Insights into the oxidation mechanisms of Ni particles using environmental TEM

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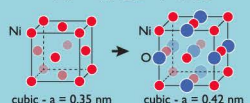
Nickel oxidation

$Ni + ½\ O2 \rightarrow NiO$



Model system to study oxidation[1]

Catalysis
Solid oxide fuel cells
Superalloys

→ Ni oxidation is difficult to prevent & leads to a degradation of the physical and electrochemical properties of the system

→ A detailed understanding of the mechanisms controlling oxidation is required

→ Need for a characterization technique that can directly relate chemistry & structure at the nm-scale under relevant oxidation conditions

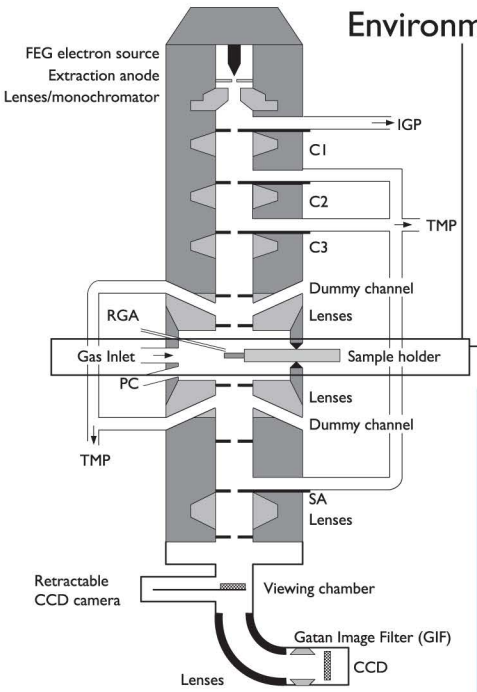
Objectives

Correlate structural & chemical changes occurring during oxidation of Ni particles to NiO using environmental TEM

Understand oxidation mechanisms of Ni & their effect on the resulting structure at the nm-scale

Transition between nonlinear & linear diffusion regimes

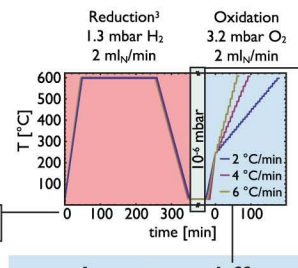
Environmental transmission electron microscopy (ETEM)



Differentially pumped 300 kV FEI TITAN²

Gatan 652 DT inconel heating holder

Commercial NiO powder on Au-SiO grids (crystallite size of ~ 100 nm by XRD)



Reduction³ & then oxidation

Characterize system evolution during oxidation inside ETEM

Imaging, diffraction, electron energy loss spectroscopy (EELS)

HRTEM in 10^{-6} mbar

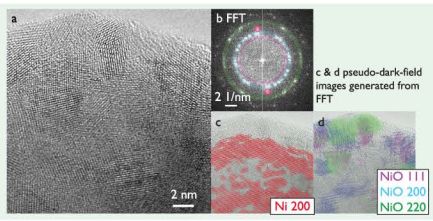
NiO nucleation on Ni due to P_{O_2}

Random Ni/NiO orientation

Built-in electric field driven NiO film growth up to 2-3 nm⁴

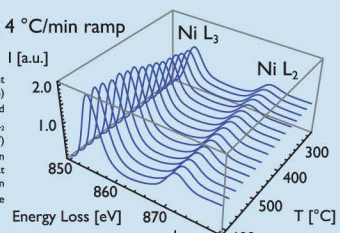
Nonlinear diffusion mechanisms passivate the surface

NiO growth rate negligible at a thickness of > 2-3 nm



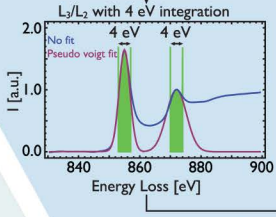
Imaging, diffraction & EELS during oxidation up to 600 °C in 3.2 mbar of O_2

EELS during 4 °C/min ramp

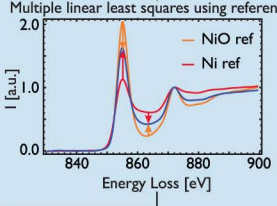


Noise reduced by principle component analysis (8 components taken)
Background subtracted
Normalized to 1 at L_2
Energy shift not accounted (- 0.2 eV)
Convoluted with point spread function to get same initial NiO L_3 resolution at 2, 4 & 6 °C/min
See Ref. [3] for procedure

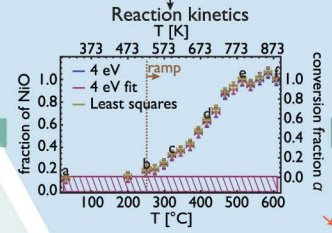
L_3/L_2 with 4 eV integration



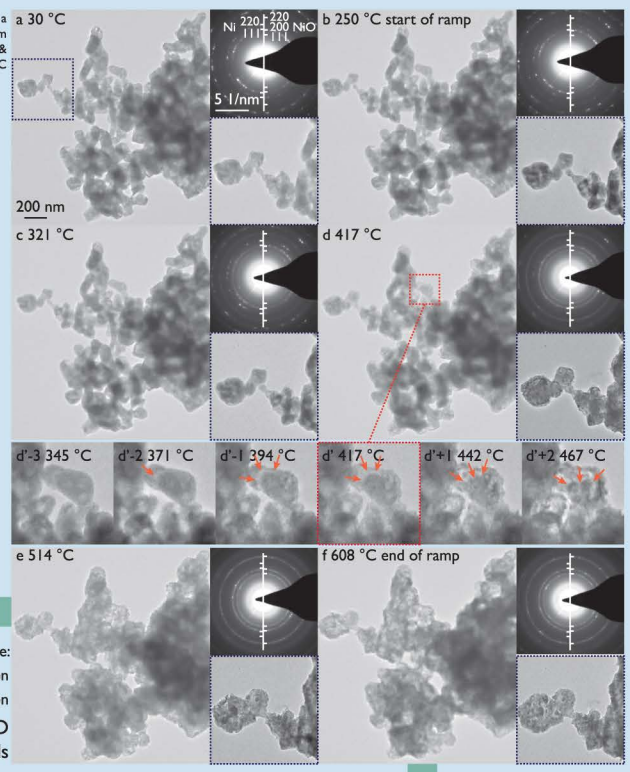
Multiple linear least squares using references



Reaction kinetics



Ni particles with a diameter of ~ 100 nm after reduction & sintering at 600 °C



We observe:

Volume expansion

Internal Ni retraction

Irregular polycrystalline NiO structures with internal voids

Analysis of kinetics obtained by EELS

2, 4, 6 °C/min — conversion fraction by EELS

activation energy?

reaction model?

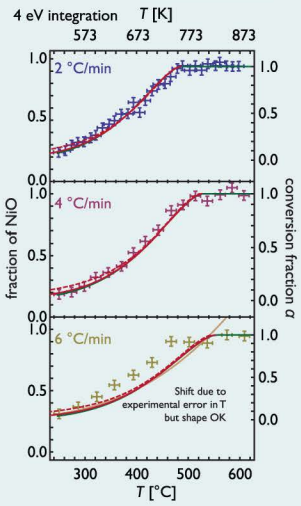
nucleation, geometrical contraction, diffusion, etc?

pre-exponential factor?

$$\beta \frac{d\alpha}{dT} = A e^{\frac{-E_a}{RT}} f(\alpha)$$

See Ref. [3] for procedure

4 eV integration



Models that describe reaction kinetics

Linear diffusion[5]

$E_a \approx 70$ kJ/mol

Nonlinear & then linear diffusion[6]

$E_a \approx 80$ kJ/mol

with

r_0 = 50 - 200 nm, particle radius (estimated from images)

L_{cr} = 10 nm, nonlinear/linear crossover oxide thickness

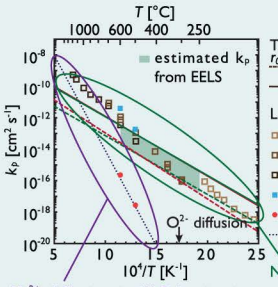
Linear diffusion of active species appears to control the reaction from an oxide thickness of ~ 10 nm up to full oxidation

Which active species? How does it diffuse?

Kinetic models allow to calculate k_p ~ reaction speed as a function of temperature

As the reaction appears mainly controlled by linear diffusion, k_p is directly related to diffusion coefficients of Ni & O in NiO

Which diffusion mechanism predicts a reaction speed that corresponds to the one predicted here?



This work

r_0 50 nm — models

200 nm — Linear diffusion

Nonlinear & then linear

Literature

7.5 nm — Karmhag[7]

2.5 μm — Experimental measurements

75 μm

planar - Atkinson[8] — Predictions $D_{g.b}$ + $D_{lattice}$

planar - Atkinson[8] — Predictions $D_{lattice}$

planar - Mrowec[9]

Ni^{2+} diffusion in NiO lattice is several orders of magnitude slower

Ni^{2+} diffusion in NiO grain boundaries controls the reaction

Linear diffusion of Ni^{2+} along NiO grain boundaries seems to be the main rate-controlling mechanism

These results are comparable to work done *ex situ*, similar to literature for oxide films > 1 μm

Does that description make sense?

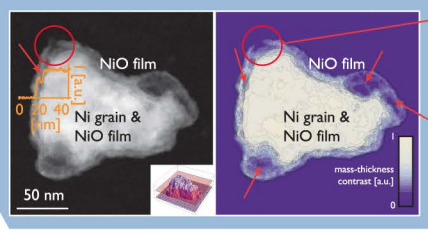
Here E_a (70-80 kJ/mol) < E_a for Ni^{2+} diffusion along NiO grain boundaries (171 kJ/mol[1])!

However, two mechanisms lower *Ea* without changing the diffusion mechanism:

1) NiO grain growth decreases the number of fast diffusion paths as the oxide film grows

2) Built-in electric field due to space charge separation at the interfaces accelerates diffusion when the oxide film is thin (< 1 μm)[1]

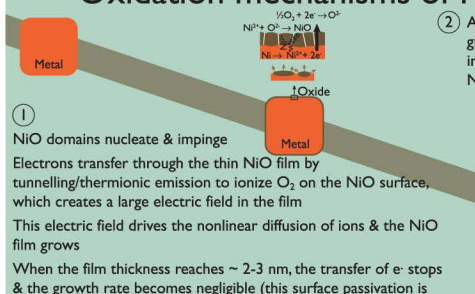
STEM HAADF at 300 °C in 3.2 mbar of O_2



Fracture of the NiO film in curved regions due to geometrically induced stress

Nucleation of voids at NiO/Ni interfaces as Ni^{2+} diffusion is several orders of magnitude faster than O^{2-} diffusion

Oxidation mechanisms of Ni particles



① NiO domains nucleate & impinge

Electrons transfer through the thin NiO film by tunnelling/thermionic emission to ionize O_2 on the NiO surface, which creates a large electric field in the film

This electric field drives the nonlinear diffusion of ions & the NiO film grows

When the film thickness reaches ~ 2-3 nm, the transfer of e^- stops & the growth rate becomes negligible (this surface passivation is not thermally activated)

② As the temperature increases, Ni^{2+} diffuses through the NiO grain boundaries. This process might be field-assisted. As O^{2-} inwards diffusion is much slower, vacancies are injected at the NiO/Ni interfaces & voids nucleate

Interface recession may annihilate these vacancies in flat regions unlike in curved areas, where NiO/Ni contact is lost quickly

The NiO film may fracture at its edges due to geometrically induced stress, O_2 permeates through the crack and reacts directly with Ni

[1] Atkinson, A., Reviews of Modern Physics, 57, 437 (1985).
[2] Hansen TW, *et al.* (2010), Materials Science and Technology 26 (11)
[3] Jeangros, Q. et al., Journal of Materials Science, 48, 2893 (2013).
[4] Mott, N. F. (1995). Theory of the oxidation of metals. 65 years in physics, Singapore, World Scientific: 163.
[5] Fromhold, A. T., Journal of Physics and Chemistry of Solids, 49, 1159 (1988).
[6] Niklasson, G.A. et al., Surface Science, 532-535, 324 (2003).
[7] Karmhag, R. et al., Journal of Applied Physics, 89, 3012 (2001).
[8] Atkinson, A. et al., Philosophical Magazine A, 45, 823 (1982).
[9] Mrowec, S. et al., Journal of Physics and Chemistry of Solids, 65, 1651 (2004).