In situ reduction and oxidation of nickel from solid oxide fuel cells in a Titan ETEM

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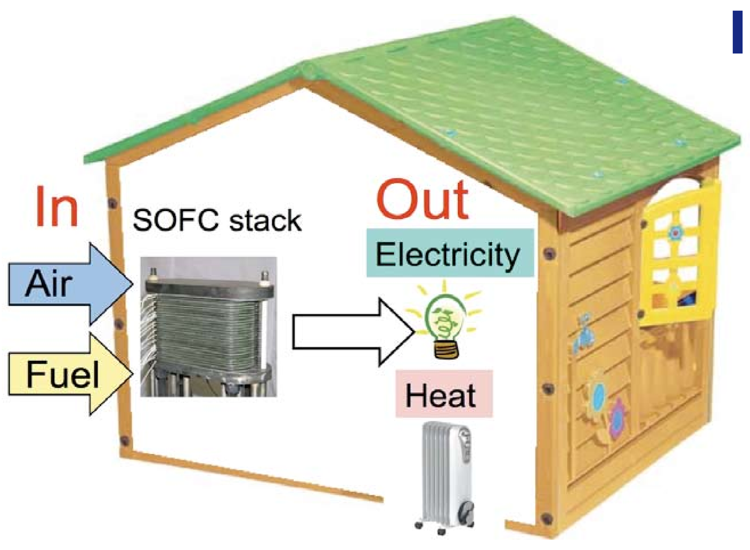
Center for Electron Nanoscopy

Introduction



Solid Oxide Fuel Cell advantages

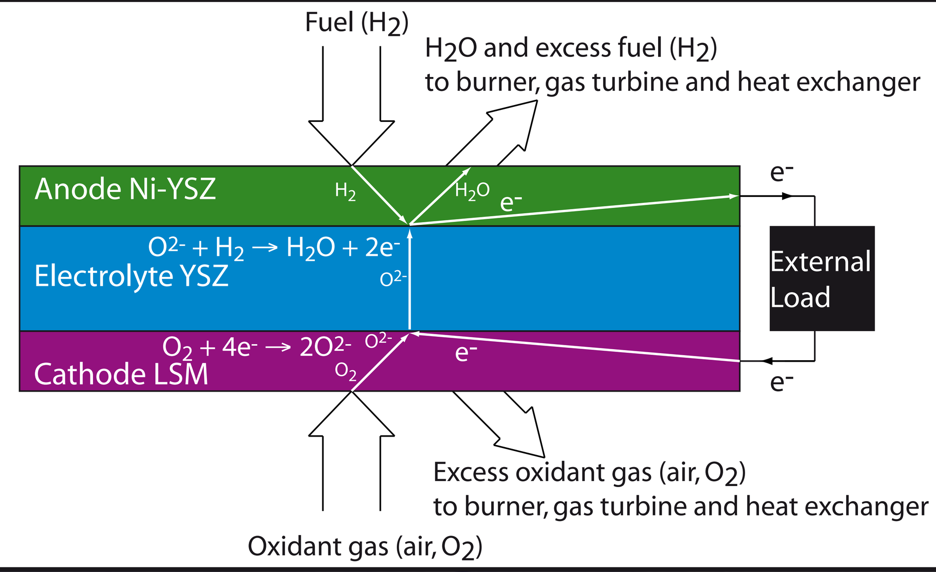
- Cogeneration (coproduction of heat and electricity)
- High electrical efficiency (> 60%)
- Fuel flexibility (renewable + fosil)
- Decentralized electricity production
- Silent
- Low SOx and NOx pollution

RedOx Instability

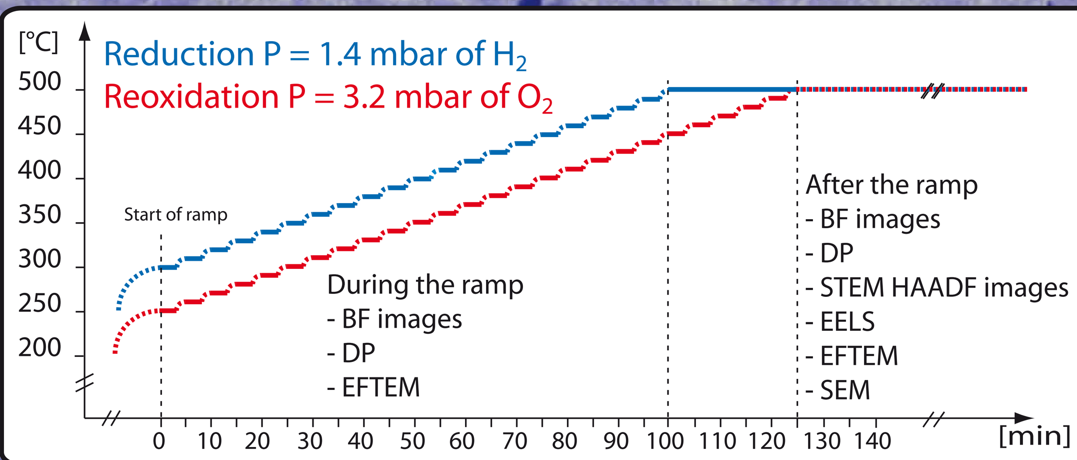
Nickel oxidation in anode produces an expansion of the support and fractures the electrolyte.

Nickel anode can re-oxidize due to:

- Air leaks
- Sealing deficiency
- Lack of fuel (shut down and startup)
- High fuel utilisation



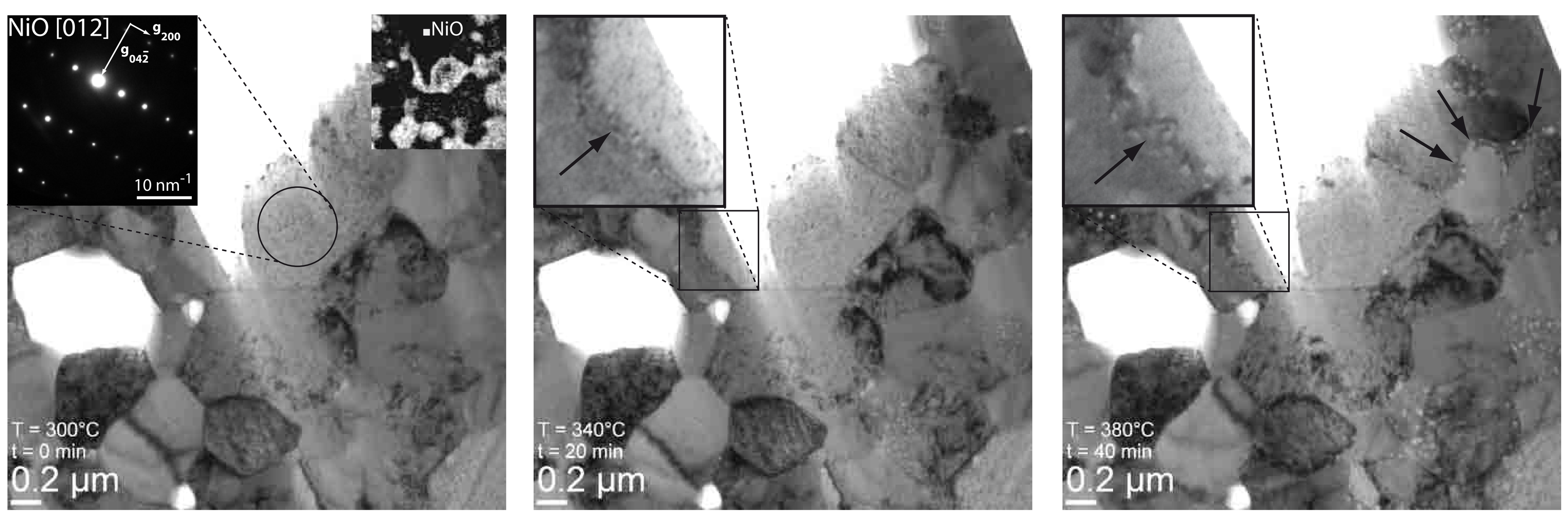
Objective **Understand the process of Ni re-oxidation in SOFC anode to find a technical solution**



Experimental

- TEM lamellas of 55 wt% NiO - 45 %wt YSZ anode were prepared by FIB lift-out method (stainless steel grid and platinum deposition).
- The NiO-YSZ cermet was reduced *in situ* during a temperature ramp from 300°C to 500°C under 1.4 mbar of H_2 in an environmental microscope FEI TITAN E-CELL™ using a inconel sample holder. Differential pumping apertures allow *in situ* S/TEM gas experiments to be performed.
- The NiO-YSZ anode was then reoxidized *in situ* during a temperature ramp from 250°C to 500°C under 3.2 mbar of O_2.
- Bright field images (BF) and diffraction patterns (DP) were acquired in order to study the evolution of the micro/nanostructure and the crystallography as function of time and temperature.

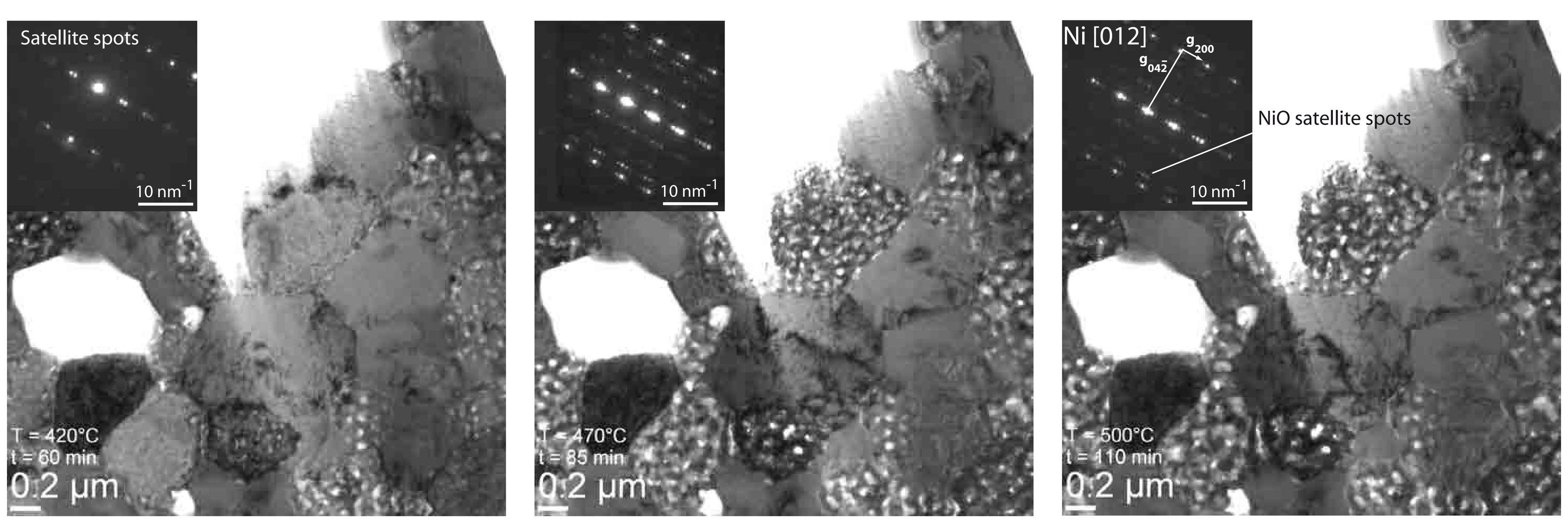
Reduction



a) Initial as-sintered microstructure under 1.4 mbar of H_2. Nickel EFTEM elemental map in the top right corner.

b) Nanovoids at the NiO-YSZ interfaces (40% volume shrinkage induced by NiO reduction). Transmission of oxygen to YSZ vacant sites, vacancies at the NiO/YSZ interface

c) Nanopores created towards the center of the grain. Hydrogen adsorption on NiO enhanced by creation of oxygen vacancy.

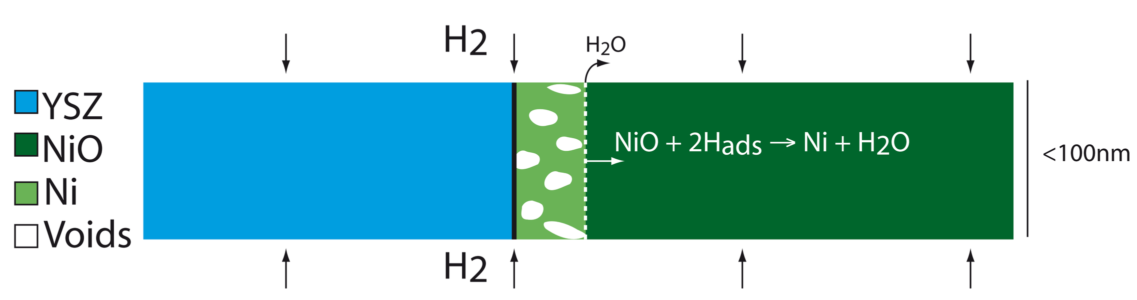


d) NiO free surface reduction enhanced by surface oxygen vacancies thermally generated. Satellite spots in the diffraction pattern. Epitaxial growth of metallic Ni on NiO.

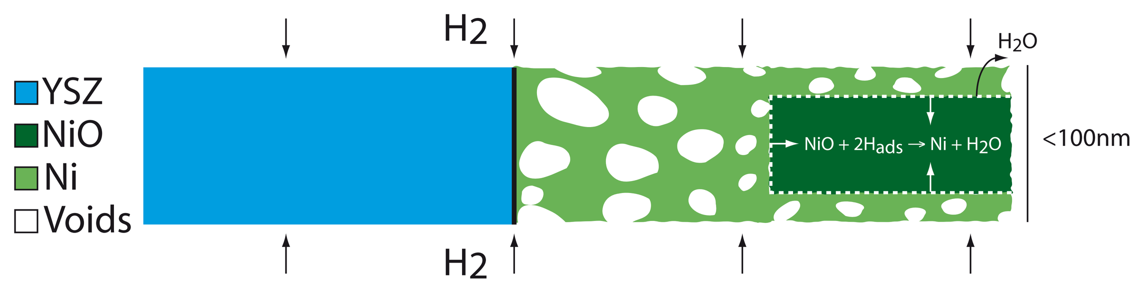
e) Pores on the surface of all nickel grains. Coalescence of voids as reduction continues.

f) NiO satellite spots due to incomplete reduction.

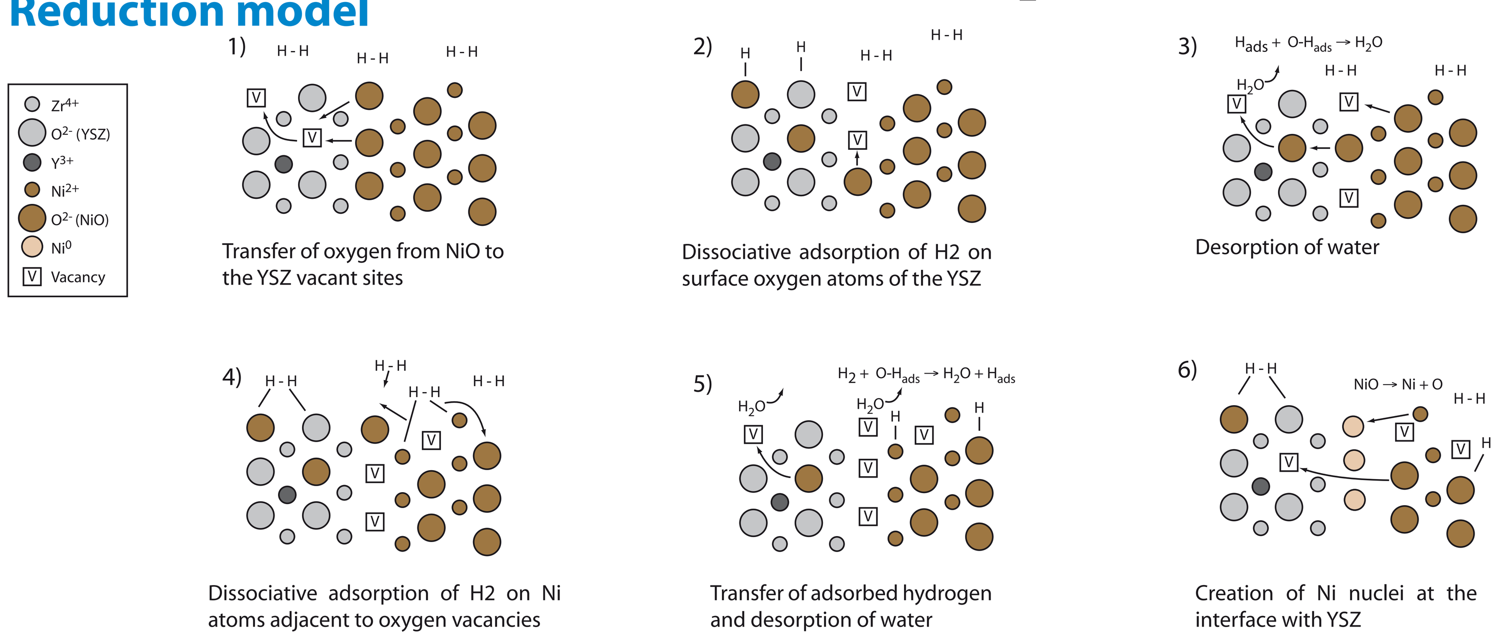
Cross-section view of the TEM lamella
NiO-YSZ interface reduction
Oxygen transmitted to YSZ vacant sites
Desorption of the externally provided oxygen, water desorption



Free surface reduction
Surface oxygen vacancies initiate the free surface reduction



Reduction model



1) Transfer of oxygen from NiO to the YSZ vacant sites

2) Dissociative adsorption of H2 on surface oxygen atoms of the YSZ

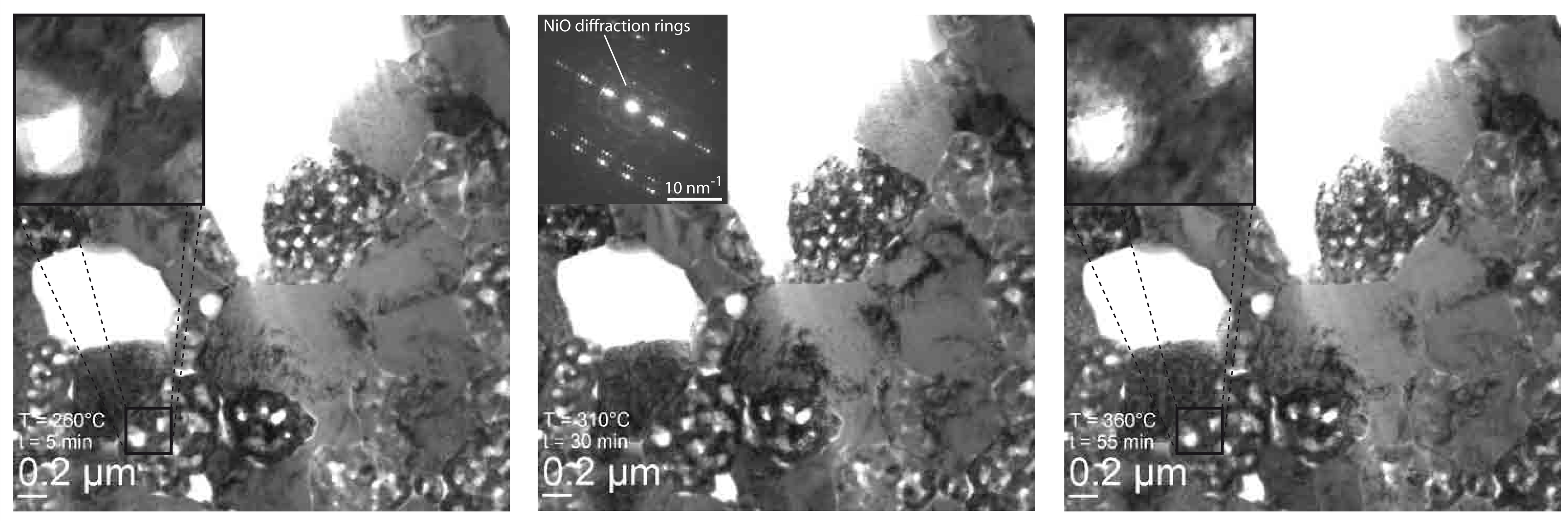
3) Desorption of water

4) Dissociative adsorption of H2 on Ni atoms adjacent to oxygen vacancies

5) Transfer of adsorbed hydrogen and desorption of water

6) Creation of Ni nuclei at the interface with YSZ

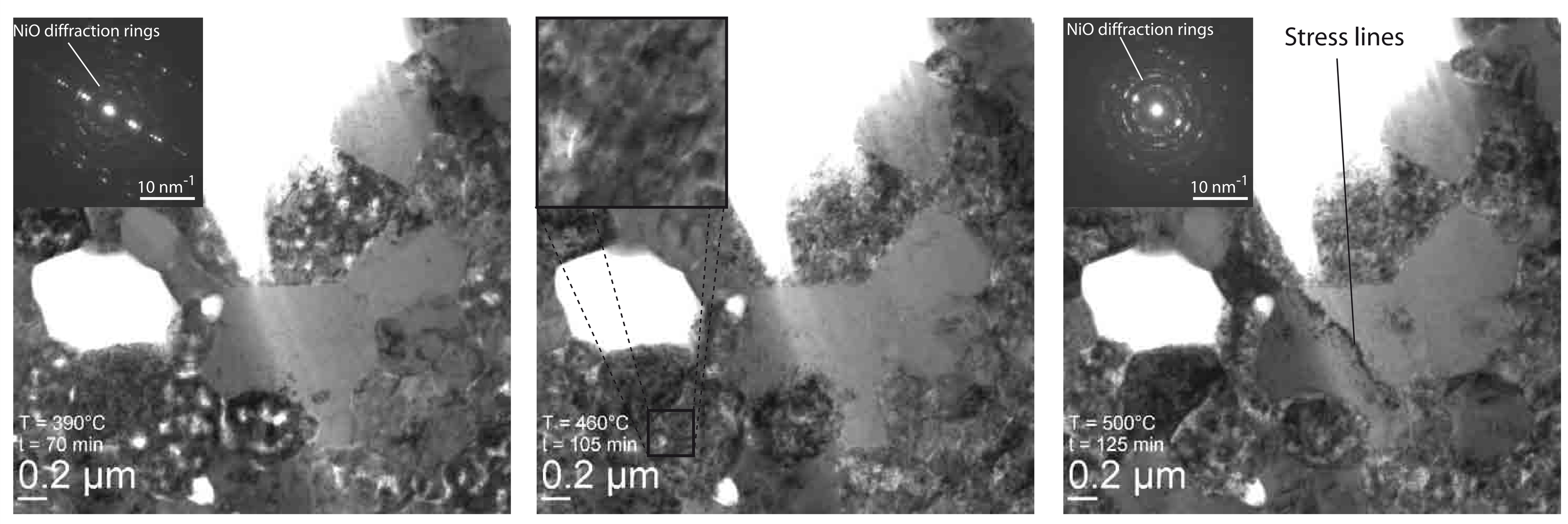
Reoxidation



a) Reduced microstructure (metallic nickel) under 3.2 mbar of O_2.

b) Diffraction rings: polycrystalline NiO structure.

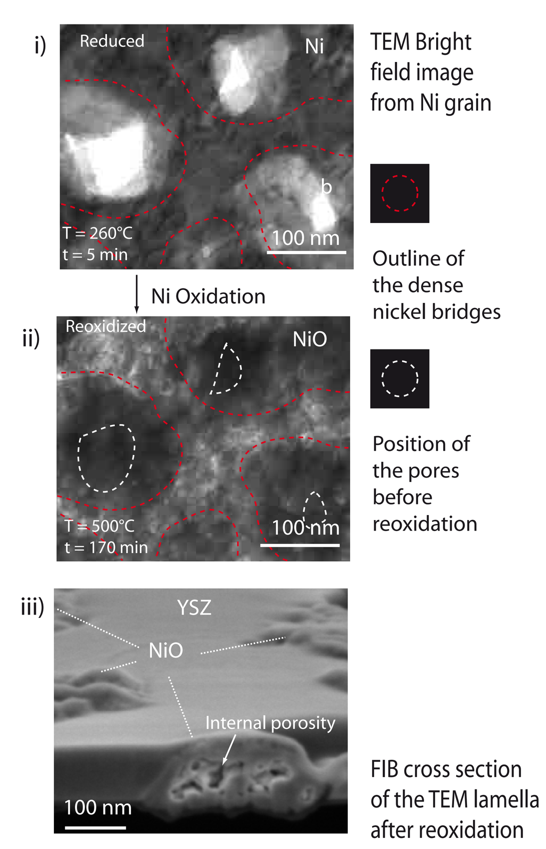
c) Intragranular porosity created during reduction filled by NiO (70% volume expansion).



d) Continuation of the surface reaction. Pores filled by NiO crystallites.

e) The pores appear almost completely filled by the growth of NiO.

f) Porous reoxidized NiO. Presence of stress in the YSZ phase underlined by bend contours.



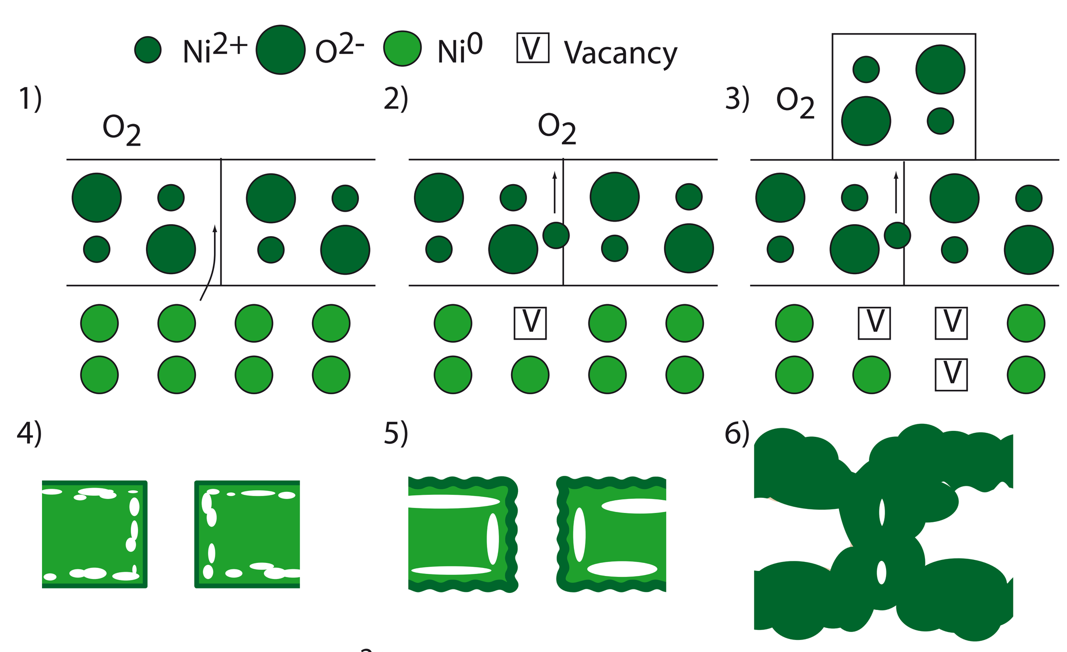
TEM Bright field image from Ni grain

Outline of the dense nickel bridges

Position of the pores before reoxidation

FIB cross section of the TEM lamella after reoxidation

Reoxidation model



Outward diffusion of Ni^{2+} through the oxide grain boundaries and dislocations is the dominant mass transport mechanism <1100°C. Negligible oxygen inward diffusion. Formation of NiO internal porosity.

Conclusion

- Start of the reduction at YSZ-NiO interface → Transfer of oxygen from NiO to YSZ.
- Formation of internal porosity during reoxidation of the nickel → Expansion upon a redox cycle.

⇨ **Intrinsic RedOx instability of dense as-sintered NiO/YSZ composite**

Microstructure RedOx solution: Introduction of fine dispersed porosity in the as sintered composite

Acknowledgments

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