Combining Synchrotron radiation and transmission electron microscopy to investigate early-stage oxidation of metallic materials

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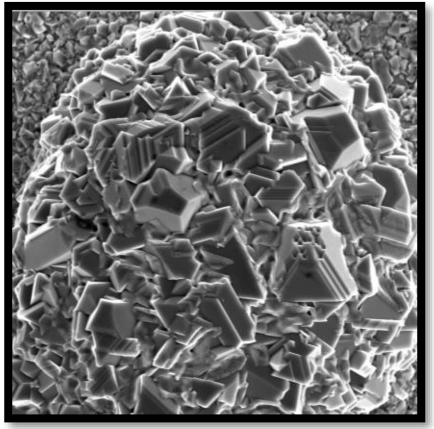
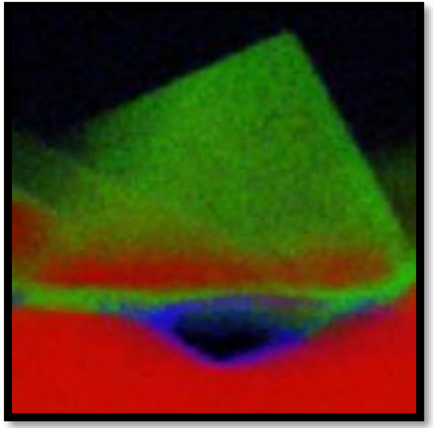
Researching early-stage oxidation of metallic materials

Electron Microscopy and Microstructural Analysis Group at TU Chemnitz (Prof. Andreas Undisz)

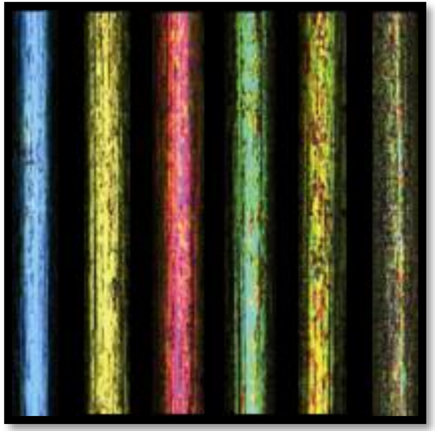
Complex alloys
(CCAs / HEAs)



Steel
(316L / Medium
Mn steels)



NiTi



➡ **Oxide layer protects the material from environmental degradation**

Researching early-stage oxidation of metallic materials

What makes an oxide layer protective?

Oxide phase	Oxide composition	Oxide morphology
• Corundum-type (e.g. Cr_2O_3) • Spinel-type (e.g. $MnCr_2O_4$) • Rock salt-type (e.g. FeO) • …	• Cr-rich / Fe-rich • Concentration gradients • …	• Dense / well-adherent • Inhomogeneous • …

➡ **Early stages of oxide growth are starting point for long-term behavior**

Combining complementary methods

Methods to investigate thin oxide layers (10 nm ~ 3 µm) formed during early-stage oxidation (5 min ~ 6 h)

- **Electron microscopy (SEM, TEM)**: Morphology, composition, phases
- **GD-OES**: concentration profiles
- **Lab-based (GI-)XRD**: oxide phases
- **Thermogravimetric analysis**: oxidation kinetics

Synchrotron radiation allows for *in-situ* studies of thin layers and short times

Complex alloys: effect of Co and Fe on oxidation

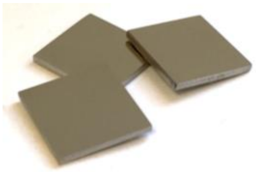
alloy	Co (at.%)	Cr (at.%)	Fe (at.%)	Ni (at.%)	Mn (at.%)	Si (at.%)	Mo (at.%)
26Co	25.9	19.3	25.9	25.9	2.0	1.0	-
13Co	12.9	19.3	38.9	25.9	2.0	1.0	-
7Co	6.5	19.3	45.3	25.9	2.0	1.0	-
0Co	-	19.3	51.7	25.9	2.0	1.0	-
316L	-	19.3	64.8	11.4	2.0	1.0	1.5

J. Apell *et al.*, Corrosion Science. 225 (2023) 111594.

induction melting, homogenization

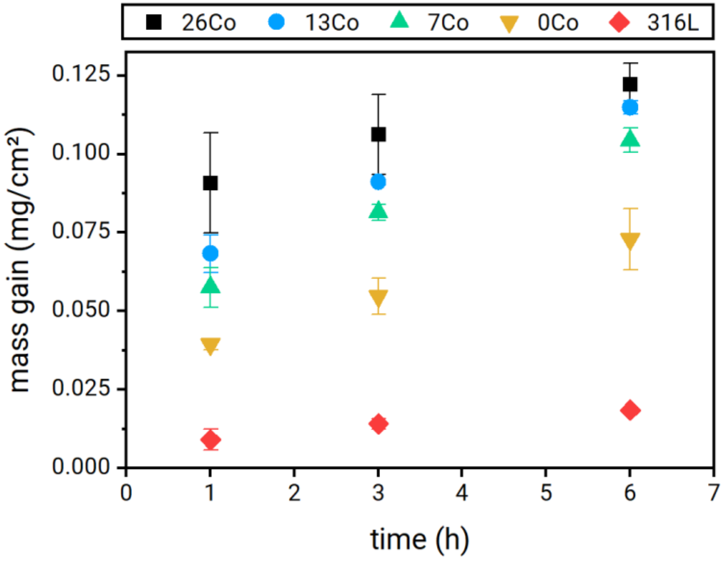
cold rolling and cutting

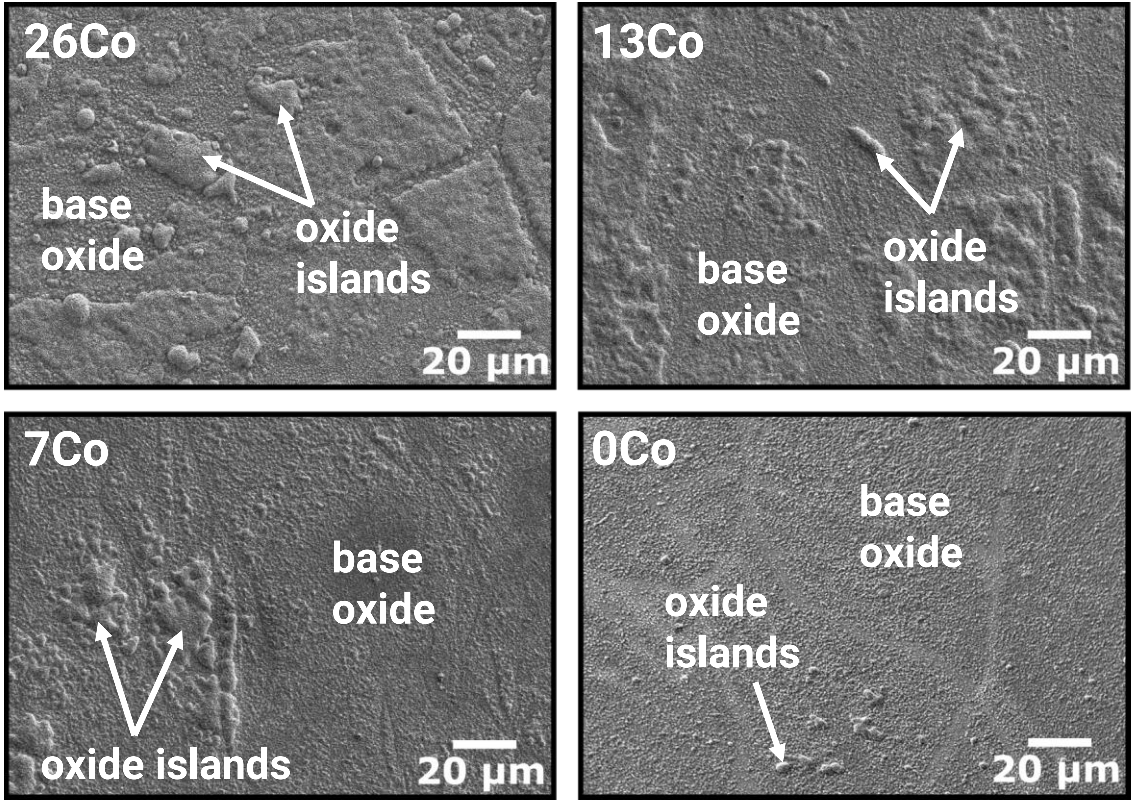
single phase FCC



oxidation for up to 6 h at 800 °C

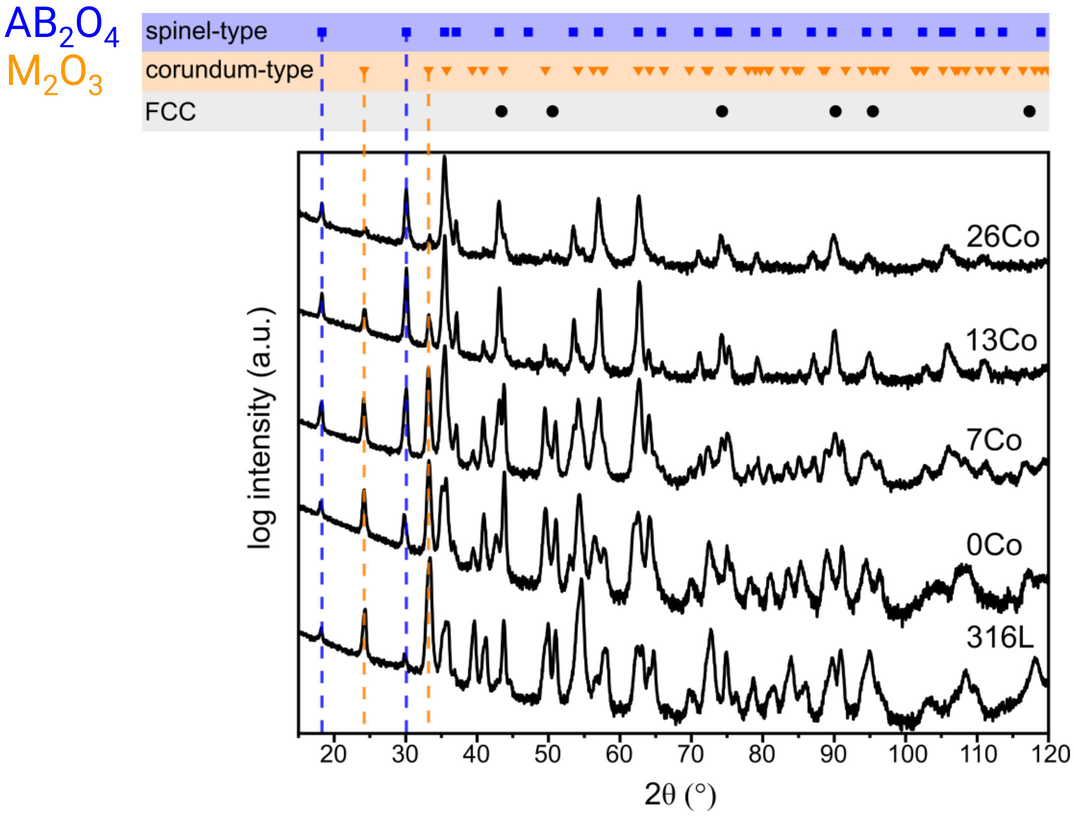
Mass gain and surface oxide morphology at 800 °C



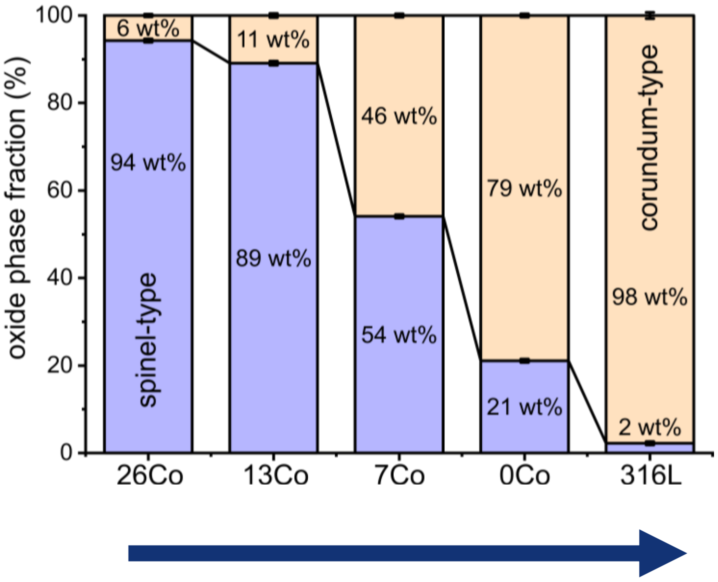


oxide phases formed during oxidation for 1 h at 800 °C

grazing incidence X-ray diffractogram



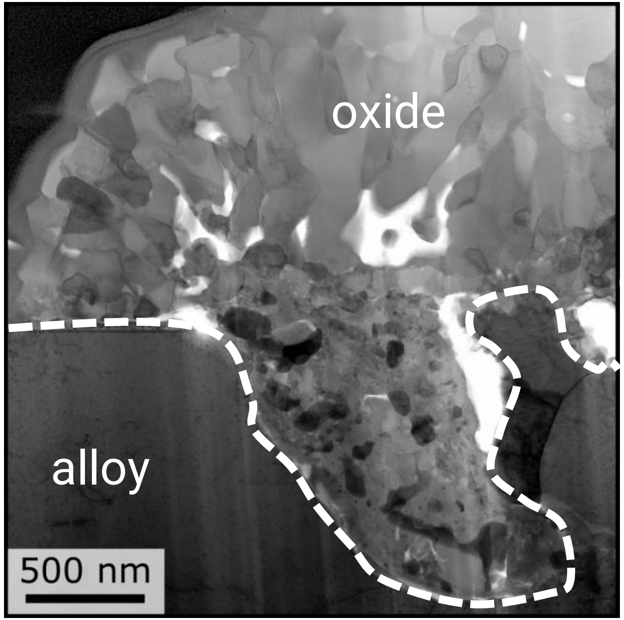
oxide phase fractions from Rietveld analysis



decreasing Co content

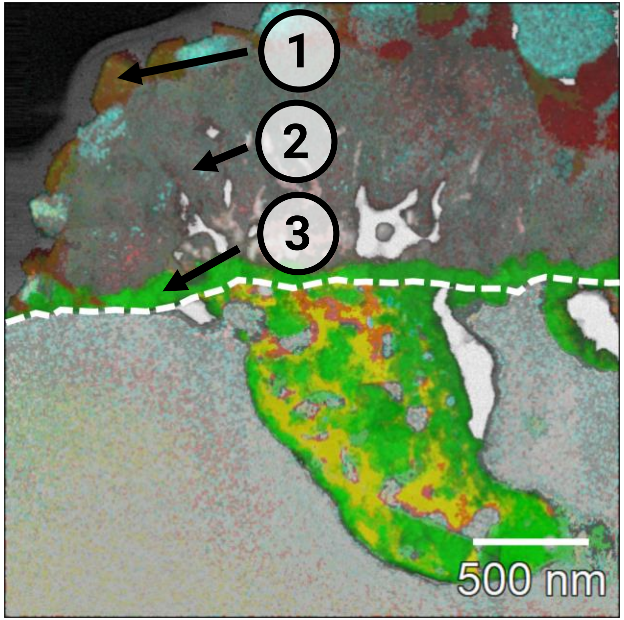
oxide island: outward grown oxide

STEM-BF



oxide island: outward grown oxide

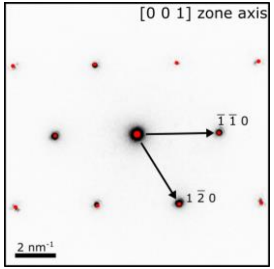
STEM-EDXS



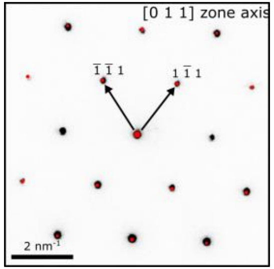
outward growth

inward growth

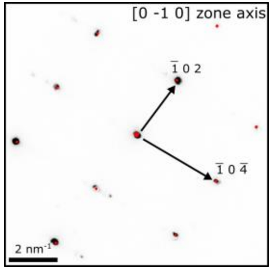
Cr Fe Co
Ni Mn



① corundum-type (Fe-rich) outer layer



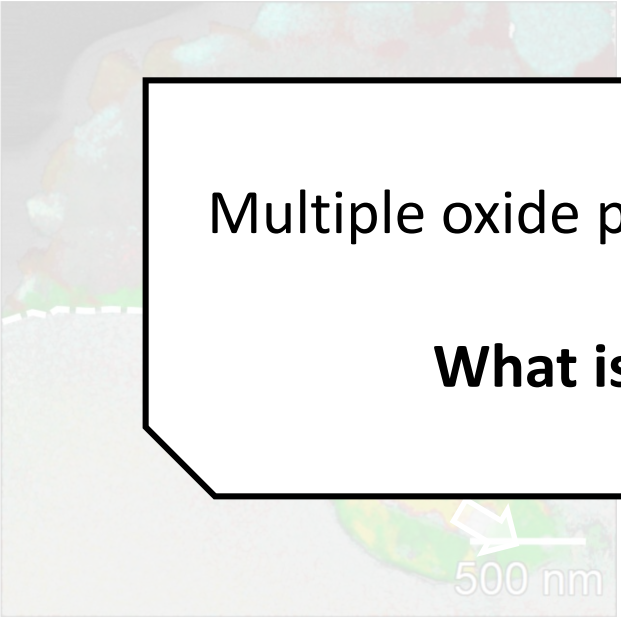
② spinel-type (Ni/Fe/Co-rich) intermediate layer



③ corundum-type (Cr-rich) inner layer

oxide island: inward grown oxide

STEM-EDXS



Cr Fe Co
Ni Mn

SAED: mixed oxide

corundum-type (Cr-rich)

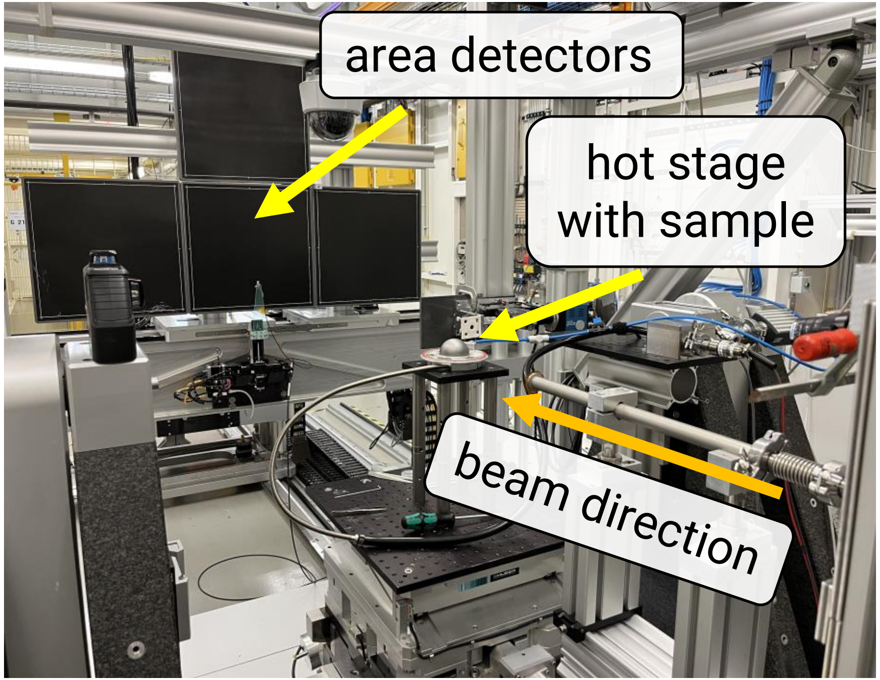
…rich)

Multiple oxide phases form during first hour of oxidation

What is the order of phase formation?

FCC (Fe/Co/Ni-rich)

in-situ Synchrotron GI-XRD oxidation experiments



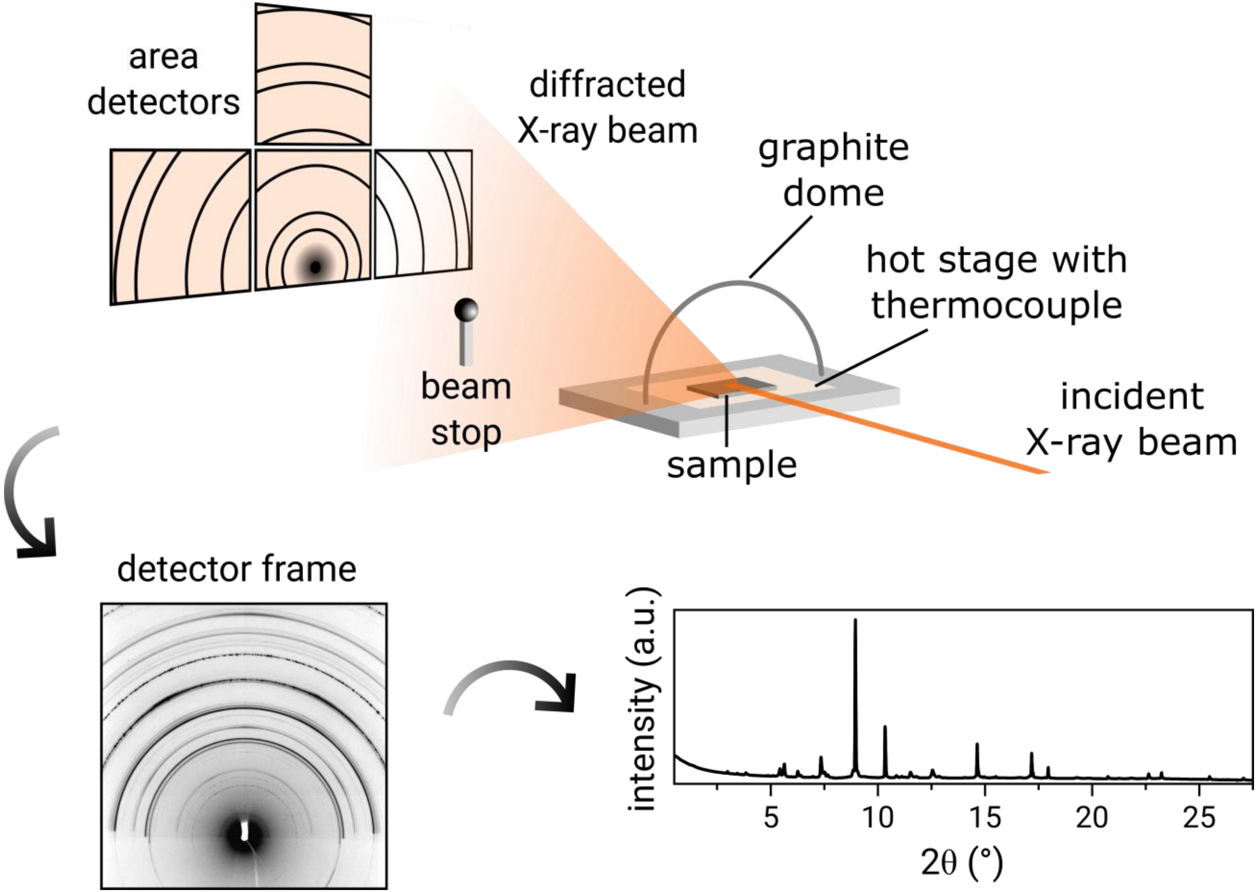
DESY Hamburg
beamline P21.2

Synchrotron radiation enables investigation of phase formation during heating

Challenges:

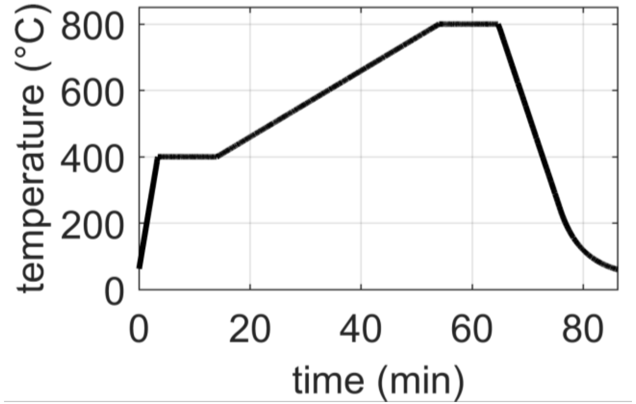
- Dynamic range of detectors (strong intensity from base material, weak intensity from thin oxide layers)
- Keeping the correct sample height during heating and cooling (thermal expansion)

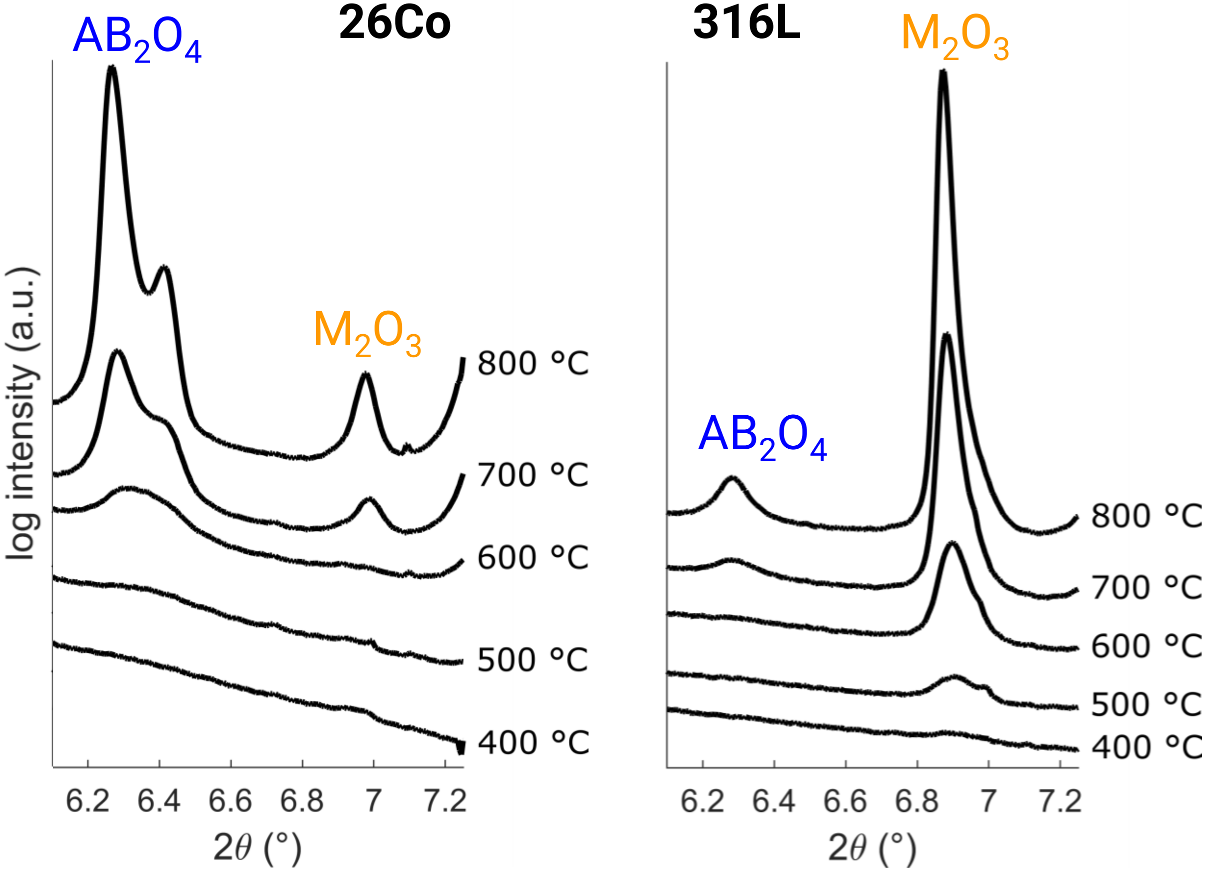
in-situ Synchrotron GI-XRD oxidation experiments



in-situ Synchrotron GI-XRD oxidation experiments

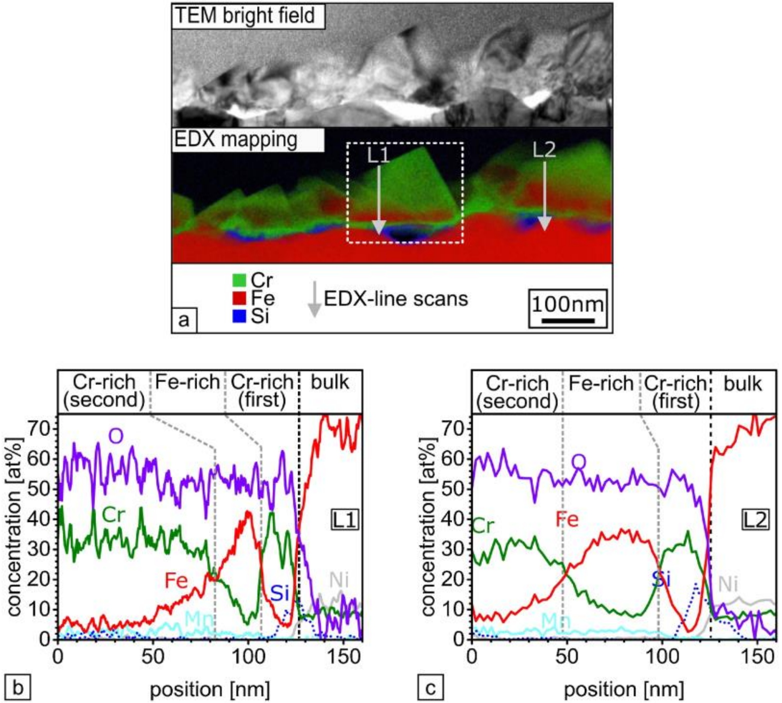
Temperature profile:
slow heating between
400 °C and 800 °C

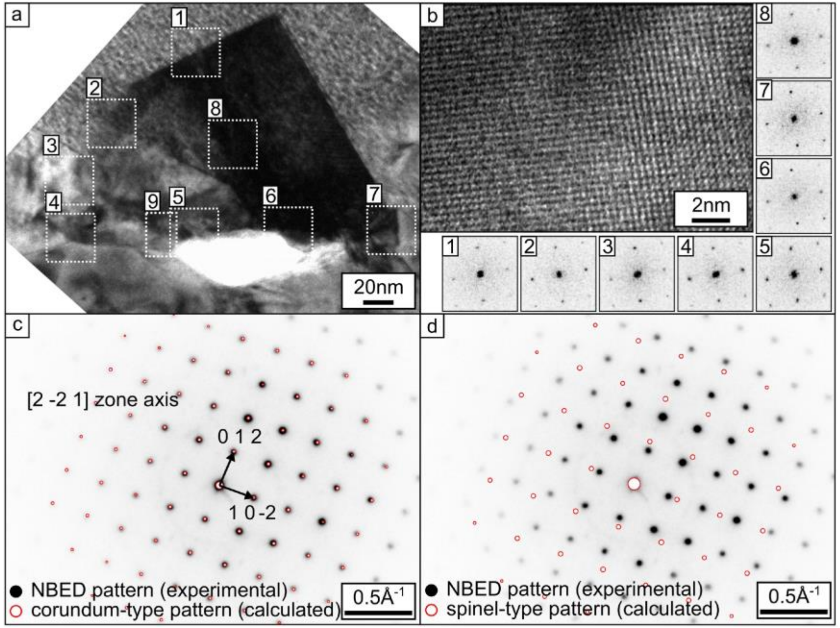




Oxidation of 316L austenitic stainless steel (X2CrNiMo17-12-2)

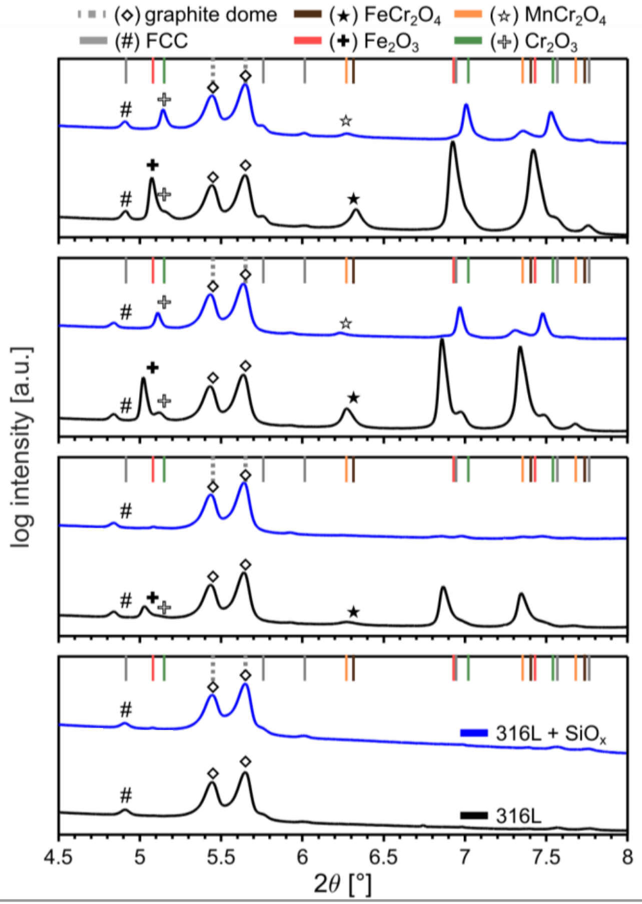
Corundum-type oxide grains with pronounced inhomogeneous elemental distribution after 1 h at 800 °C





R. Wonneberger *et al.*, Corrosion Science. 149 (2019) 178-184

Deposition of a ~20 nm SiO_x layer: only Cr incorporated in oxide



After cooling (20 °C)

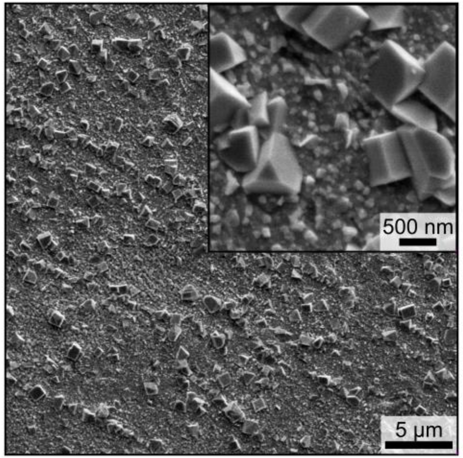
End of oxidation after 1 h (800 °C)

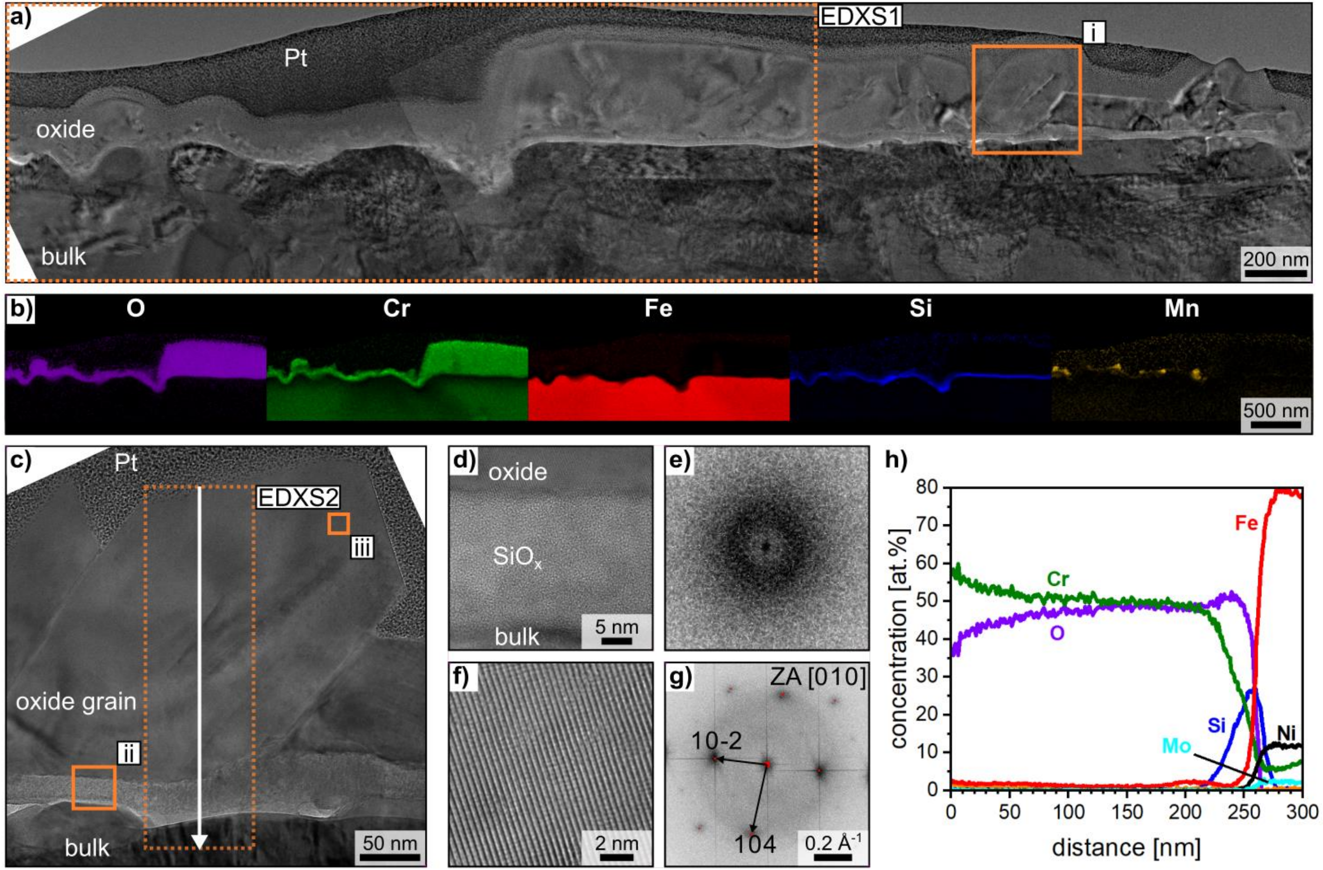
Beginning of oxidation (800 °C)

Start (20 °C)

TEM reveals oxide morphology and confirms pure Cr oxide

Oxide surface (SEM)





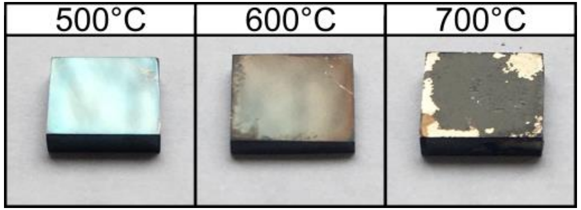
Outlook: Oxidation phenomena of medium-Mn steels

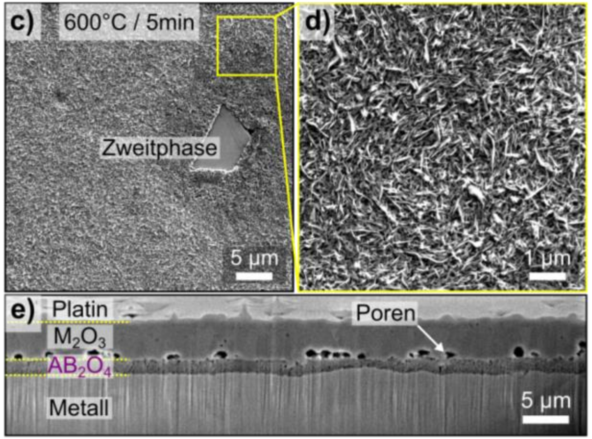
$FeMn_{4-6}Al_{0-2}Si_{0-2}$ as 3rd generation AHSS

- **Mn-rich oxides** form during thermomechanical processing (intercritical annealing, Q&P), impairing adhesion during hot-dip galvanizing

- Effect of Mn, Al, and Si on **phase formation and kinetics during early-stage oxidation (~ 5 min)** is not well understood in medium-Mn steels

- Experimental data are used as basis for **numerical modelling**



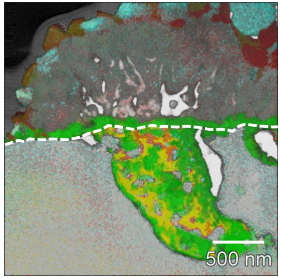


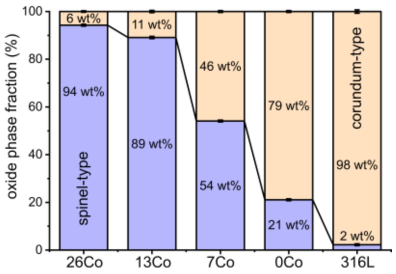
summary

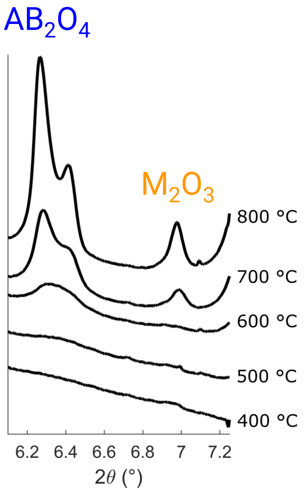
1) **Early-stage oxidation** of metallic materials is investigated using complementary methods

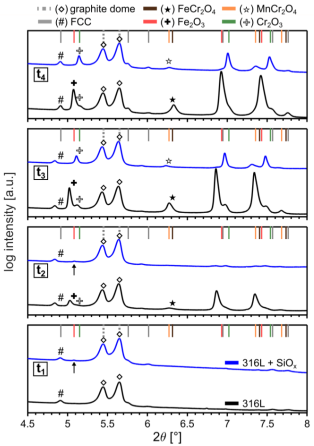
2) Short times (5 min ~ 6 h) and thin layers (10 nm ~ 3 µm) pose a **methodological challenge**

3) Combining **Synchrotron radiation** and **electron microscopy** allows for new and detailed insights into oxide layer formation









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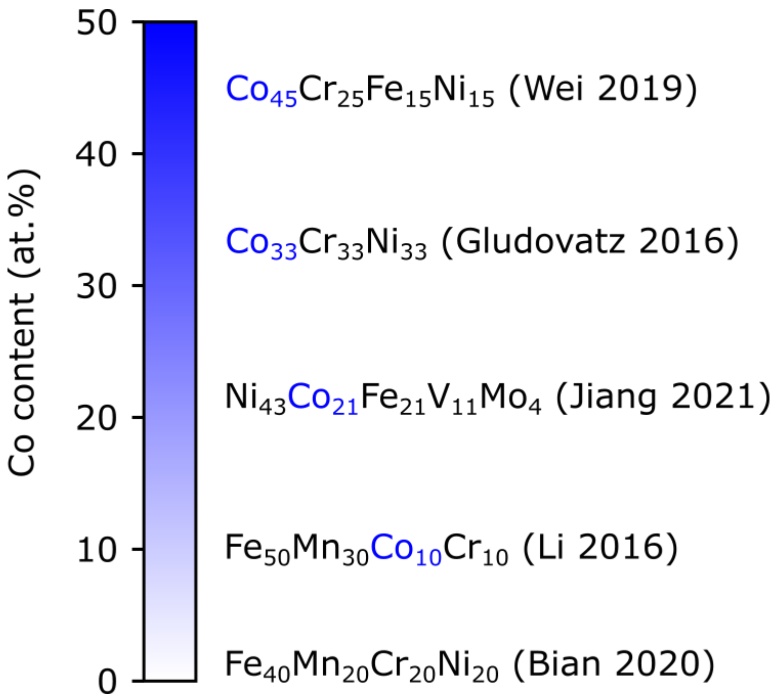
Co content in complex concentrated alloys (CCAs)



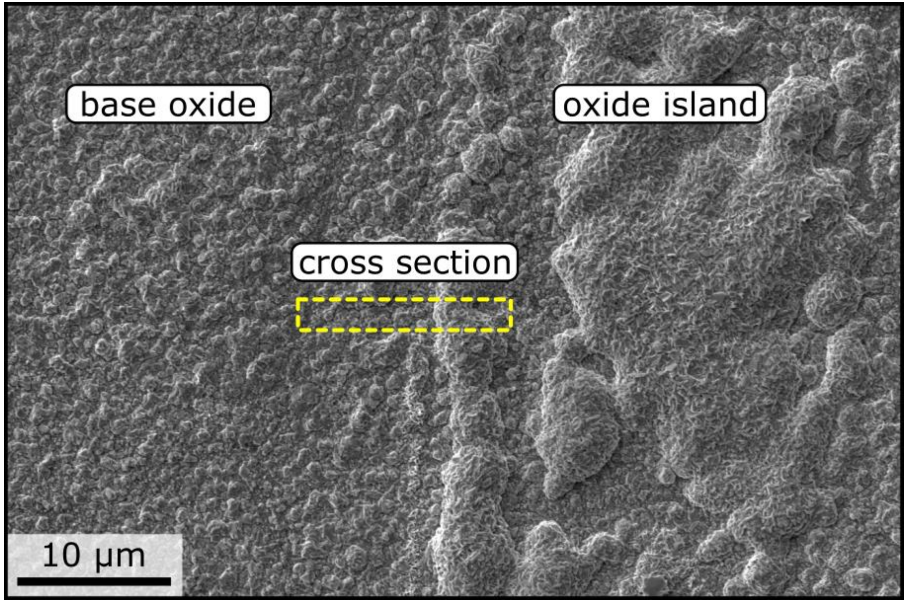
3d transition metal CCAs are candidate materials for high-temperature applications

high Co content in many CCAs poses economic and ecological challenges

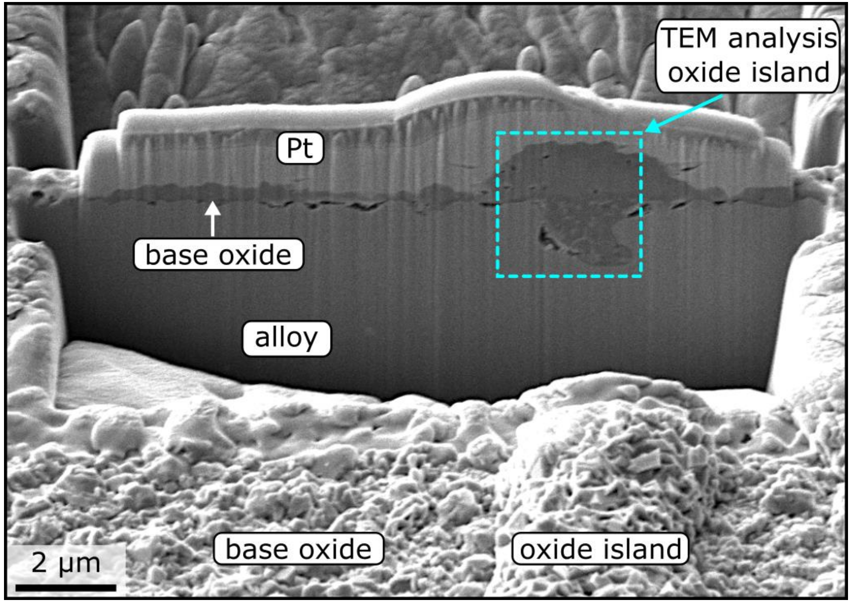
Co is substituted to reduce costs, *e.g.*, by adding Fe

dedicated oxidation studies are needed

oxide microstructure: 7Co sample after 1 h at 800 °C

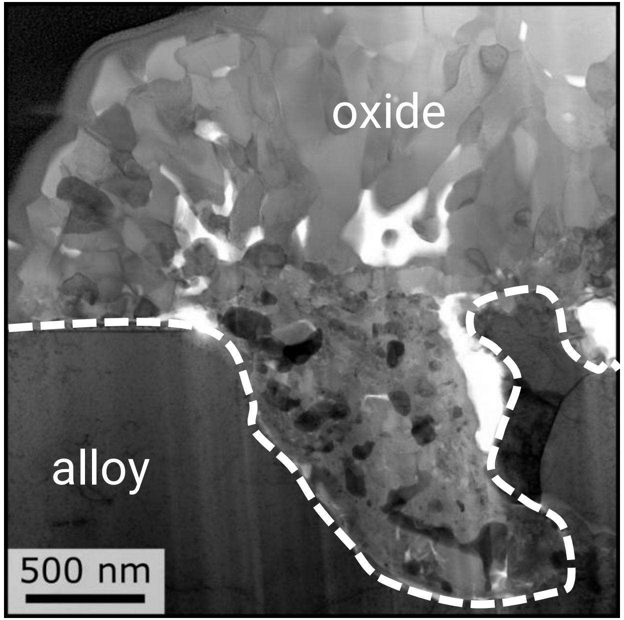


FIB cross section of 7Co sample

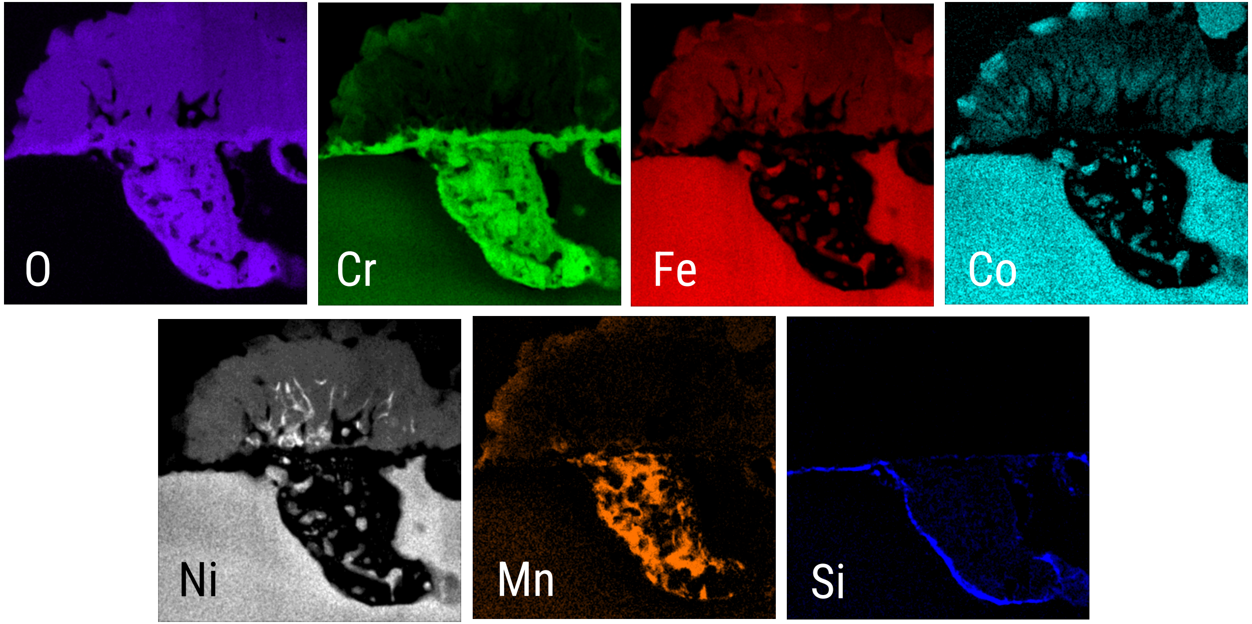


oxide island: microstructure and composition

STEM-BF



STEM-EDXS maps

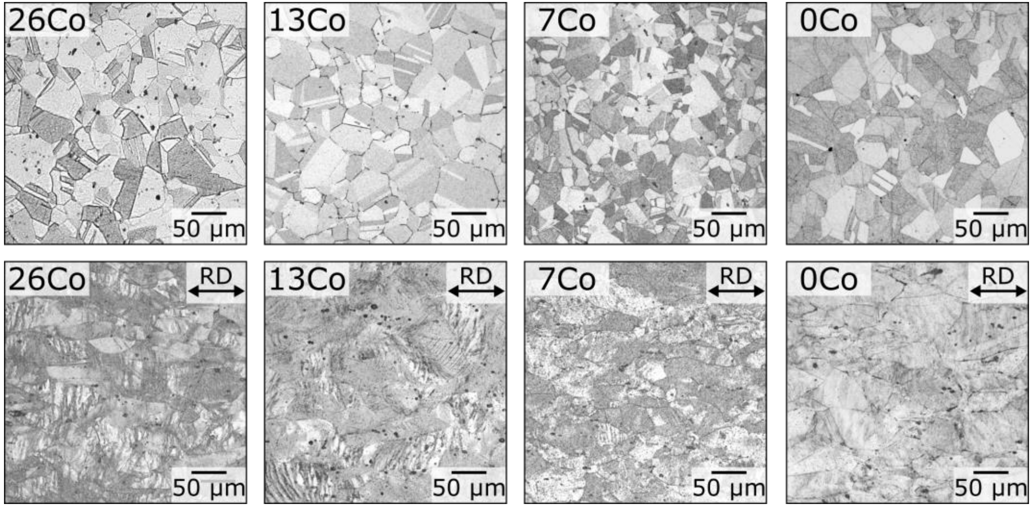


complex oxide microstructure with all alloying elements present in the oxide

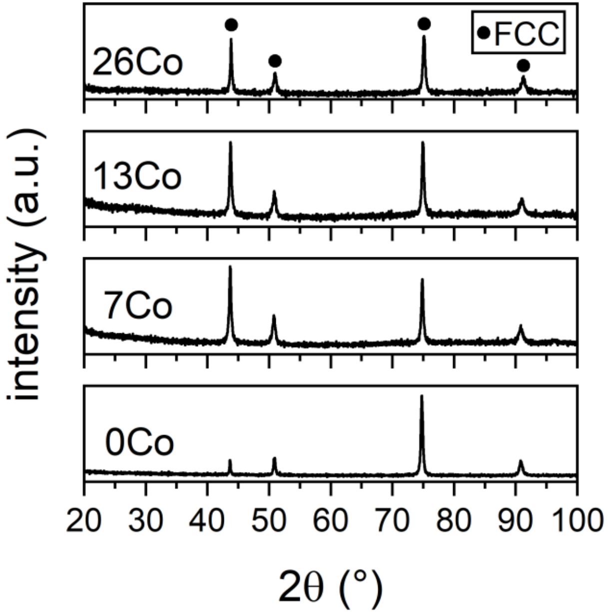
CCA microstructure and oxidation parameters

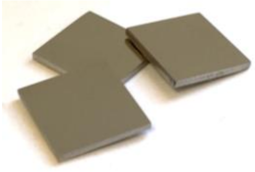
recrys-
tallized

cold rolled



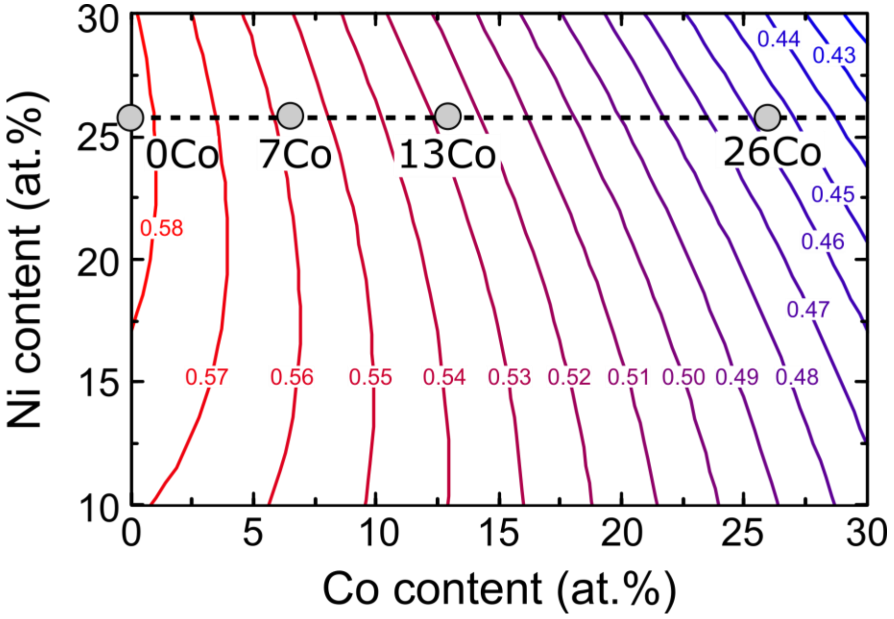
single-phase FCC





CCAs and 316L:
oxidation for 1 h at 800 °C in air

thermodynamic calculations: effect of Co, Fe, and Ni on Cr activity



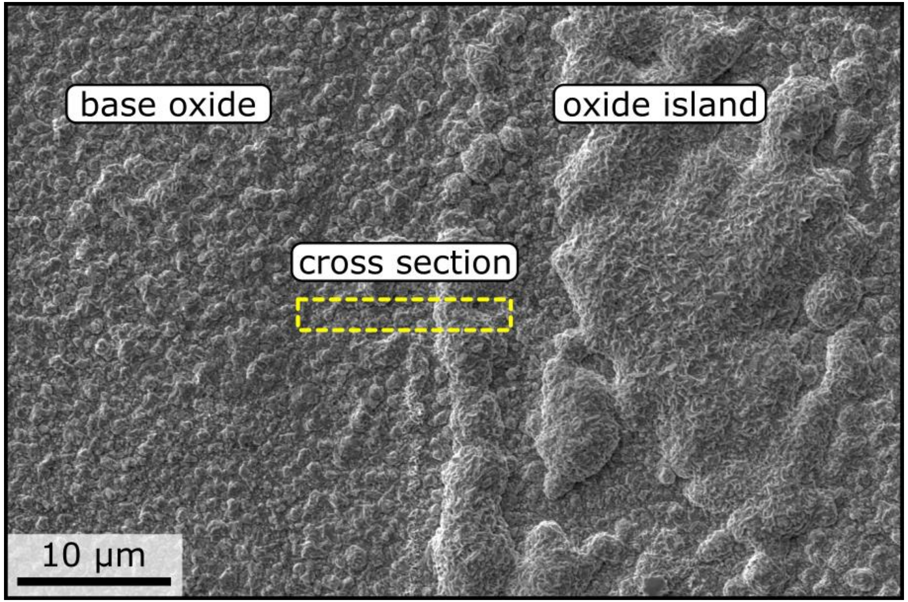
Cr activitiy in the FCC alloy with 19 at.% Cr, 2 at.% Mn and 1 at.% Si at 800 °C calculated with FactSage (CALPHAD method)

despite no change in Cr content: higher Co content decreases Cr activity by ~20%

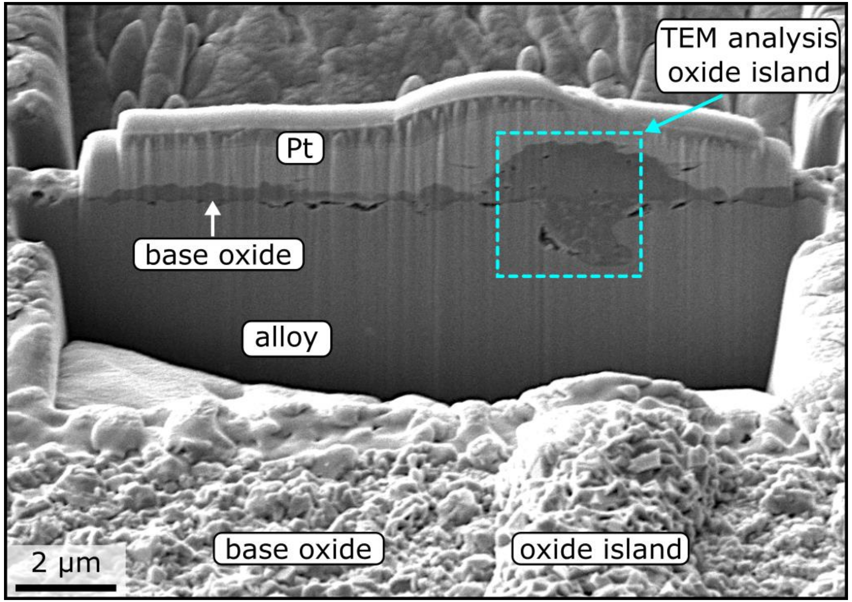
alloys with high Co content behave like alloys with lower Cr content

calculation inspired by recent work (V. Asokan *et al.*, Corrosion Science. 179 (2021) 109155.)

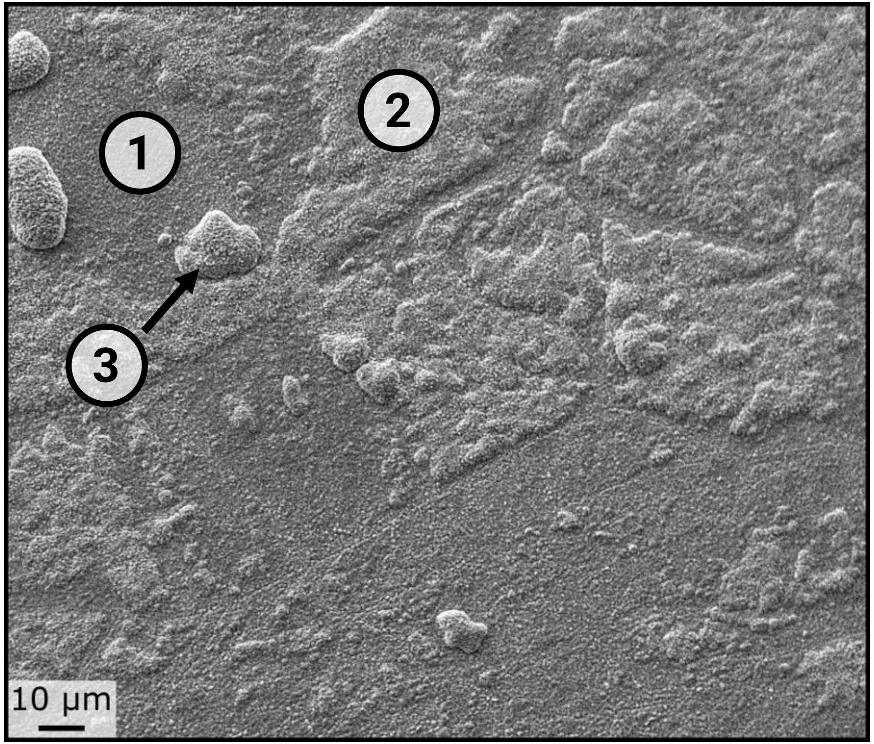
oxide microstructure: 7Co sample after 1 h at 800 °C



FIB cross section of 7Co sample



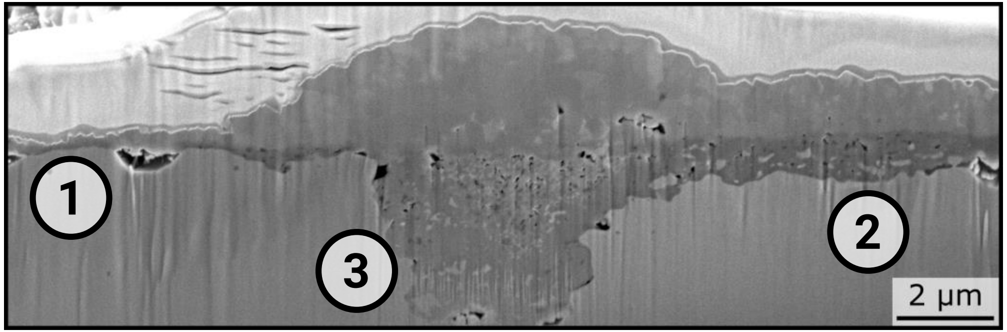
surface oxide: morphological features



1 thin base oxide

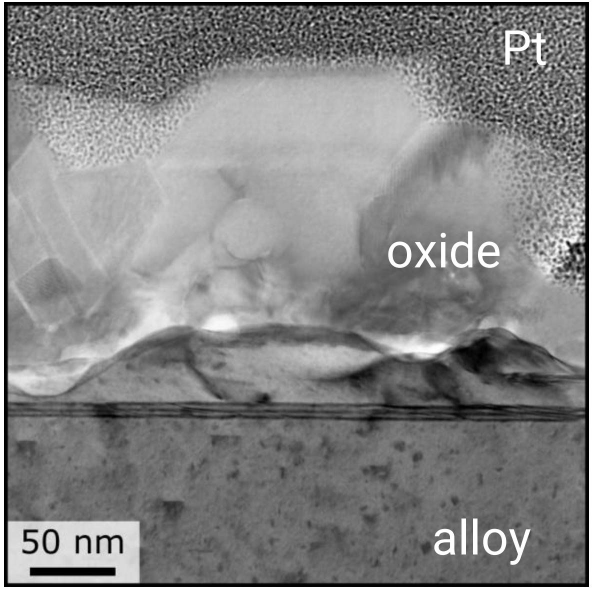
2 thick oxide covering entire grains

3 rounded oxide islands

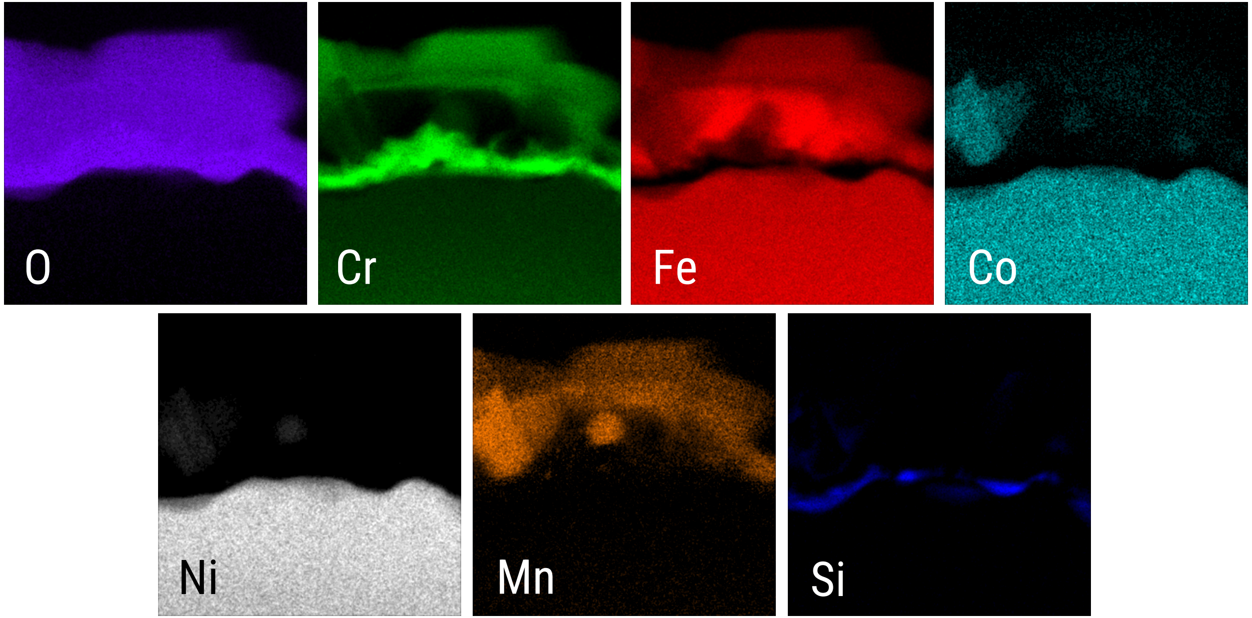


Base oxide: microstructure and composition

STEM-BF



STEM-EDX maps



all alloying elements present in the oxide

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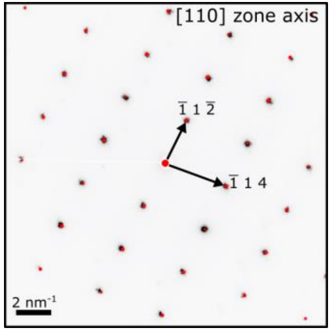
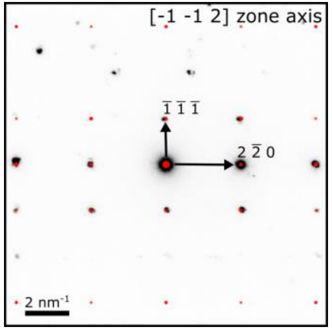
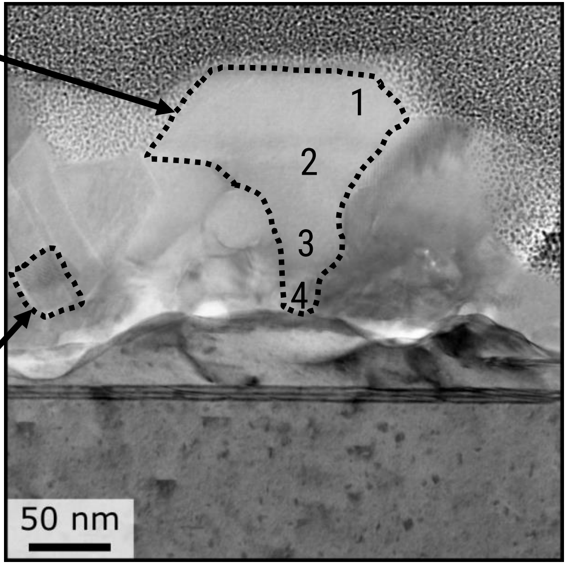
Base oxide: composition and oxide phases

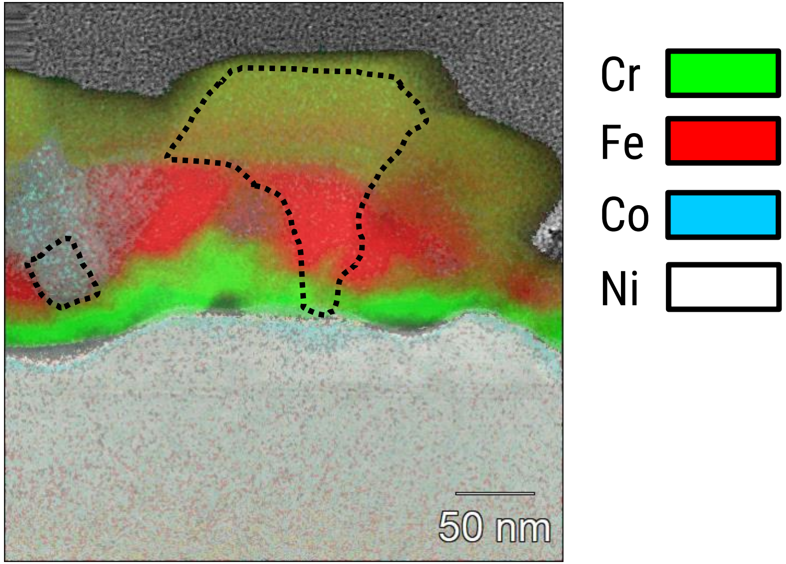
corundum-type



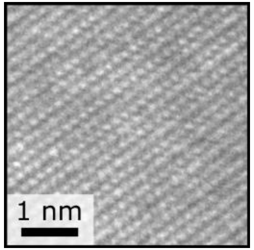
spinel-type







HRTEM



FFTs