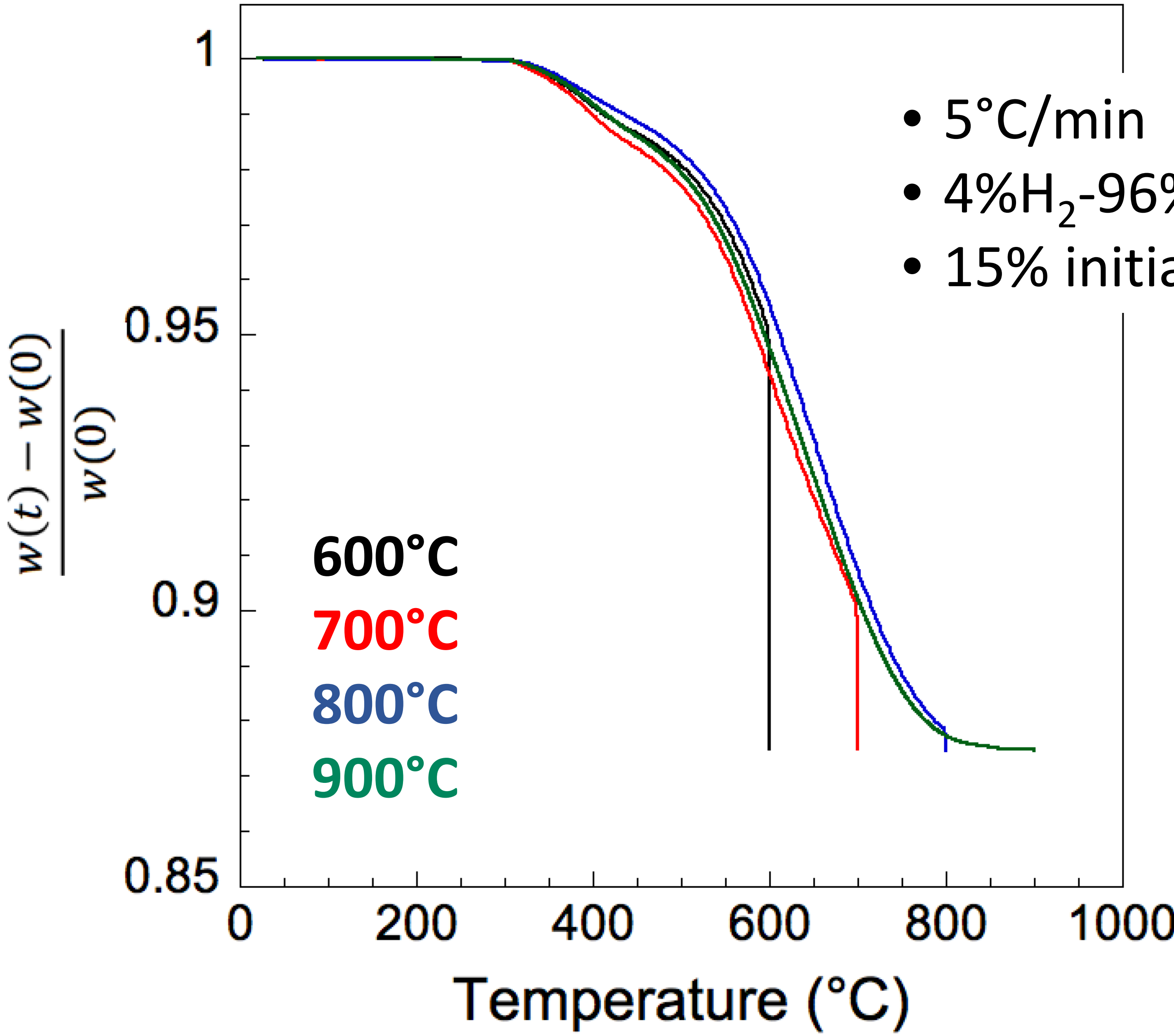
Reduction of NiO-YSZ



- 5°C/min
- 4%H_2-96%Ar
- 15% initial porosity

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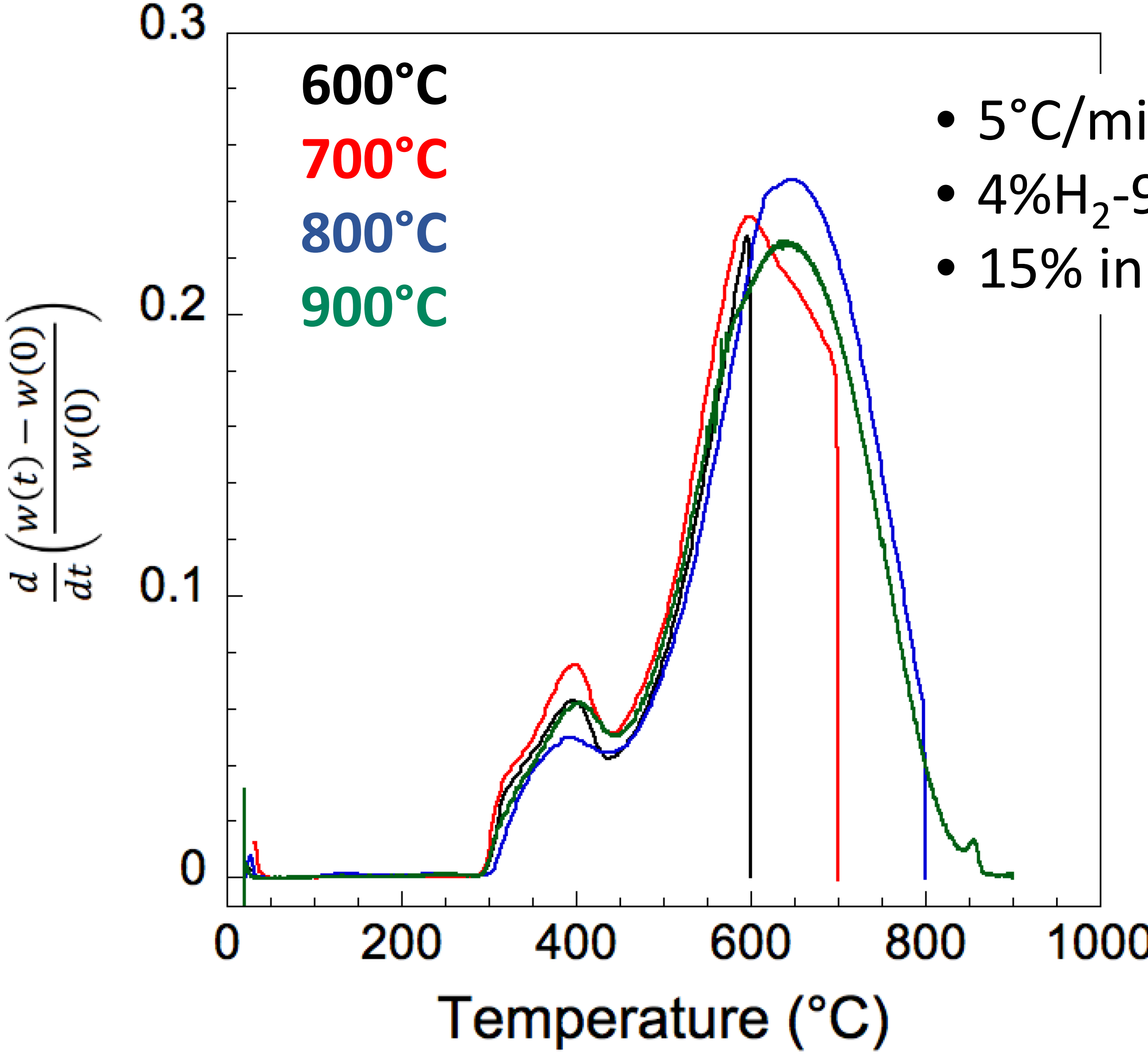
Reduction of NiO-YSZ



- 5°C/min
- 4%H_2-96%Ar
- 15% initial porosity

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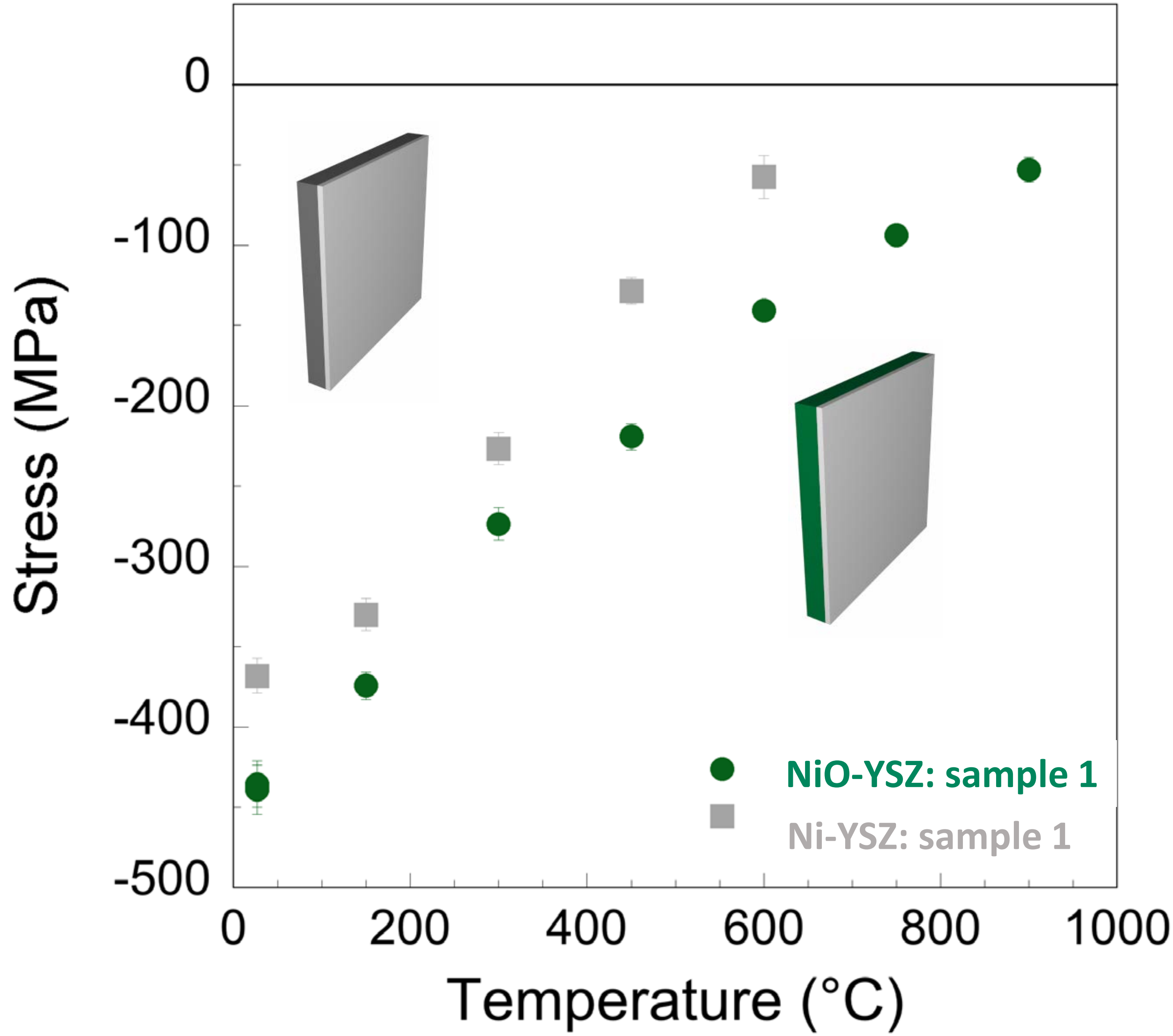
Effect of NiO Reduction Temperature on Residual Stresses

Reduction of NiO-YSZ

Reduction Temperature: 600°C



Porosity

- NiO-YSZ: 15%
- Ni-YSZ: 34%

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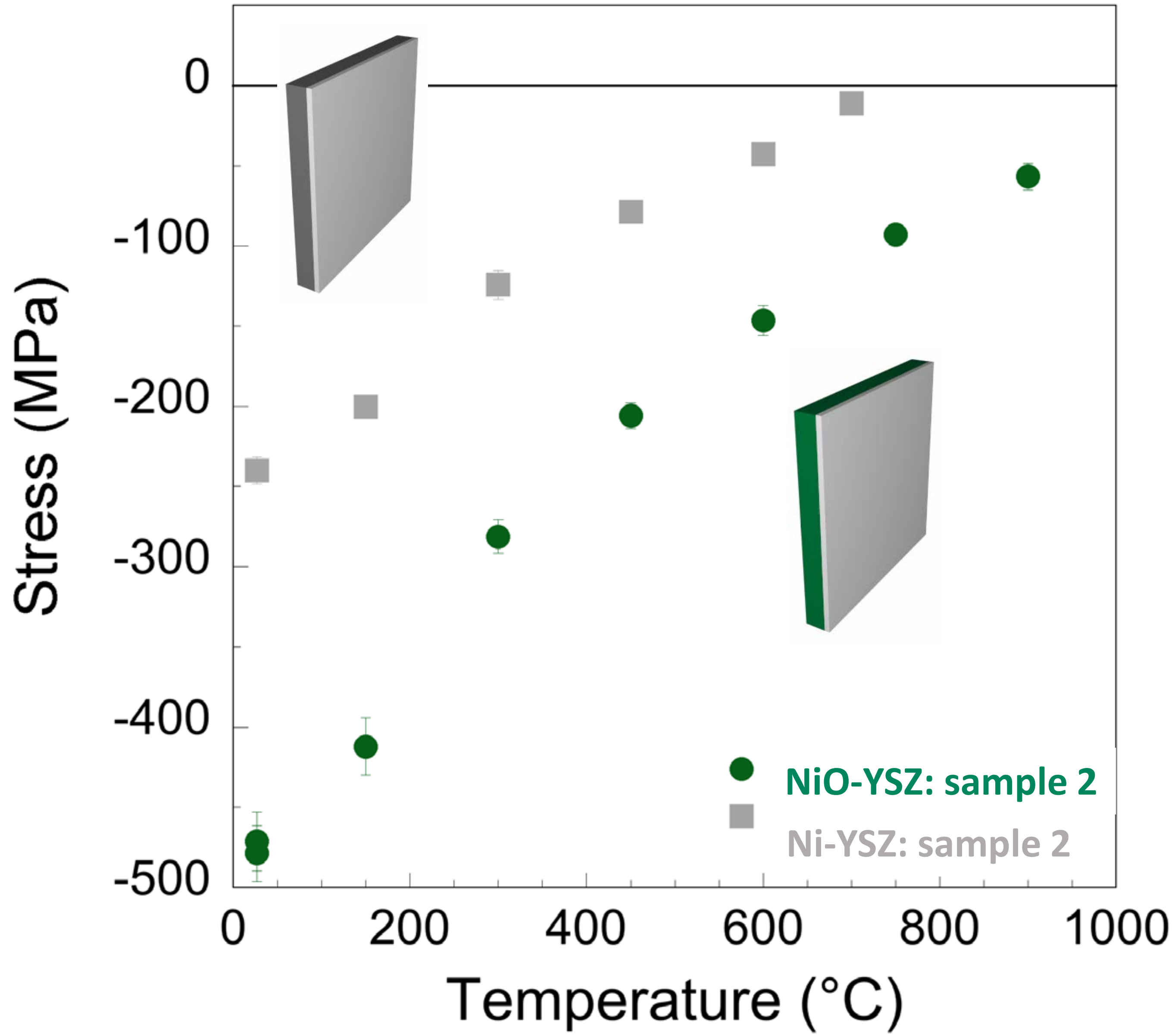
Reduction of NiO-YSZ

Reduction Temperature: 700°C



Porosity

- NiO-YSZ: 15%
- Ni-YSZ: 34%

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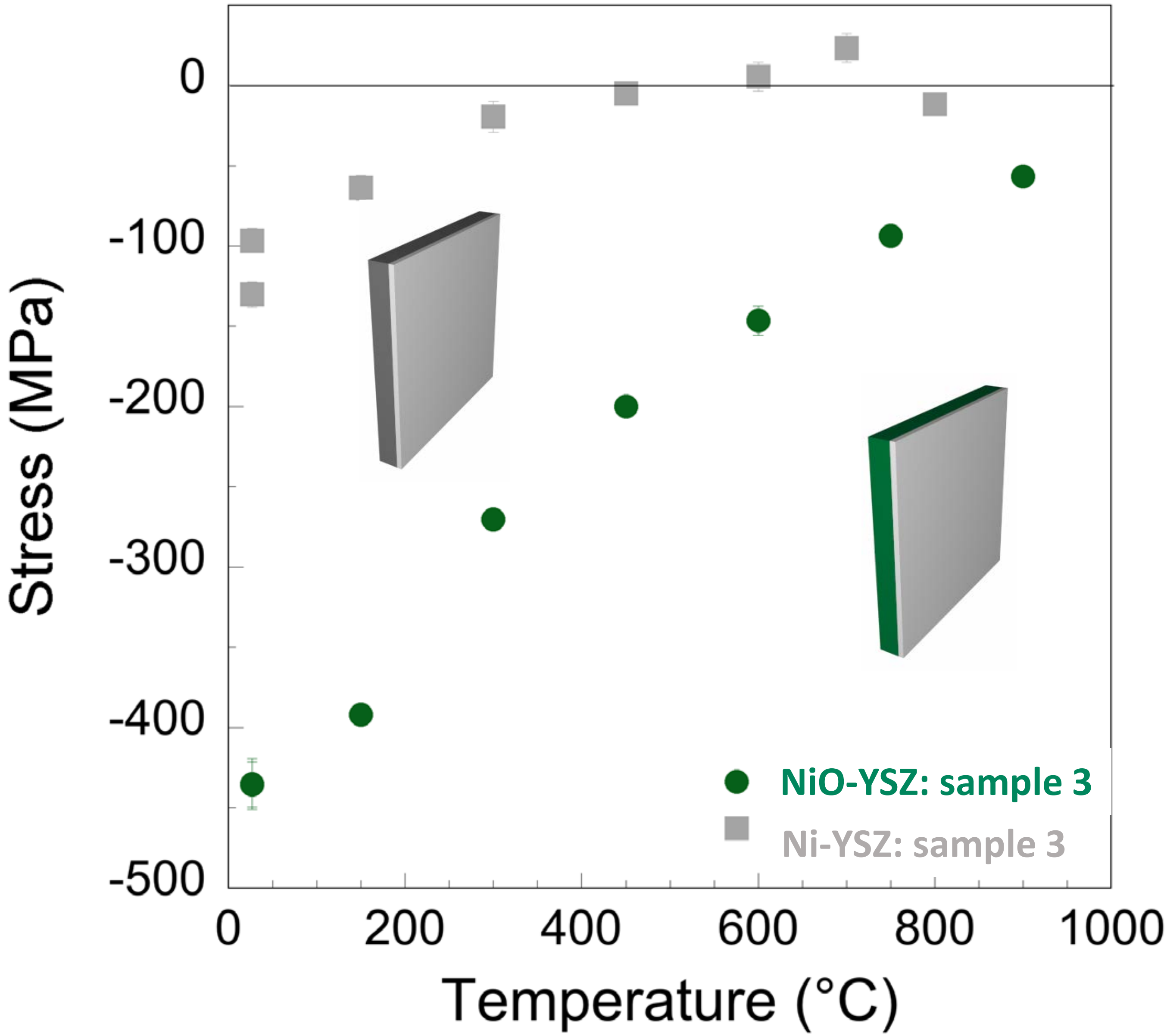
Reduction of NiO-YSZ

Reduction Temperature: 800°C



Porosity

- NiO-YSZ: 15%
- Ni-YSZ: 34%

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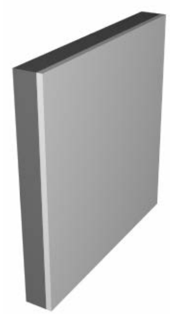
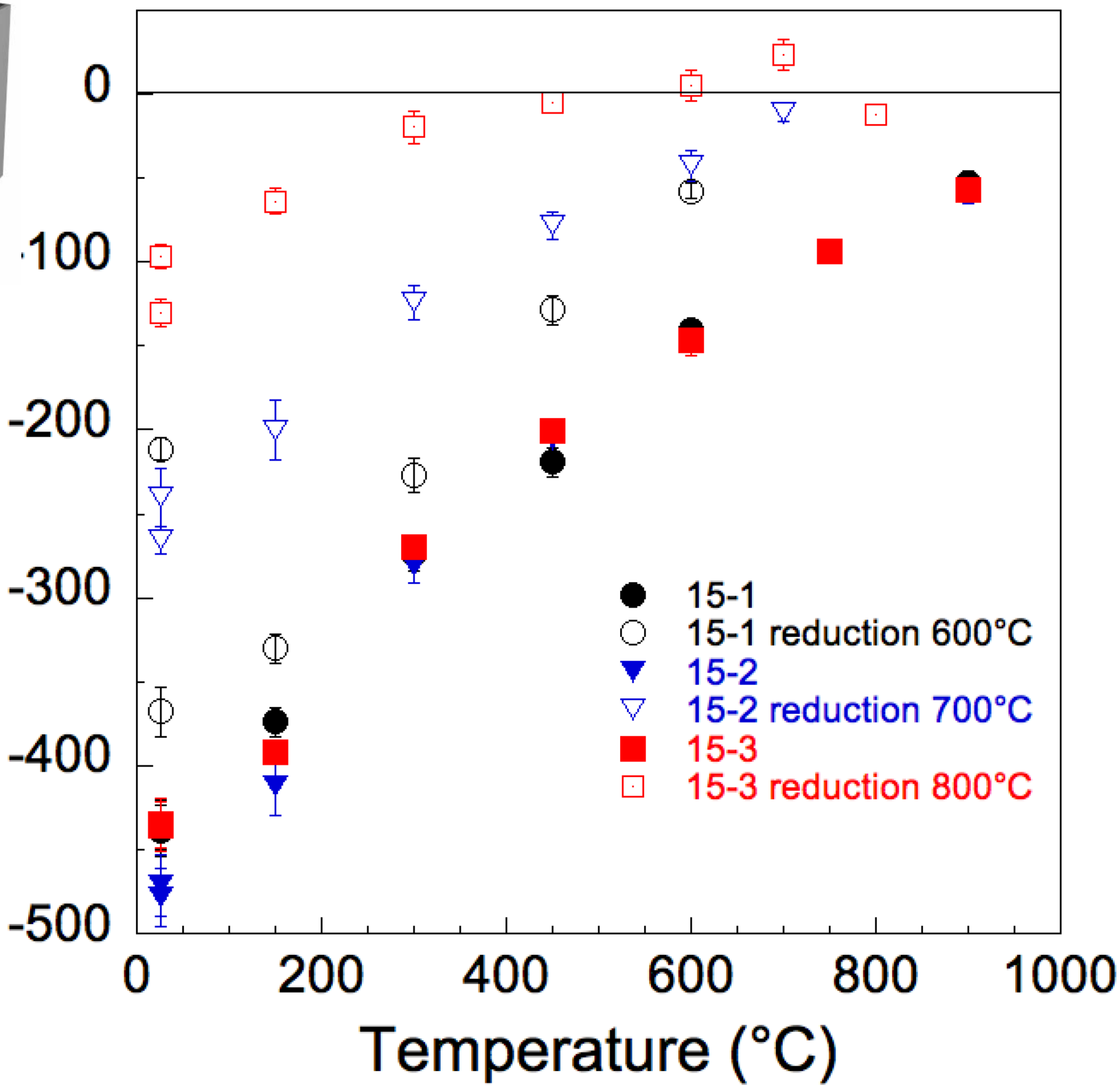
Reduction of NiO-YSZ

Effect of Reduction Temperature





Porosity

- NiO-YSZ: 15%
- Ni-YSZ: 34%

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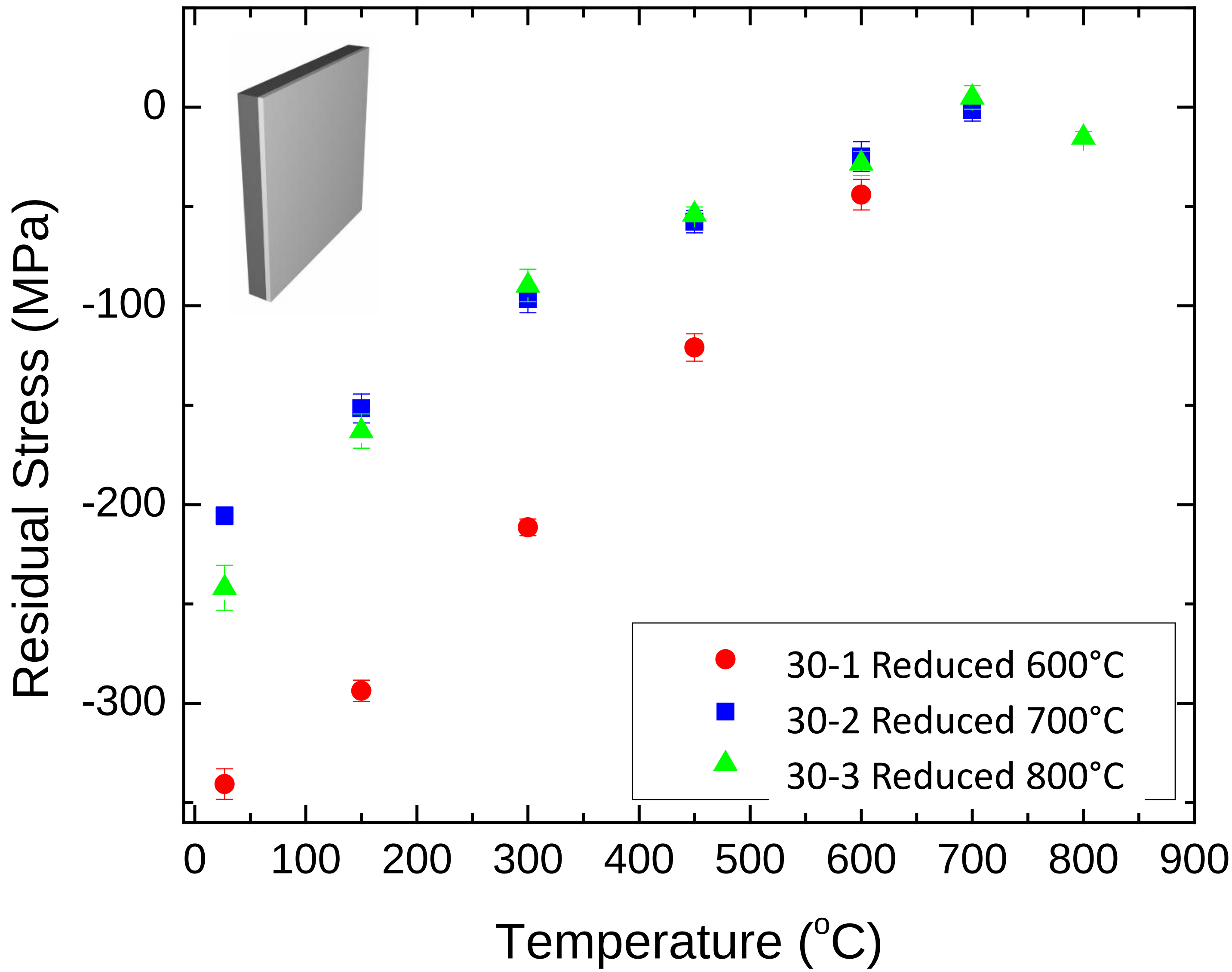
Reduction of NiO-YSZ

Effect of Reduction Temperature



Porosity

- NiO-YSZ: 30%
- Ni-YSZ: 45%

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Creep Behavior of Ni-YSZ

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Questions

- Do **operational** stresses induce creep deformation?
- Does creep deformation change the microstructure of anode materials?
- If yes, how do these changes affect the functionality of the anode?
- If the layers bonded to the anode (e.g., electrolyte and interconnect) creep less than the anode, how do stresses experienced by the anode get redistributed to the neighboring layers?

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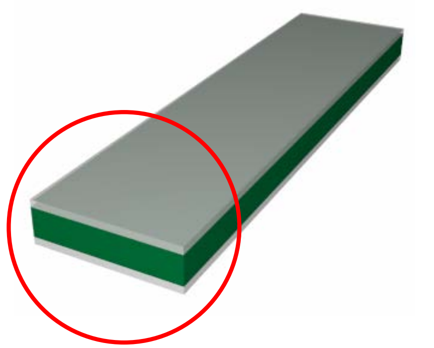
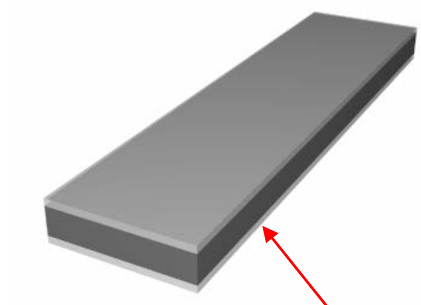
Materials for Creep testing (Sandwich Configuration)

As-processed

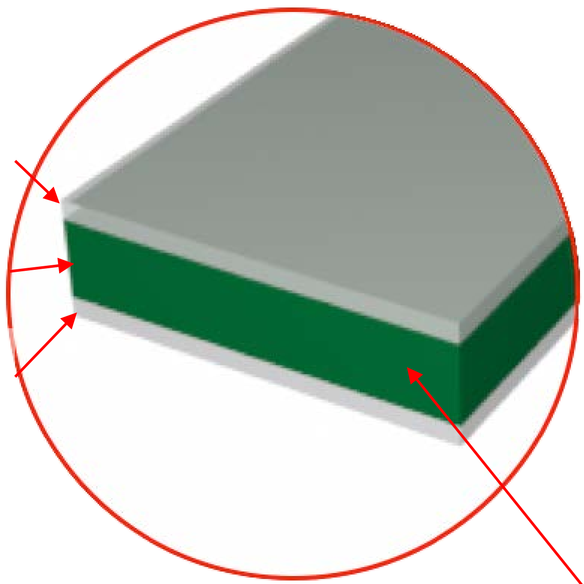


After reduction



YSZ thickness
~2µm
~20 µm
~40 µm

Porosity
34%
45%
53%



Porosity
15%
30%
40%

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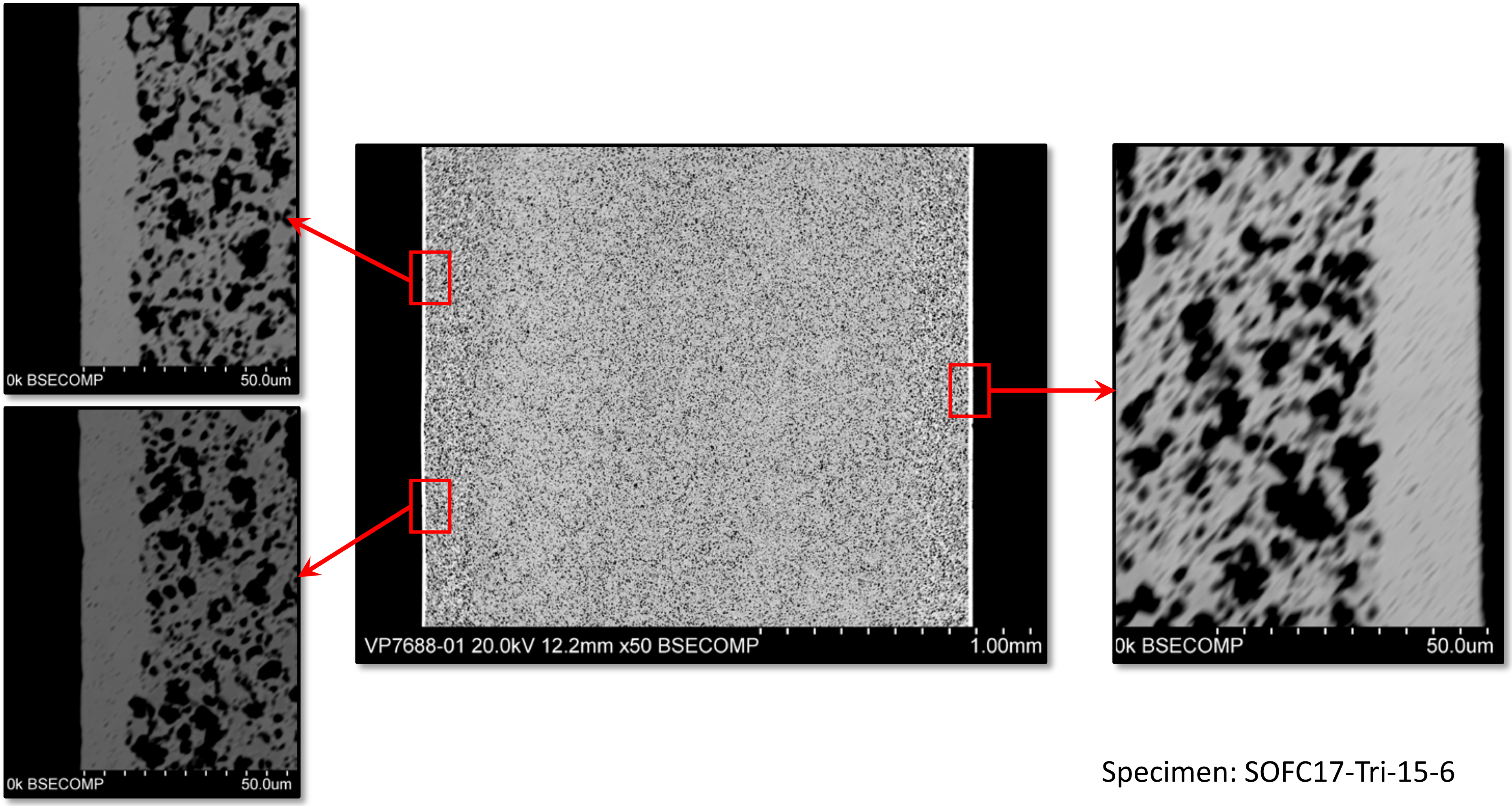
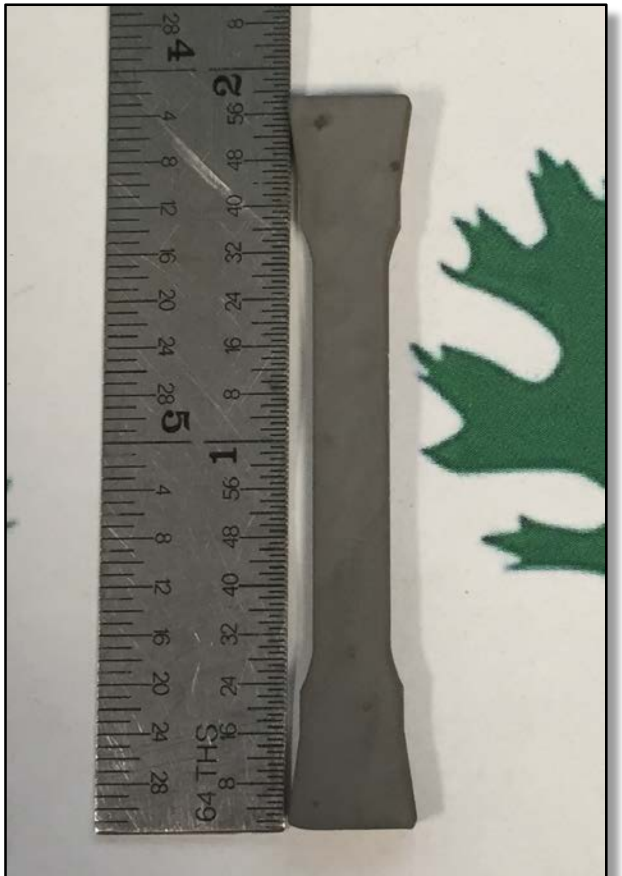
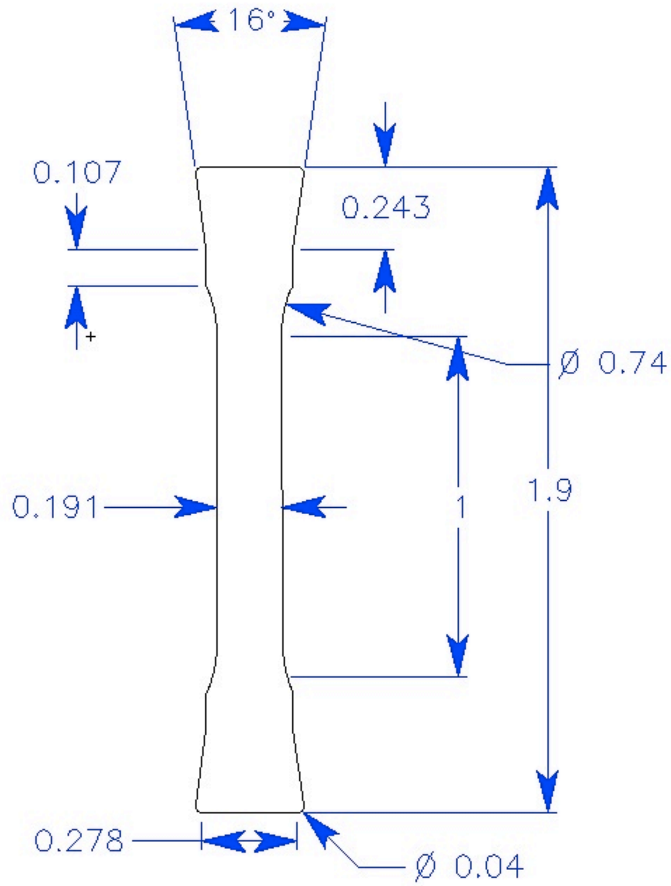
YSZ/Ni-YSZ/YSZ Sandwich Specimen



Specimen: SOFC17-Tri-15-6

Shoulder-loaded Tensile Specimen





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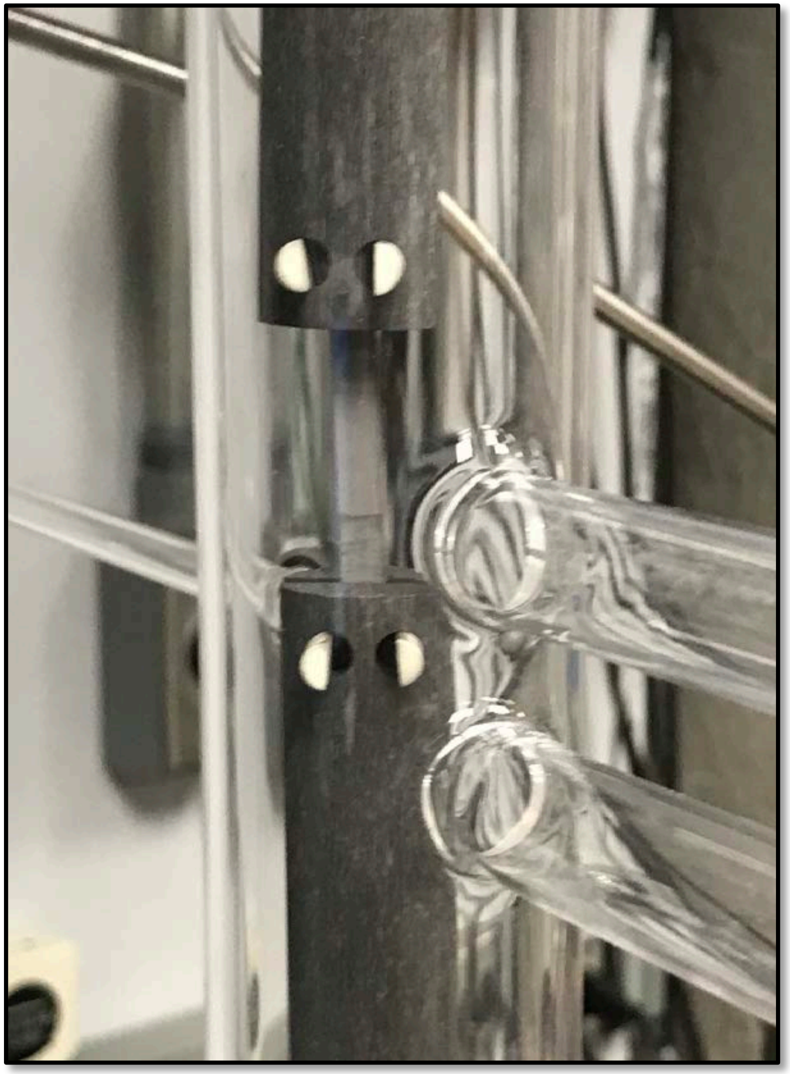
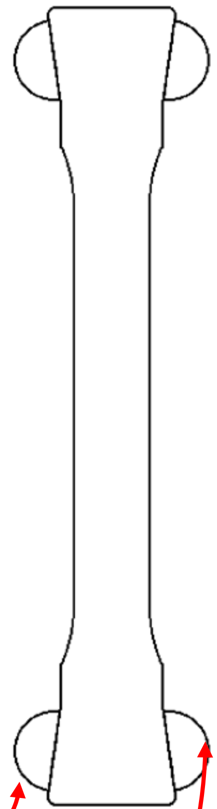
Creep Testing Facility





Load is transferred to the test specimen through its shoulders

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Creep Testing Facility

- High temperature
- Controlled environment

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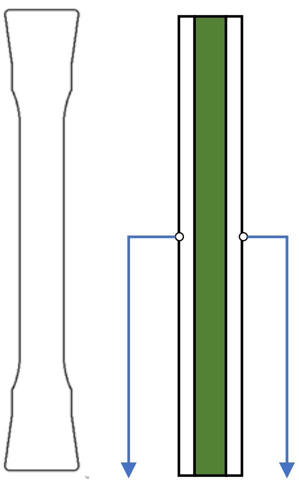
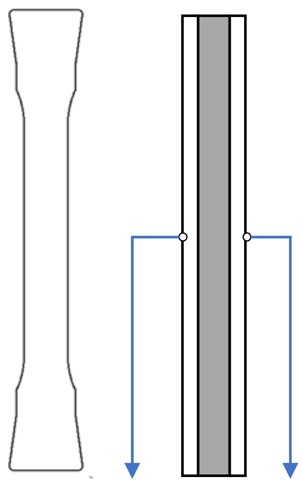
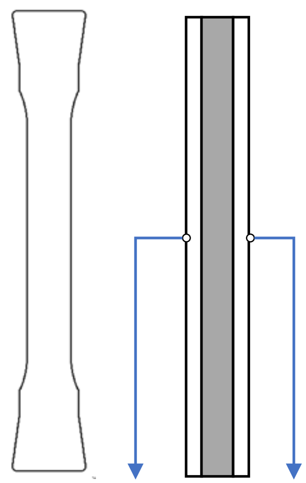
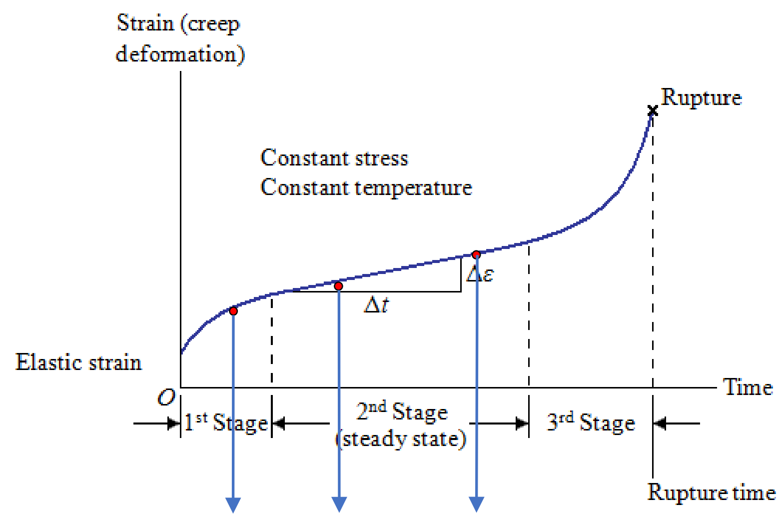
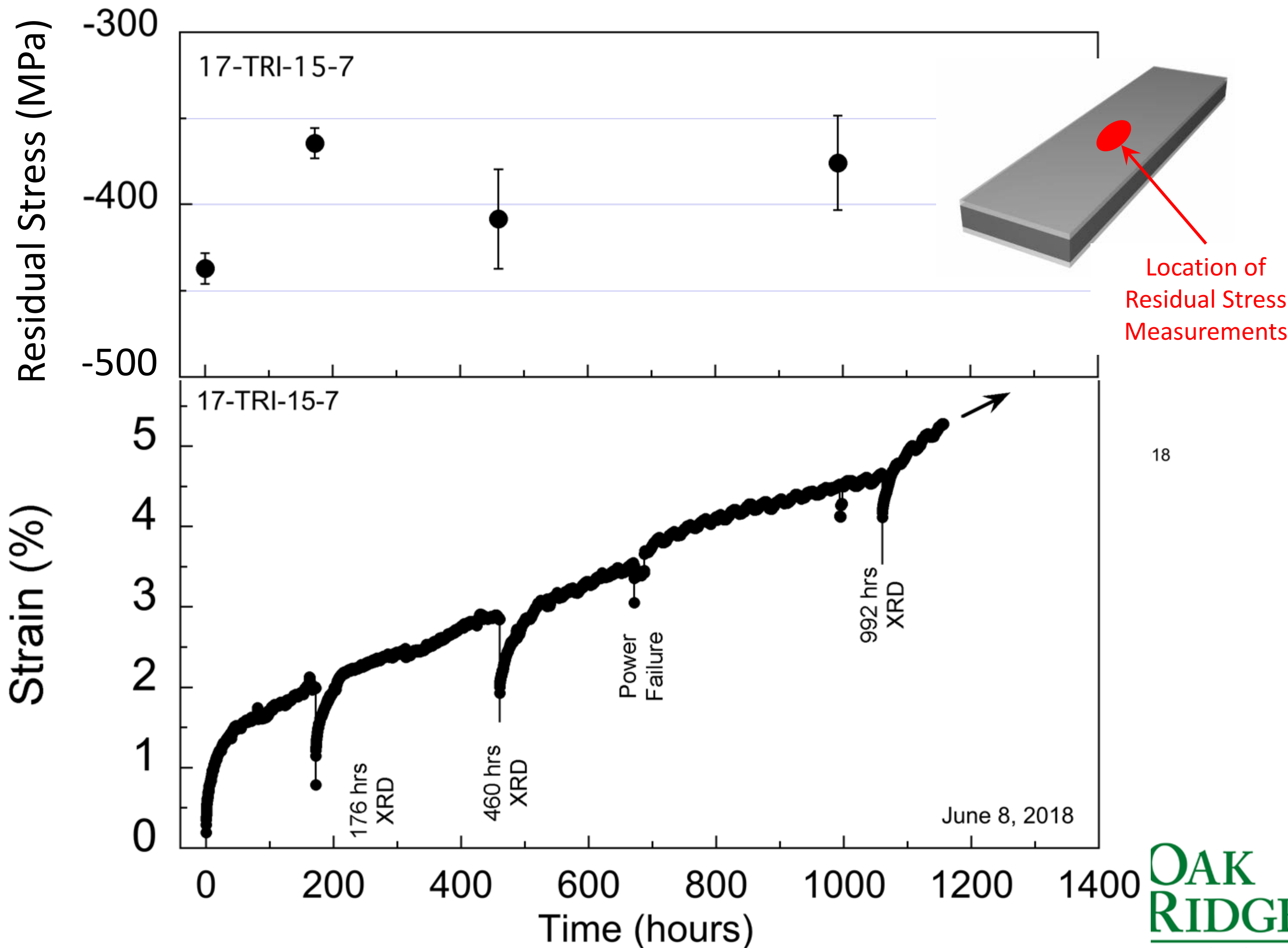
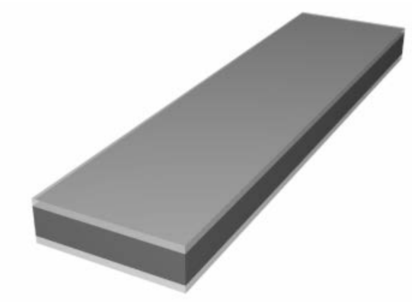
Methodology (Residual Stress Measurements)

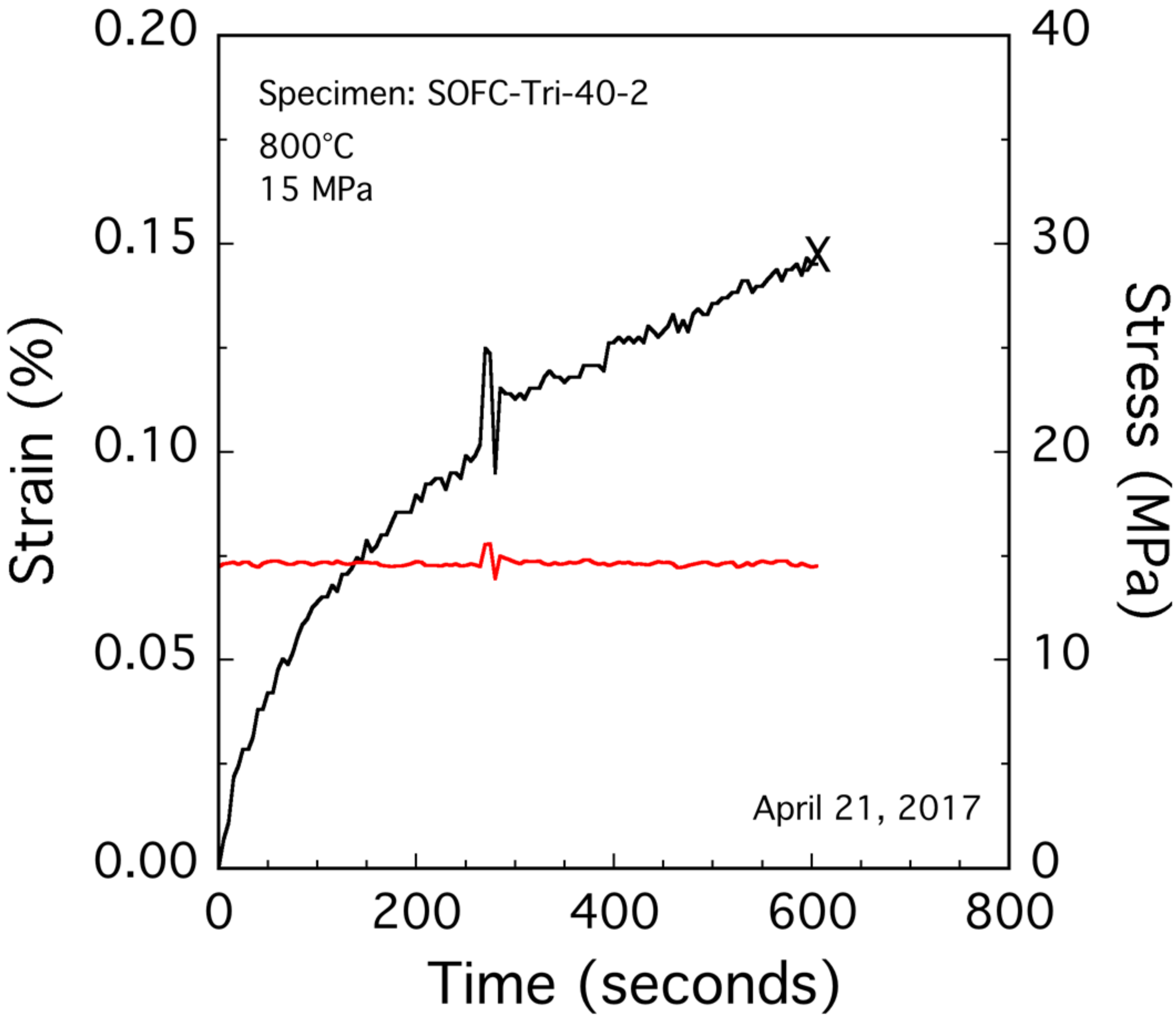
As-processed	After Reduction	After Creep Deformation (by interrupting creep tests)	
			
Residual Stress Measurement	Residual Stress Measurement	Residual Stress Measurement	Interrupted creep test

Creep-Induced Redistribution of Residual Stresses



Creep Testing Results





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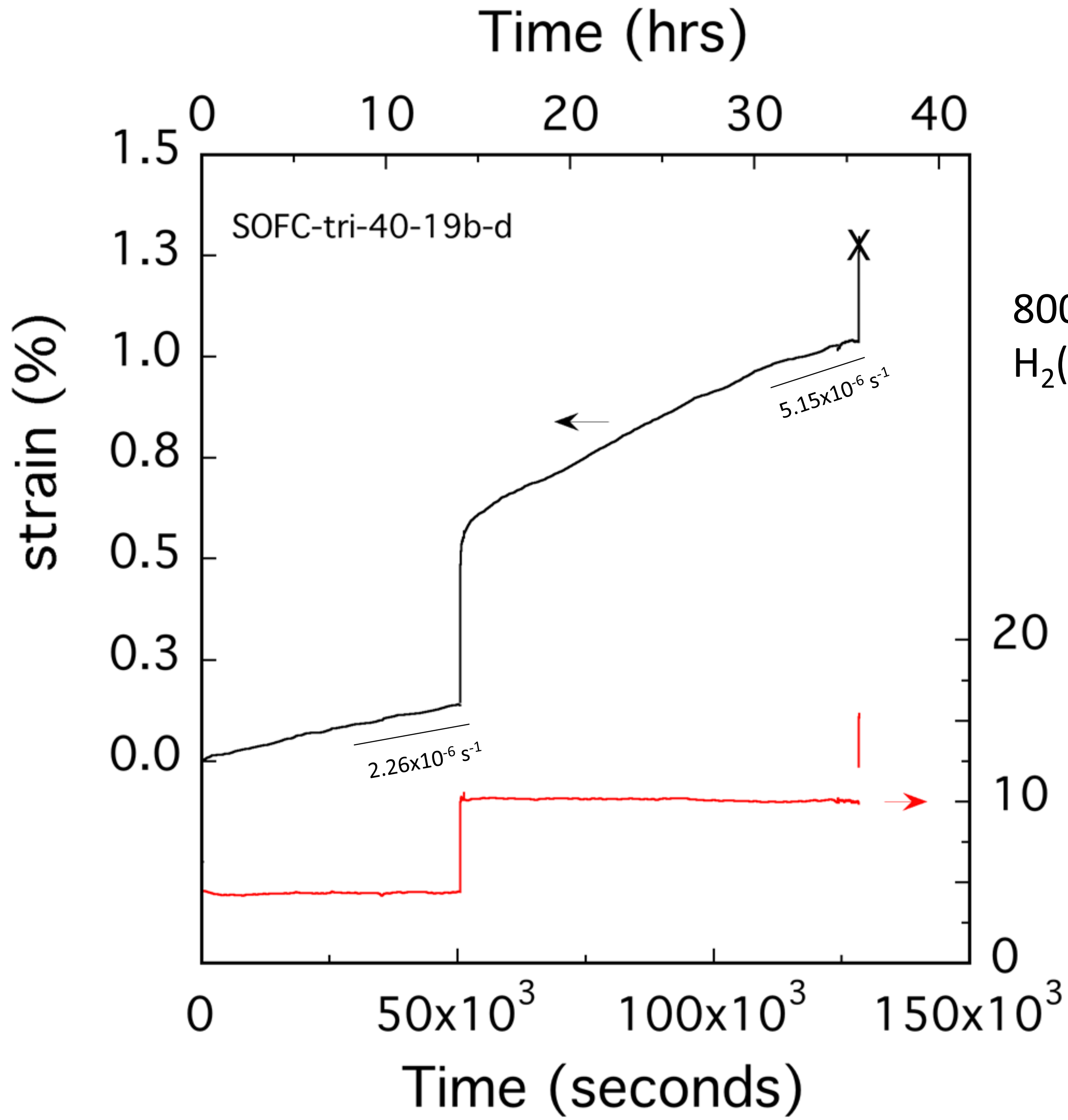
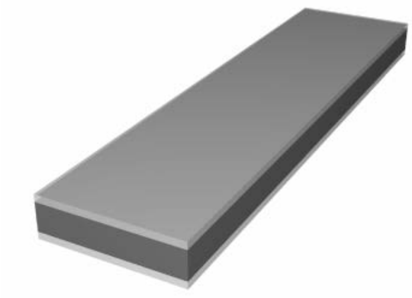
Creep Testing Results

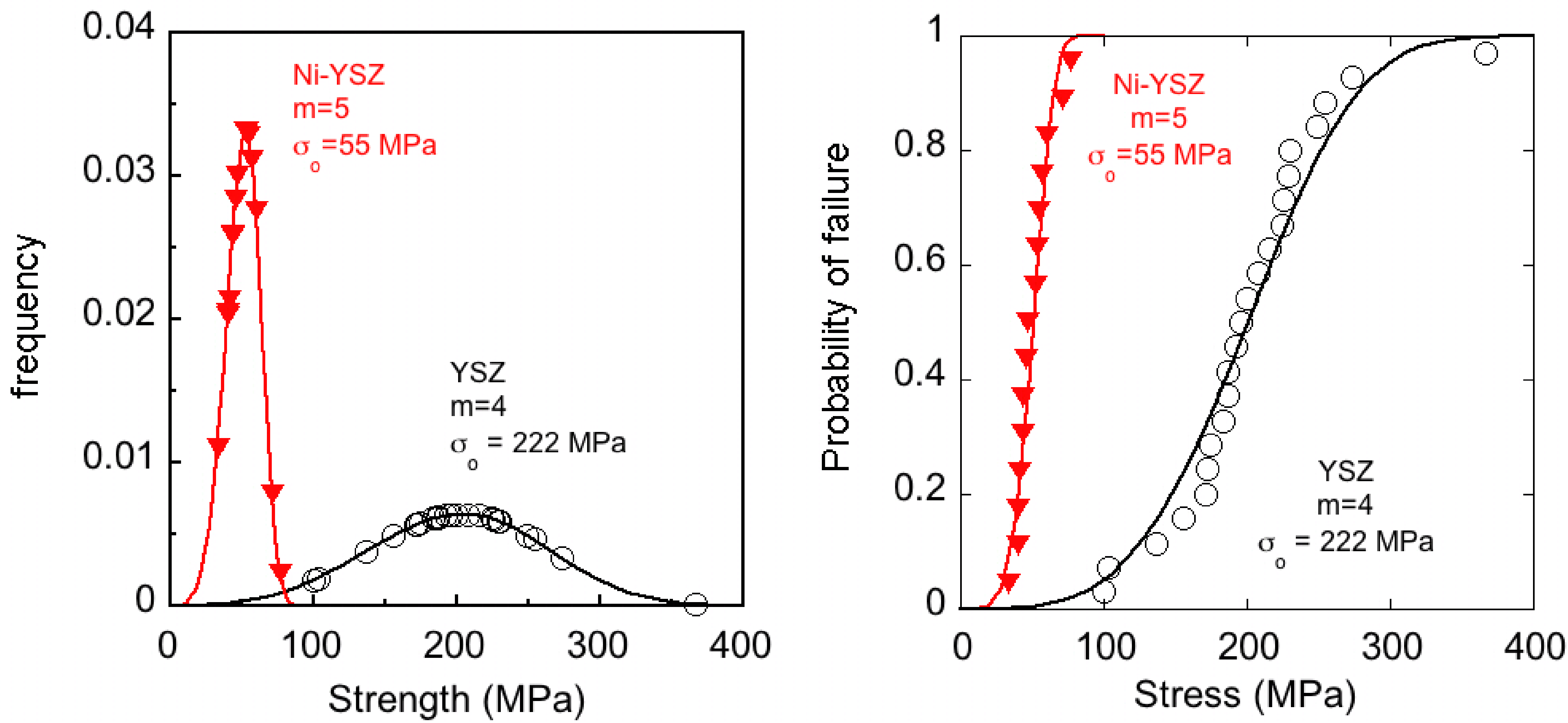




800°C
$H_2(4\%)$-Ar(96%)

Lara-Cu

Strength of SOFC materials



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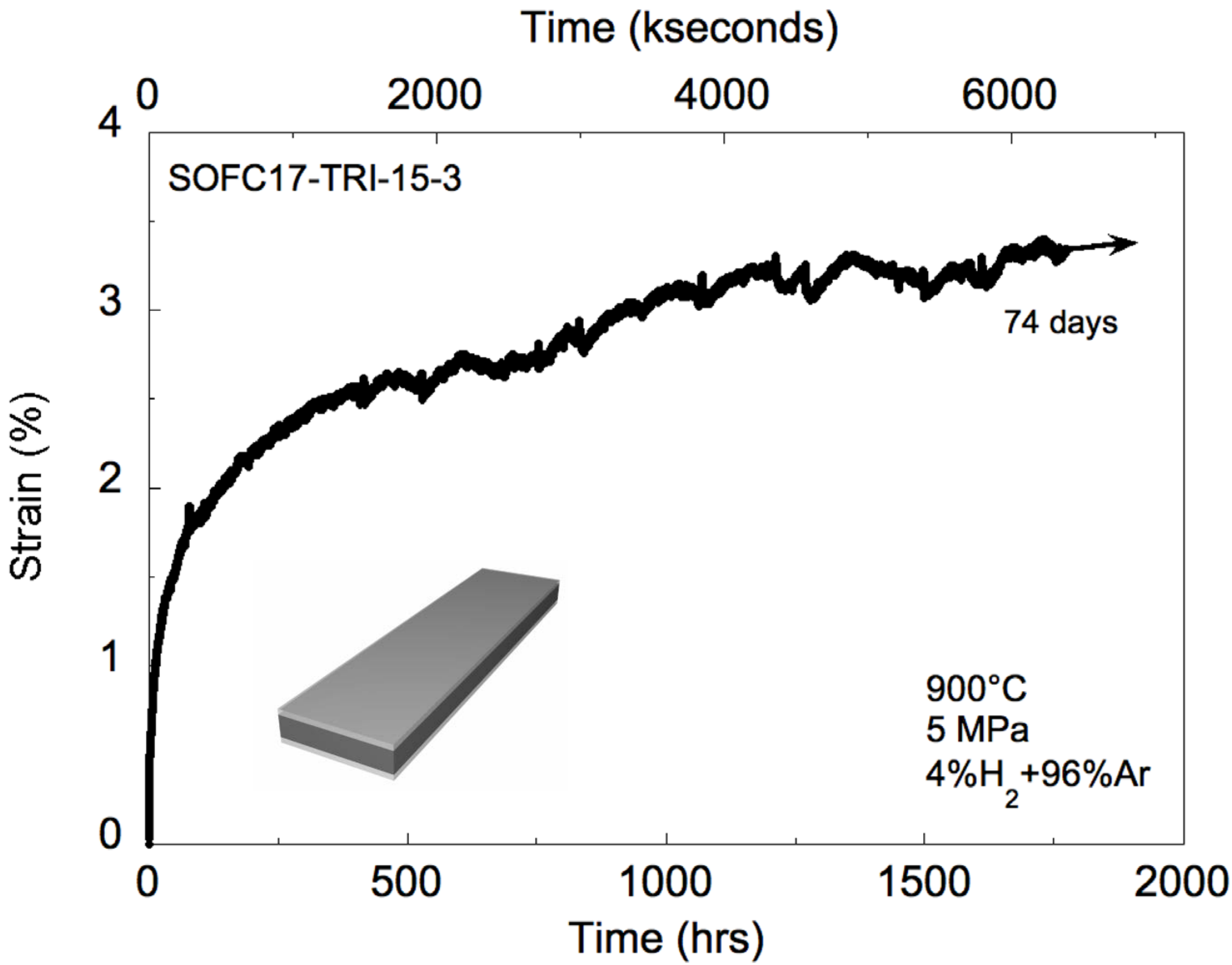
Creep Behavior of YSZ/Ni-YSZ/YSZ



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Summary

- The state of residual stresses of YSZ/Ni-YSZ bilayers depends on reduction temperature
- The magnitude of residual stress decreases with increasing reduction temperature and porosity

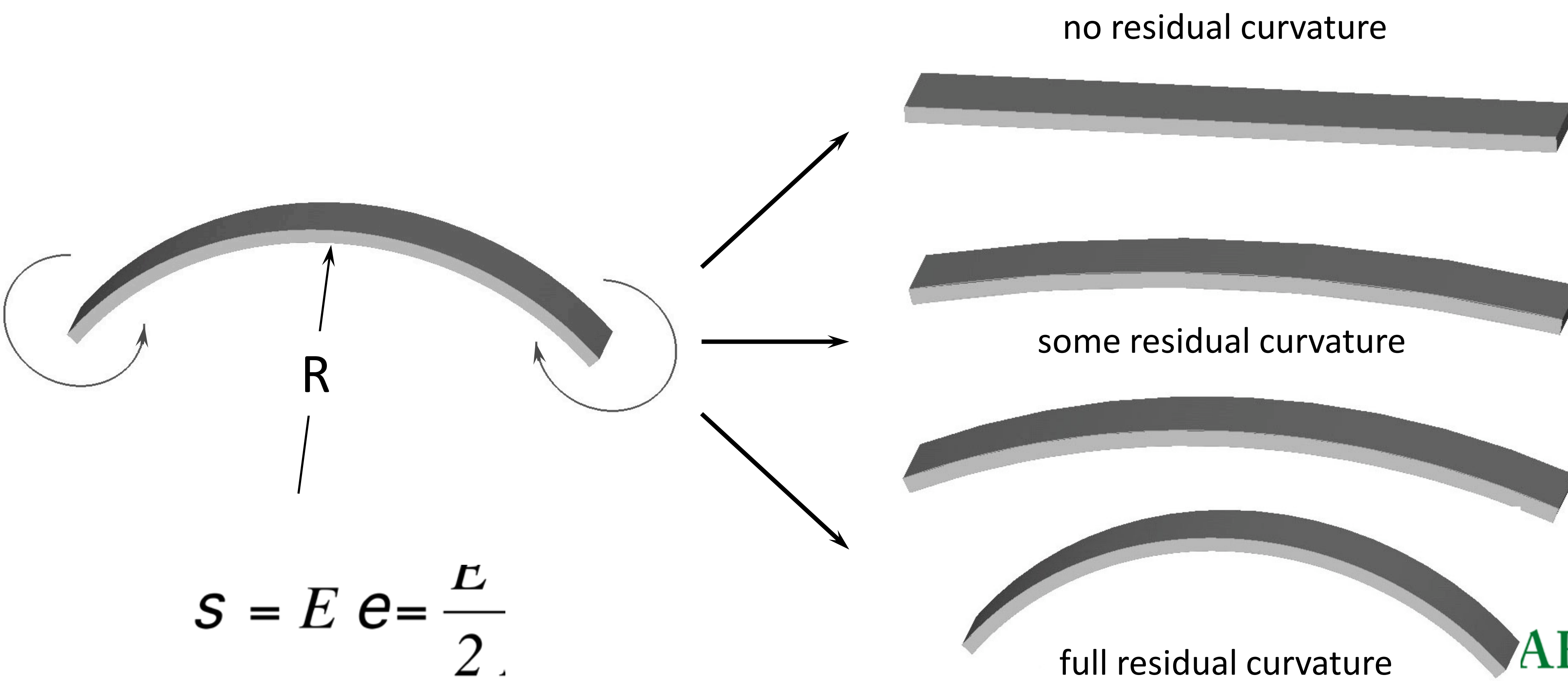
Summary

- Effect of creep deformation on the microstructure and functionality of anode materials is being investigated.
- The redistribution of stresses in SOFCs as a result of anode creep deformation is being measured using interrupted creep tests and x-ray diffraction.
- Preliminary results show that stresses get redistributed within a cell, which has implications on SOFC durability and reliability.

Time-dependent deformation

Let's subject a beam under a constant bending moment at a given temperature for a predetermined period of time.

At the end of the thermal treatment, let's remove the bending moment and measure the residual curvature of the beam by laser profilometry.



$$s = E\ e = \frac{E}{2}$$

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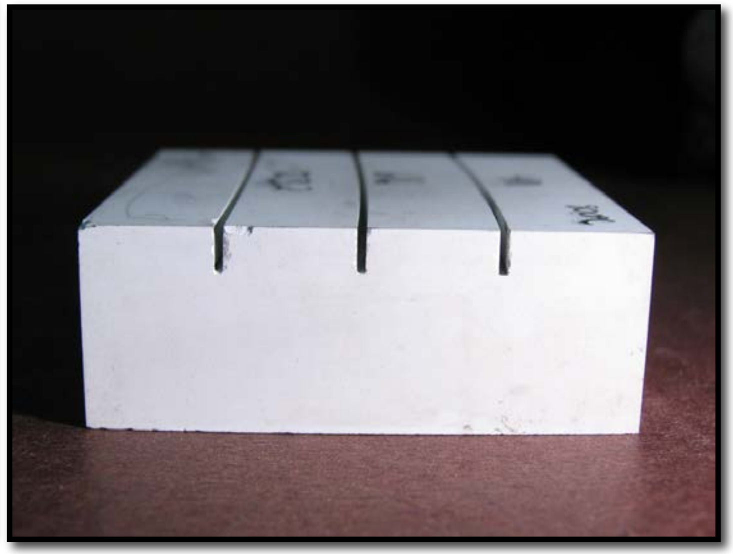
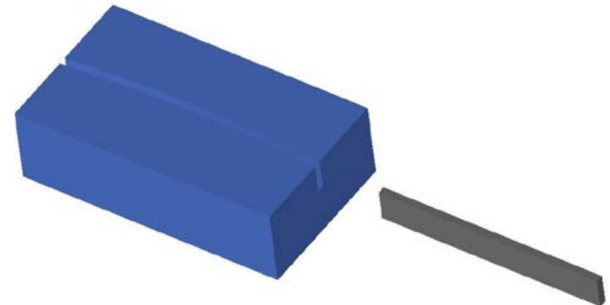
Time-dependent deformation Ni-YSZ (30% porosity)





alumina fixtures

- 600° C
- 800° C
- 900° C
- 15, 30 and 45 MPa
- 4%H_2+96%Ar

sample dimensions:

- 0.7 mm
- 4 mm
- 40 mm

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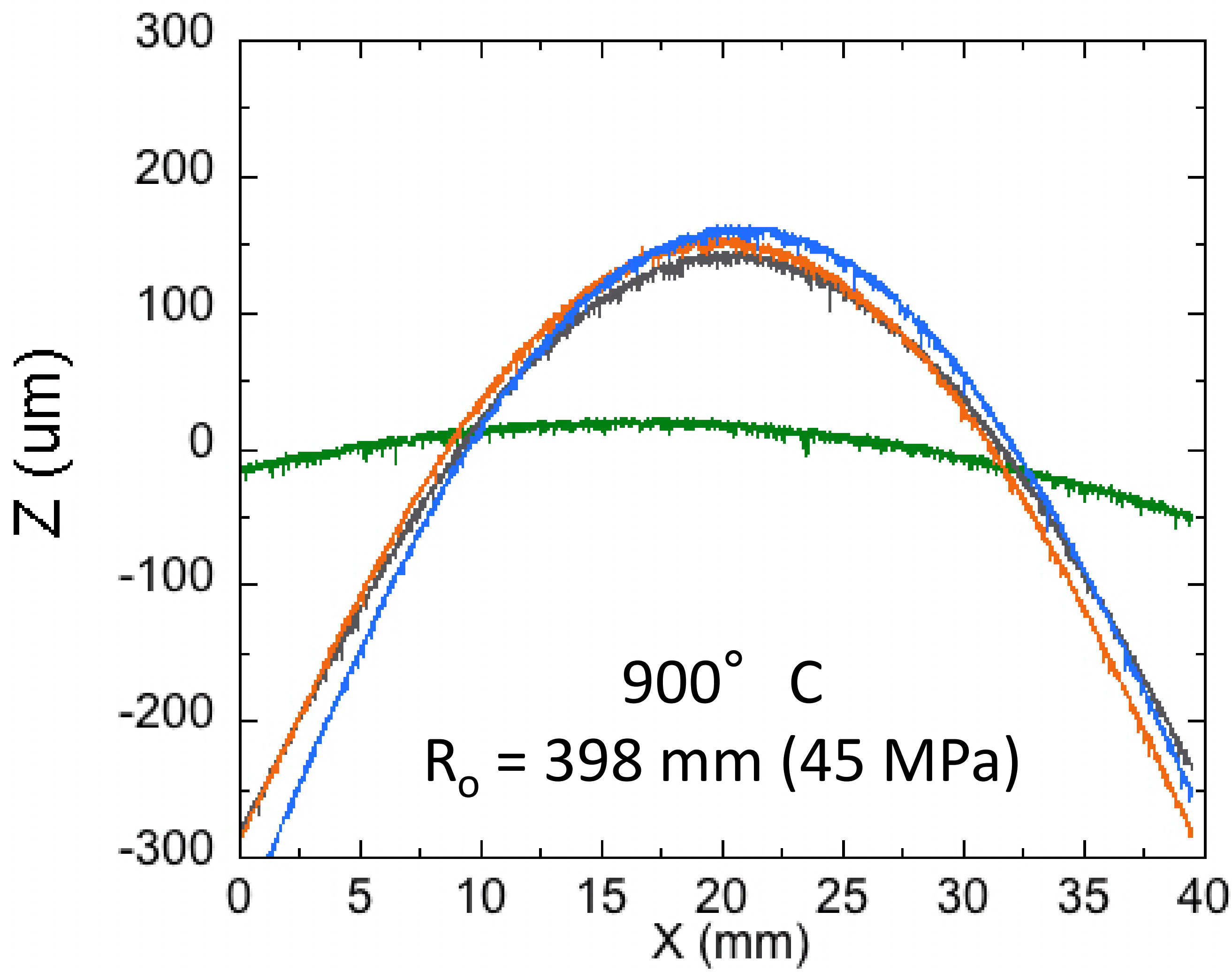
Time-dependent deformation of Ni-YSZ



0	37
1	47
10	43
50	41

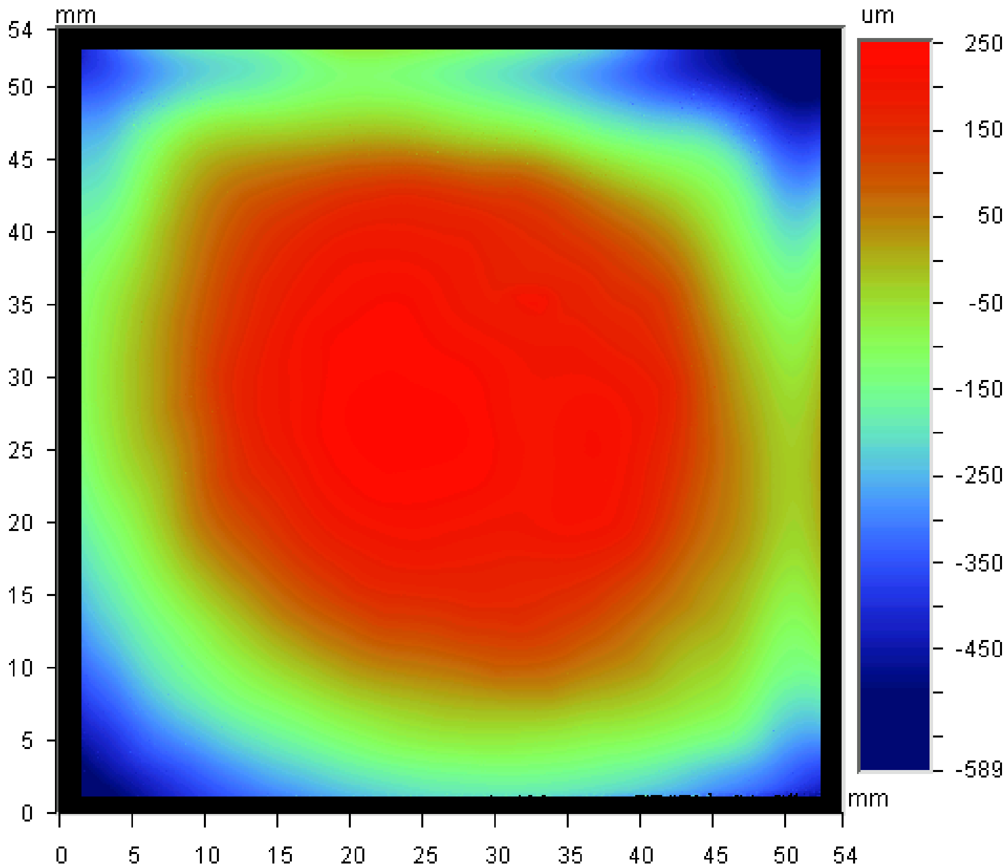
Background

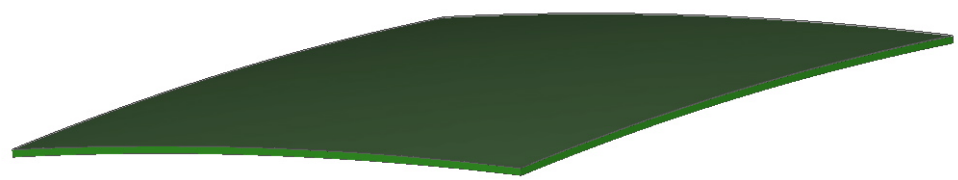
The reliability and durability of materials and components for solid-oxide fuel cells is determined by their state of stress, which consists of the superposition of:

- Residual stresses
- Assembly and Conditioning stresses
- Operational stresses

Ni-YSZ exhibits creep deformation at temperatures relevant to the operation of SOFCs

Curvature of NiO-YSZ/YSZ bilayer: optical profilometry





reconstructed object from profilometric data

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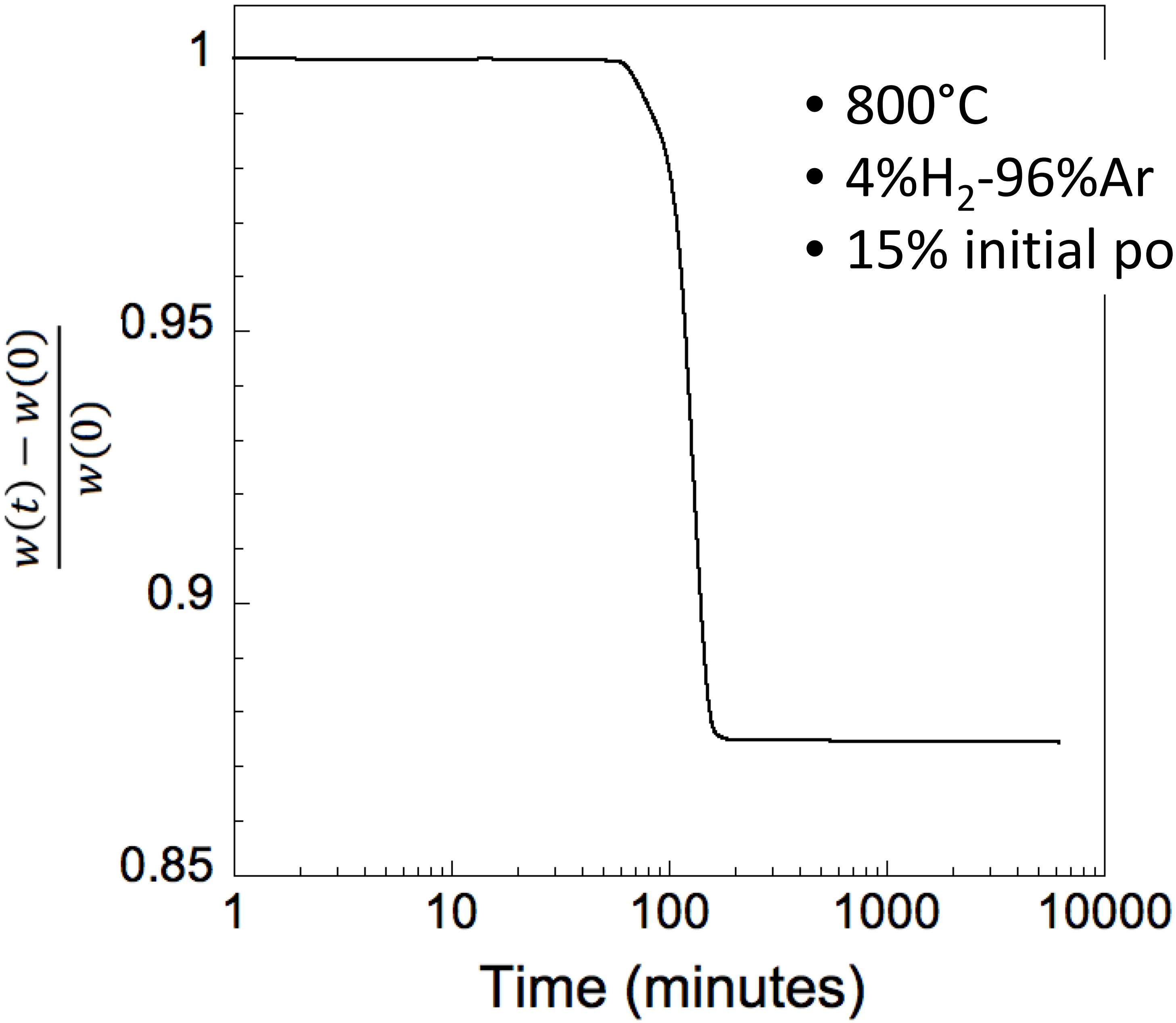
Reduction of NiO-YSZ



- 800°C
- 4%H_2-96%Ar
- 15% initial porosity

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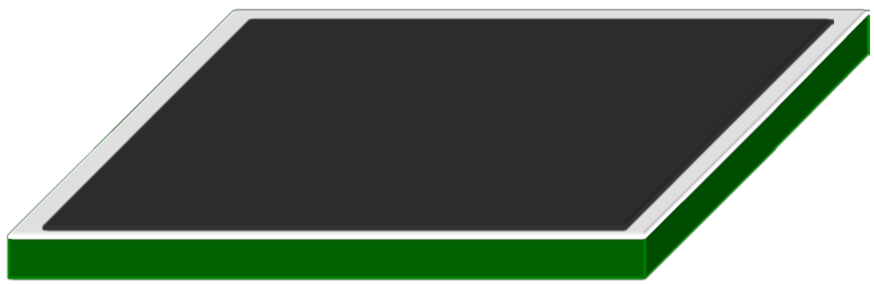
Stresses in SOFCs: residual and "reduction" stresses

anode-supported cell

LSM

YSZ

NiO-YSZ



sintering

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Stresses in SOFCs: residual and “reduction” stresses

anode-supported cell

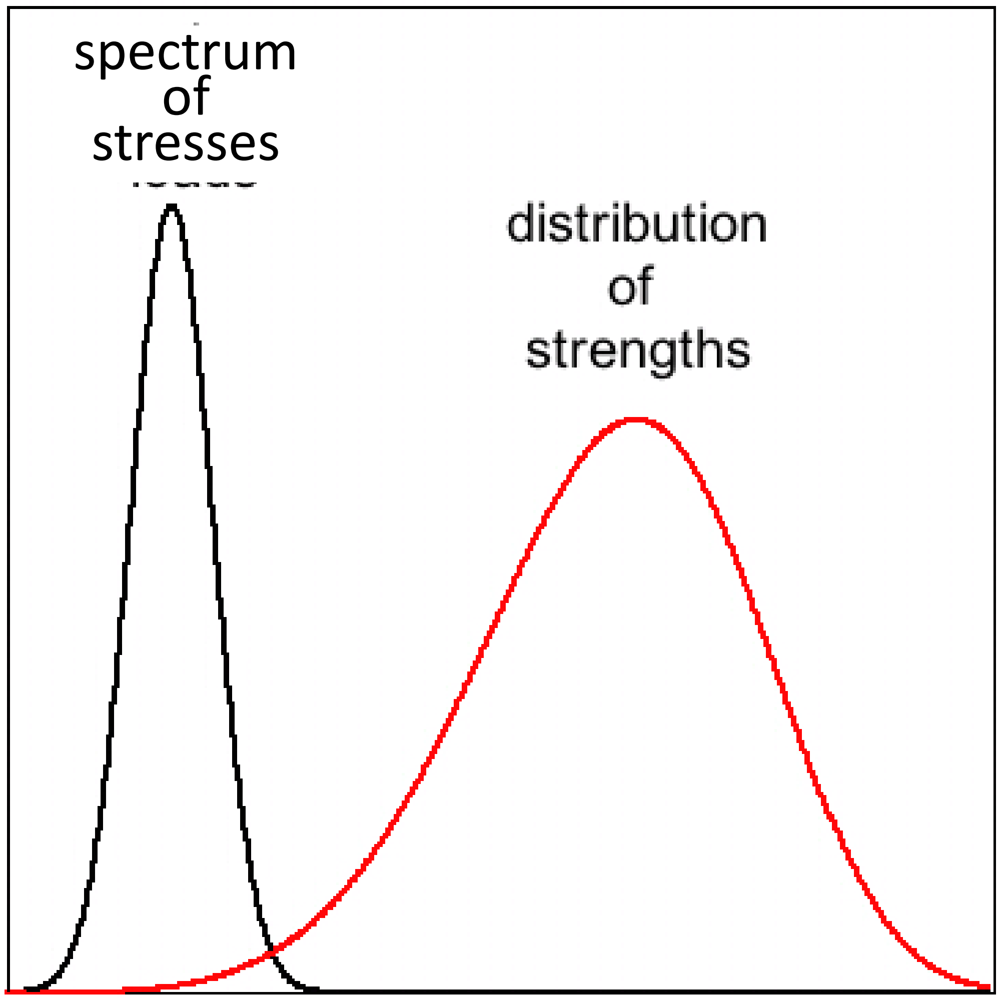
LSM

YSZ

Ni-YSZ

reduction

Failure, Reliability and Durability of Systems



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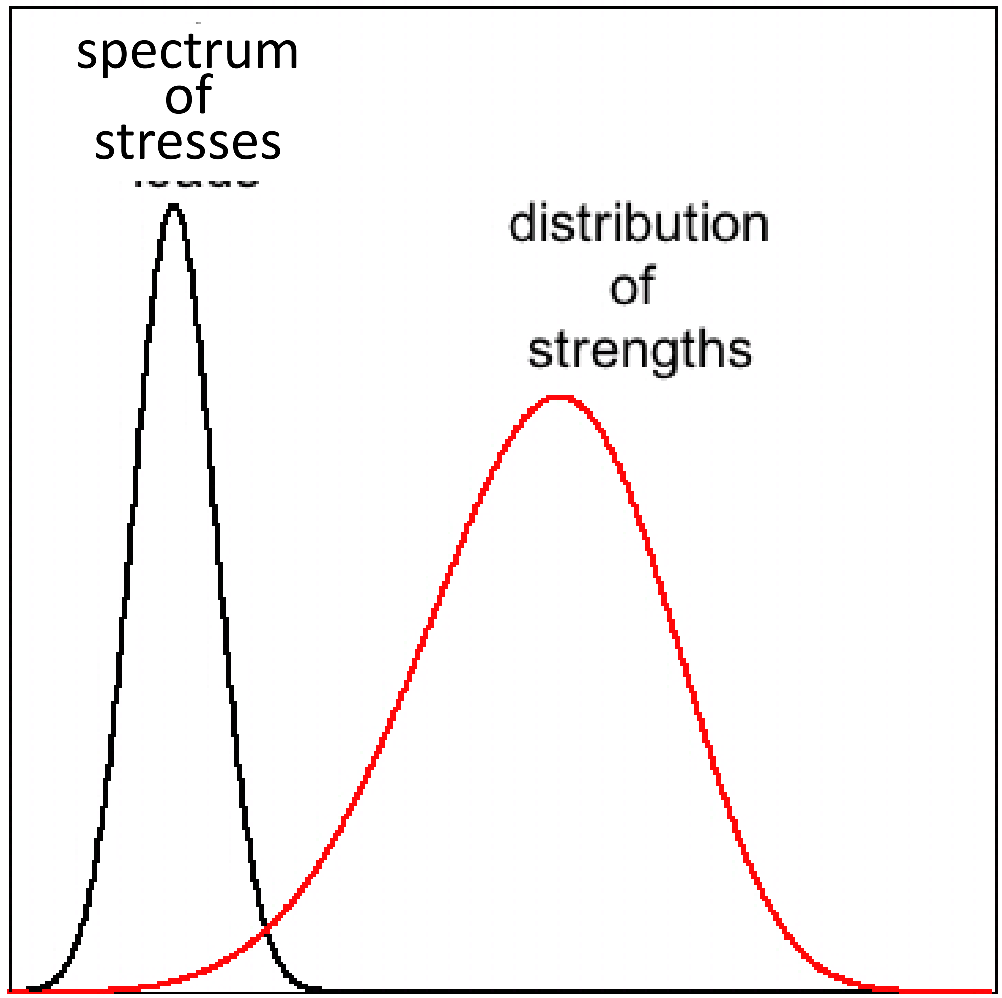
Failure, Reliability and Durability of Systems



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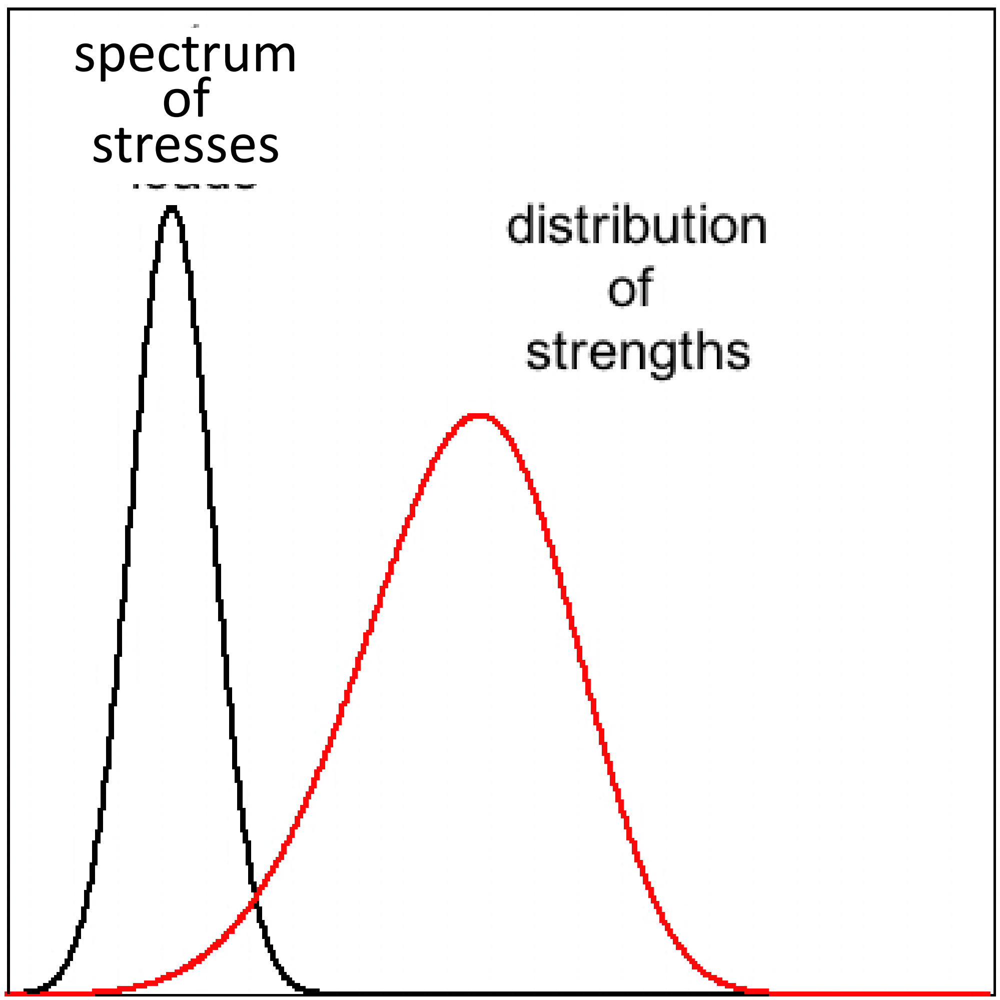
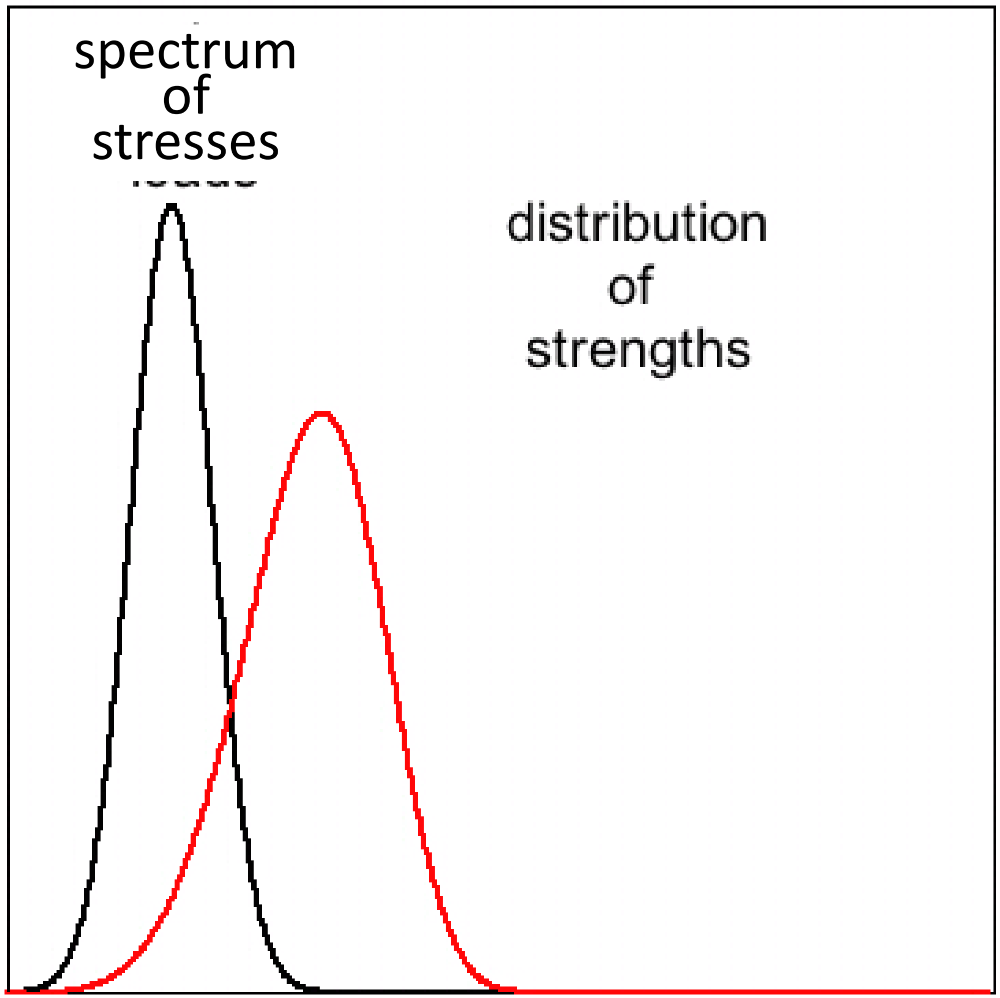
Failure, Reliability and Durability of Systems



Failure, Reliability and Durability of Systems



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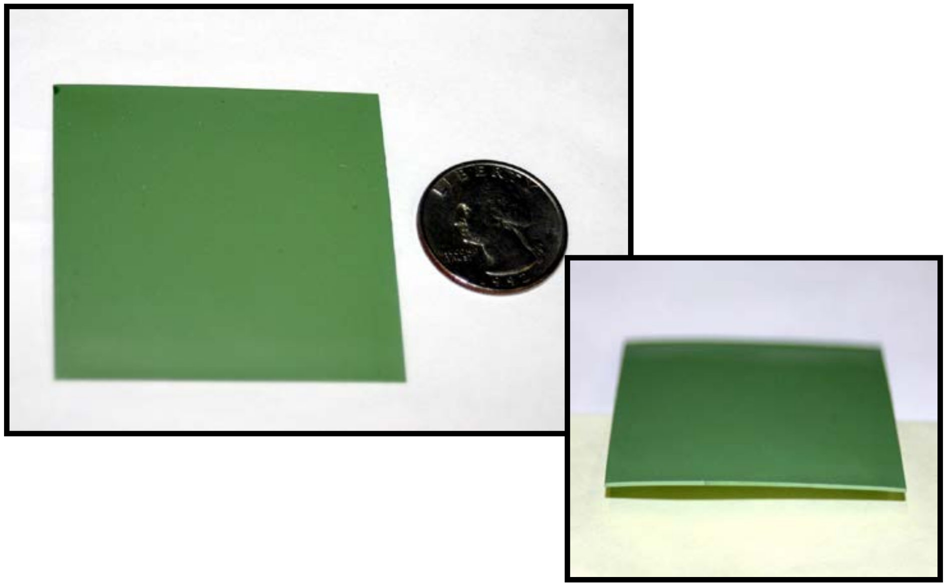
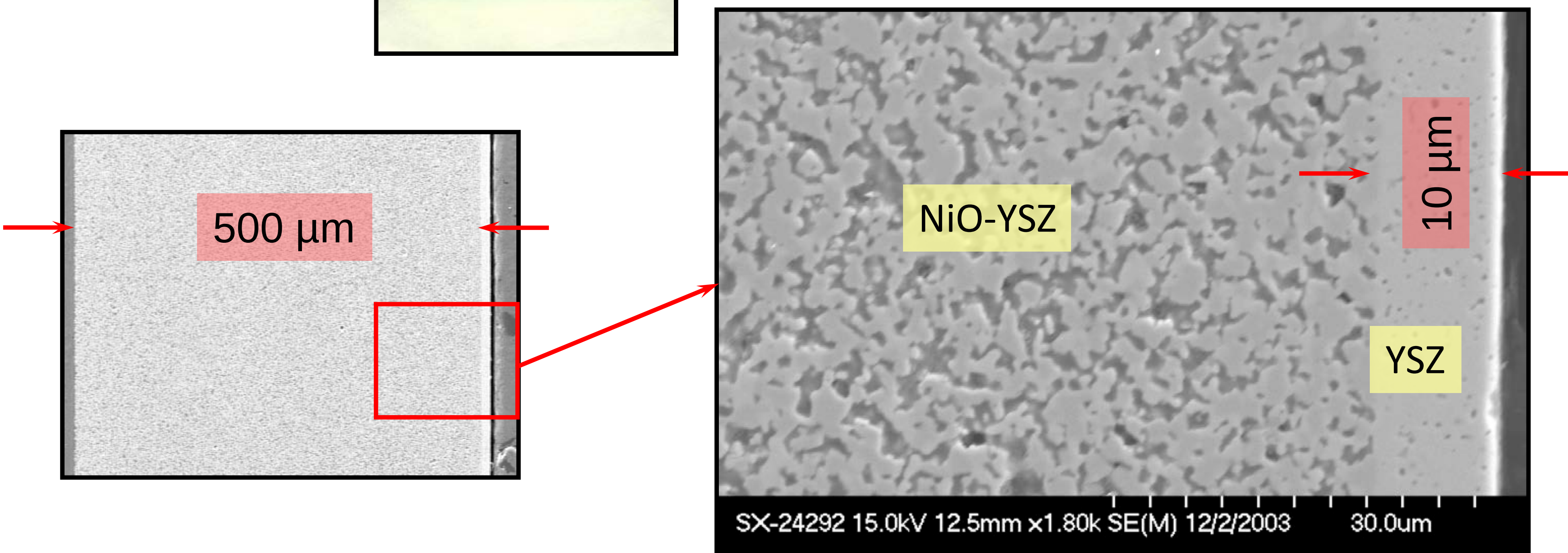
NiO-YSZ/YSZ bilayer



50 mm X 50 mm X 510 μm

Co-sintered in air at 1,400°C for 2 hours



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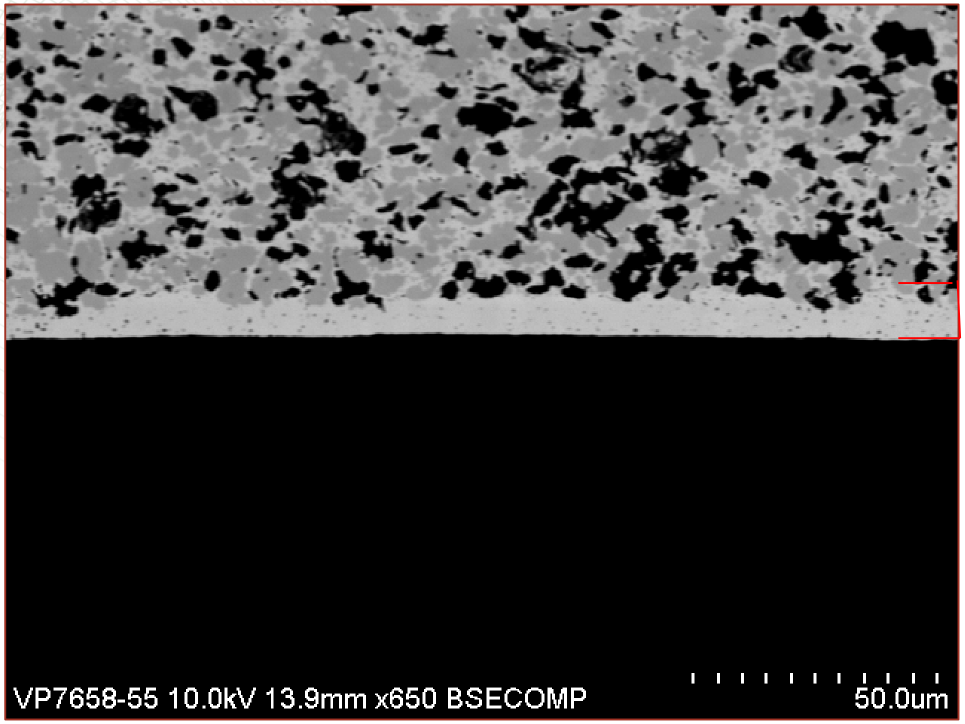
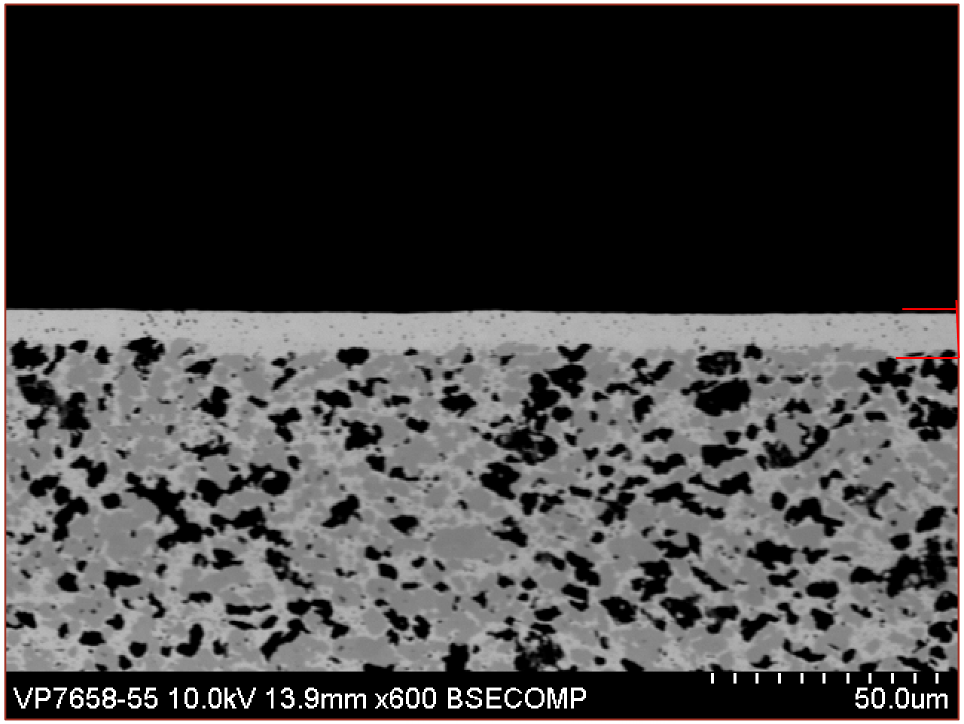
SOFC17S-Dual-3-1





- Average ZrO_2 thickness: 9.82 μm

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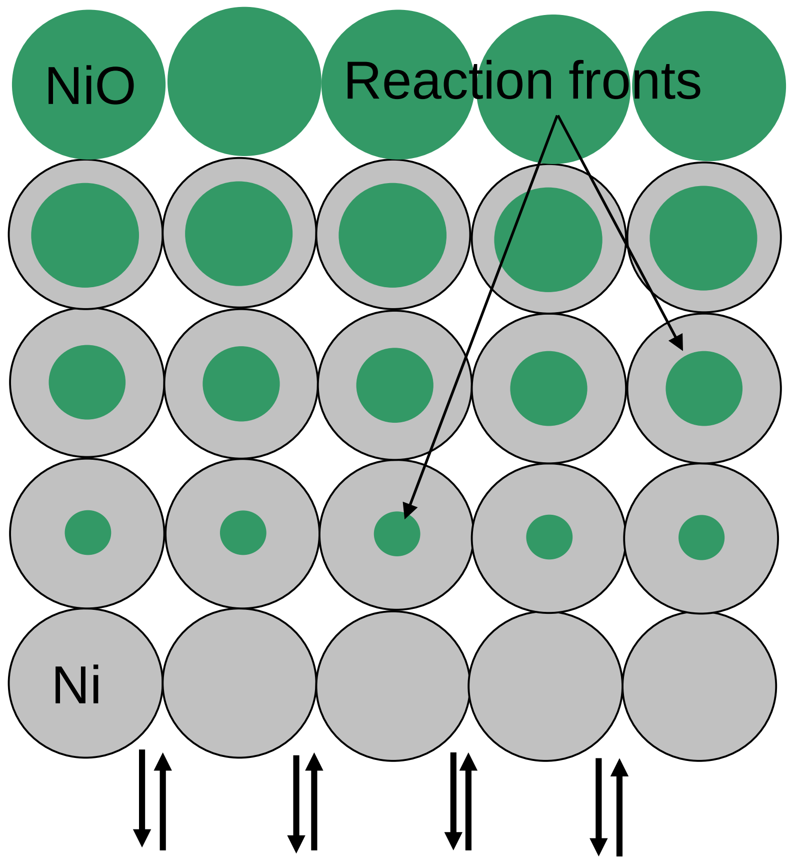
journal

J. Am. Ceram. Soc., 87 [12] 2242–2246 (2004)

Elastic Properties of Nickel-Based Anodes for Solid Oxide Fuel Cells as a Function of the Fraction of Reduced NiO

Miladin Radovic* and Edgar Lara-Curzio*

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6069



Gas phase mass transfer of reactants (H_2) and products (H_2O)

Porosity in Reduced NiO-YSZ

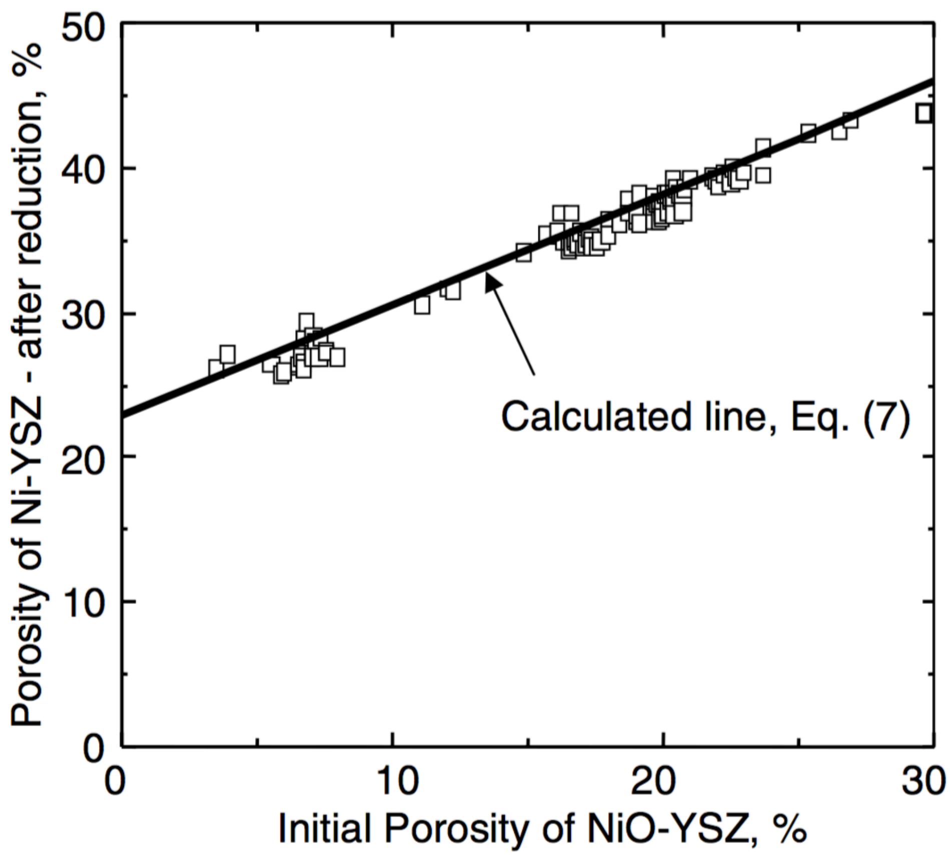
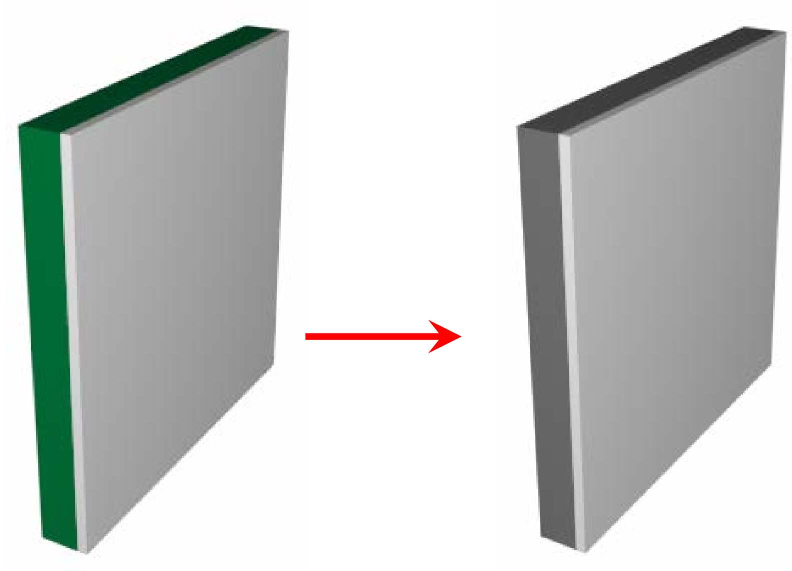


Fig. 1. Relationship between relative porosity of the reduced anode samples and initial porosity of the samples before reduction. Open square symbols represent experimental results determined by alcohol immersion method, while the solid line corresponds to Eq. (7).



M. Radovic, E. Lara-Curzio / *Acta Materialia* **52** (2004) 5747–5756

THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
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Nickel Oxide Reduction by Hydrogen: Kinetics and Structural Transformations

Khachatur V. Manukyan,*[†,‡] Arpi G. Avetisyan,[‡] Christopher E. Shuck,[§] Hakob A. Chatilyan,[‡] Sergei Rouvimov,[#] Suren L. Kharatyan,[‡,⊥] and Alexander S. Mukasyan*[,§]

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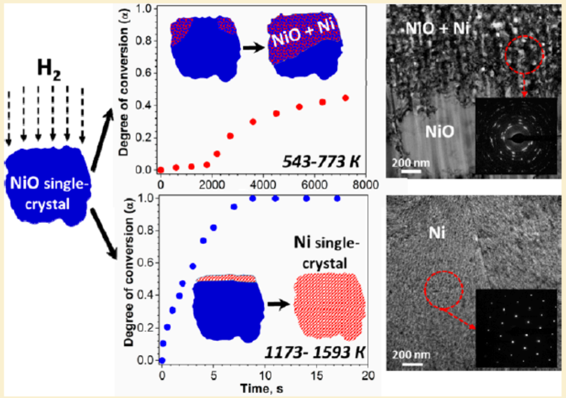
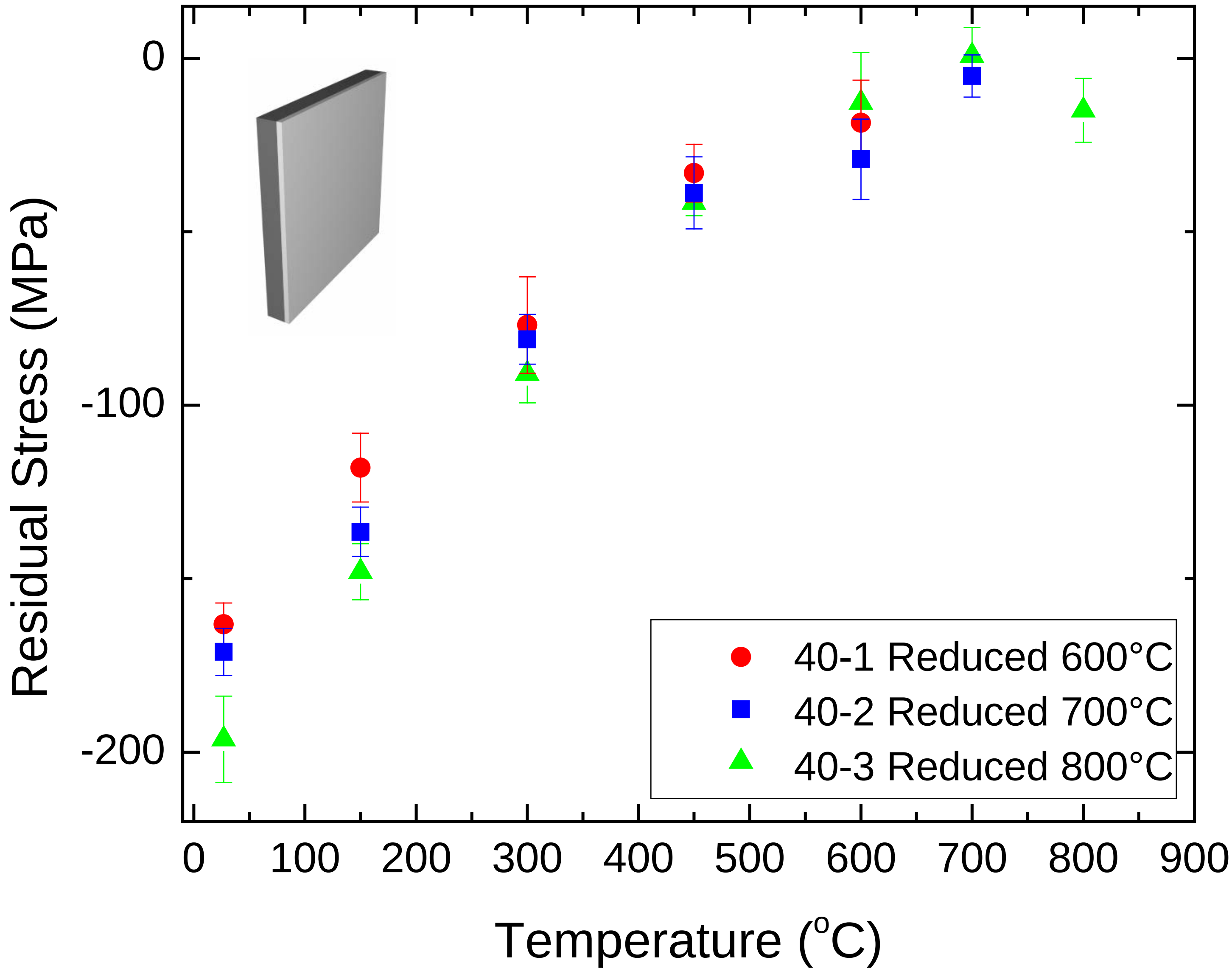
Web-Enhanced Feature *Supporting Information*

ABSTRACT: We studied the reduction kinetics of bulk NiO crystals by hydrogen and the corresponding structural transformations in the temperature range of 543−1593 K. A new experimental approach allows us to arrest and quench the reaction at different stages with millisecond time resolution. Two distinctive temperature intervals are found where the reaction kinetics and product microstructures are different. At relatively low temperatures, 543−773 K, the kinetic curves have a sigmoidal shape with long induction times (up to 2000 s) and result in incomplete conversion. Low-temperature reduction forms a complex polycrystalline Ni/NiO porous structure with characteristic pore size on the order of 100 nm. No induction period was observed for the high-temperature conditions (1173−1593 K), and full reduction of NiO to Ni is achieved within seconds. An extremely fine porous metal structure, with pore size under 10 nm, forms during high-temperature reduction by a novel crystal growth mechanism. This consists of the epitaxial-like transformation of micrometer-sized NiO single crystals into single-crystalline Ni without any crystallographic changes, including shape, size, or crystal orientation. The Avrami nucleation model accurately describes the reaction kinetics in both temperature regimes. However, the structural transformations during reduction in both nanolevel and atomic level are very complex, and the mechanism relies on both nucleation and the critical diffusion length for outward diffusion of water molecules.



Reduction of NiO-YSZ

Effect of Reduction Temperature



Porosity

- NiO-YSZ: 40%
- Ni-YSZ: 53%