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Industrial Processes -
New challenges for high temperature materials

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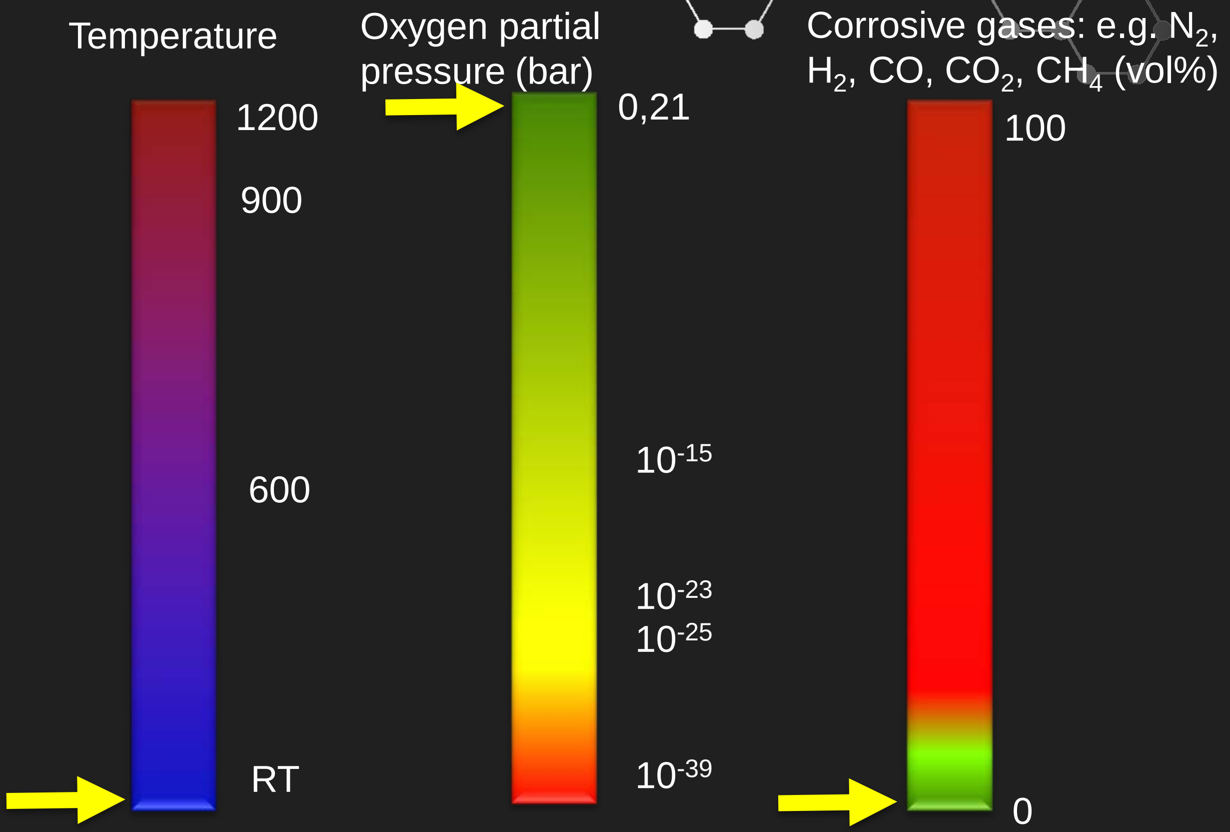
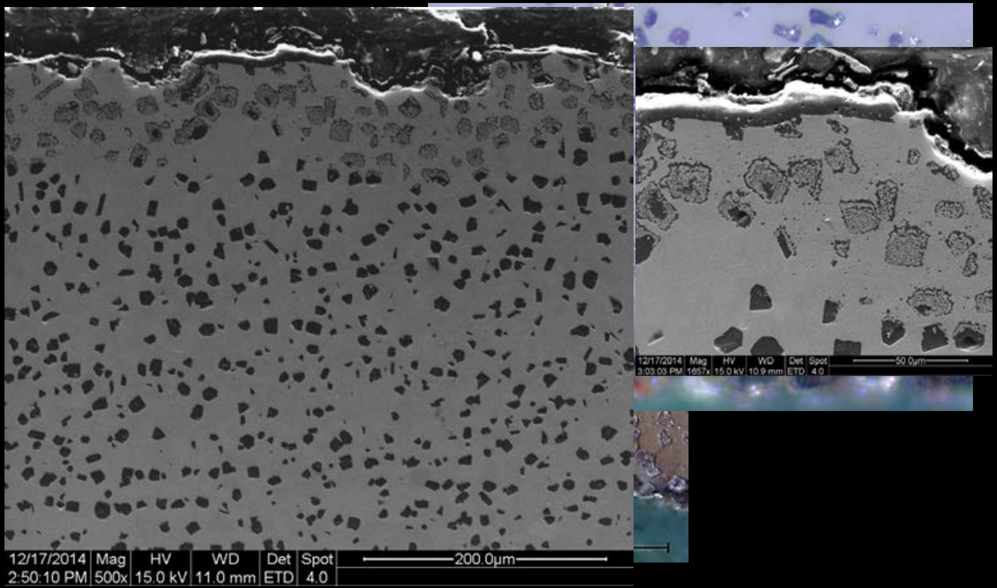
High Temperature Corrosion Centre


Temperature
1200
900
600
RT
Oxygen partial pressure (bar)
0,21
10^{-15}
10^{-23}
10^{-25}
10^{-39}
Corrosive gases: e.g. N_2, H_2, CO, CO_2, CH_4 (vol%)
100
0

Some of the best alumina forming alloys degrade extremely rapidly under these conditions

Furnaces for heat treatments under inert conditions

- ‚inert' conditions N_2/H_2
- high temperature 900-1200ºC

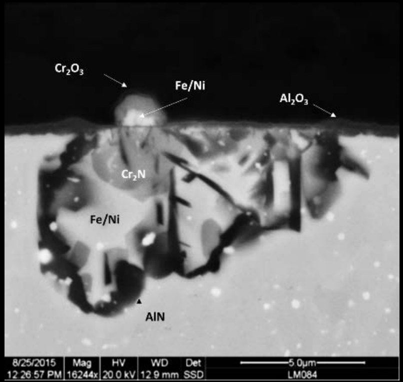


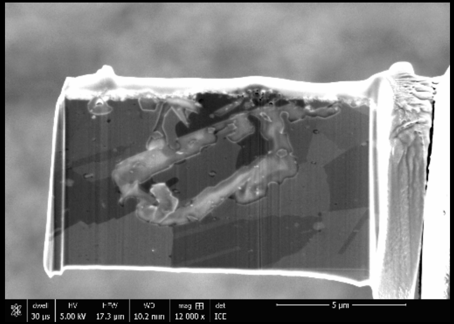
What did we look at

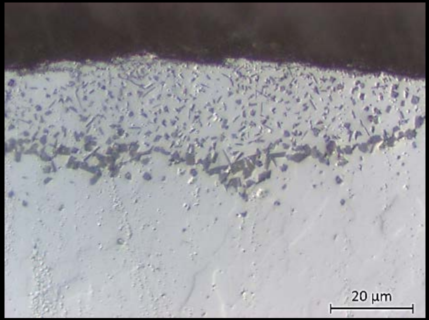
Two major topics:

Nitridation

The uncontrolled formation of internal nitride precipitates

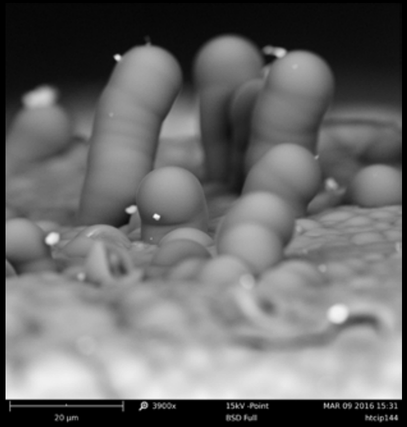


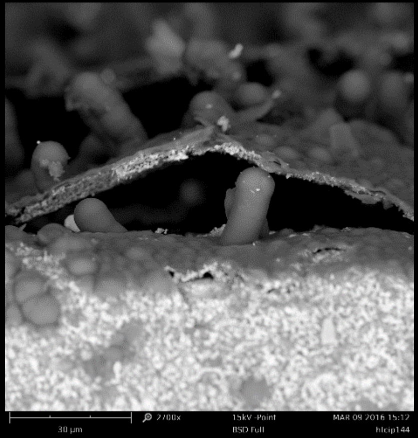


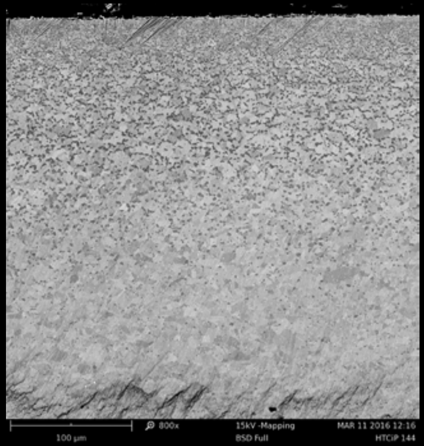


Carburization/Metal Dusting

The uncontrolled uptake of carbon into alloys and formation of graphite internally and externally.







What did we look at

Nitridation

- Model alloys
- Effect of secondary oxides in alumina scale

A novel high temperature hydrogen embrittlement mechanism triggered by internal nitridation

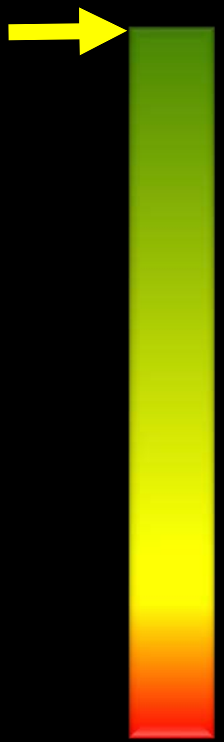
Oxidation

- Alumina Scaling Behavior in low pO2 in the presence of RE-particles

Carburization – initial investigations in highly carburizing environments

What did we look at

Oxygen partial pressure (bar)



0,21

10^{-15}

10^{-23}

10^{-25}

10^{-39}

Application of N_2-5%H_2 with ~35 ppm H_2O as impurity

iron and nickel oxide are not stable

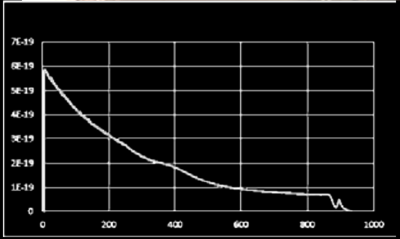
In this regime chromia, alumina, yttria and zirconia are stable

Materials investigated within this projects are:

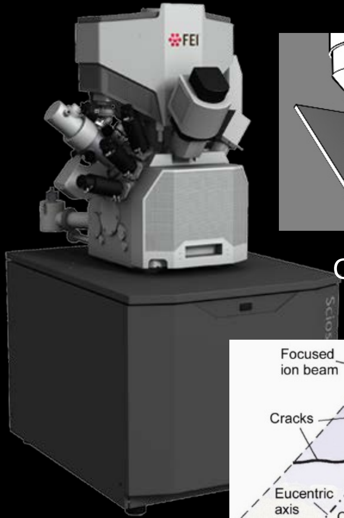
- FeCrAl(RE) – most works focused on Kanthal APMT™ (Fe-21Cr-5Al-3Mo)
- FeNiCrAl(RE)
- NiCr
- and stainless

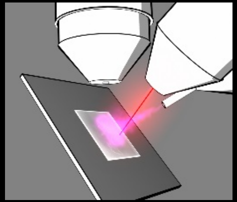
Exposures and State-of-the-Art Analysis

Well controlled high temperature exposures

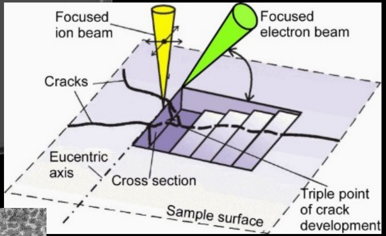


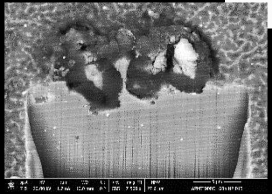
FIB (Focused Ion beam)





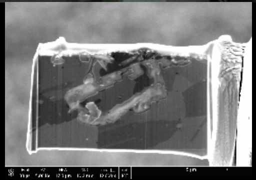
Gallium Ion Beam





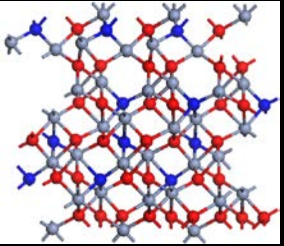
For more selective and site-specific cross-section (around 30×50 µm)

TEM (Transition Electron Microscope)

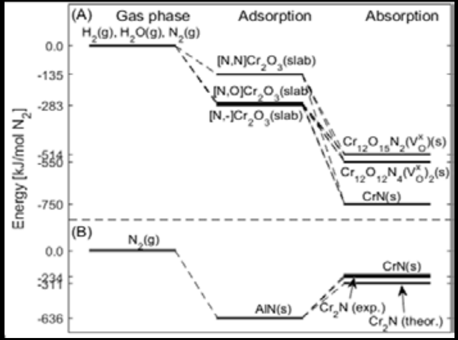


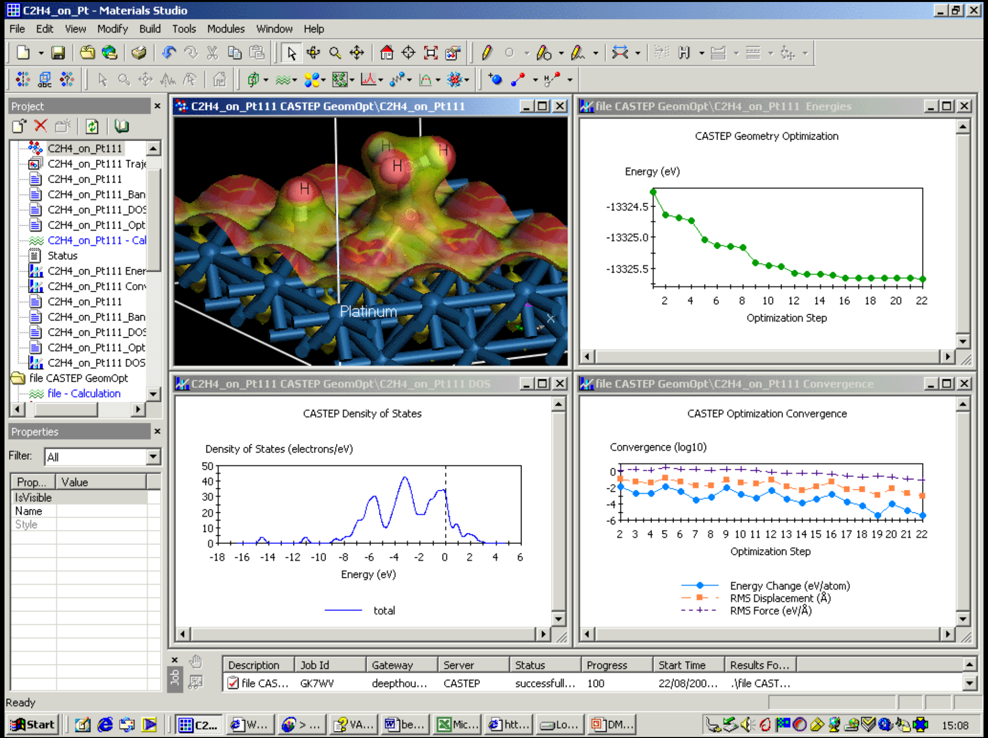
High resolution analysis

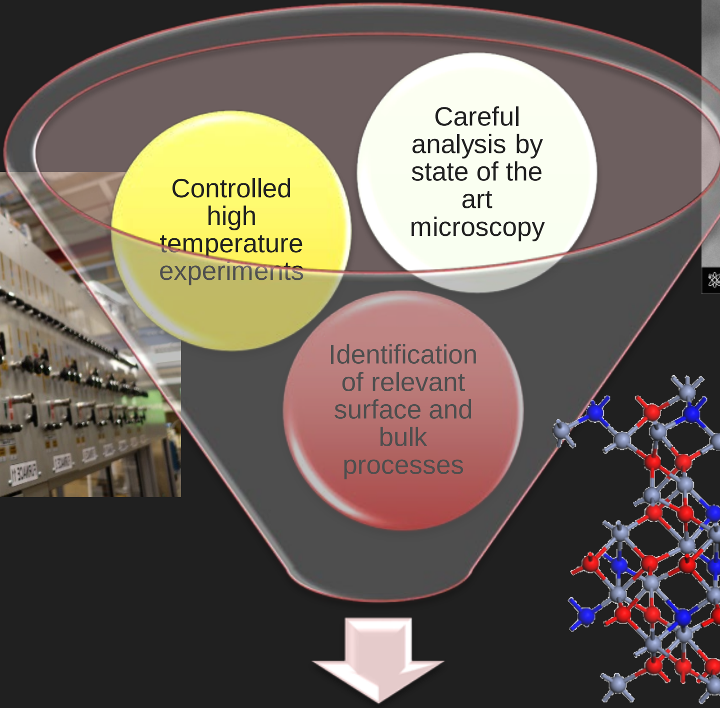
Investigation of the energy landscape of corrosion processes by ab initio methods for mechanistic insight

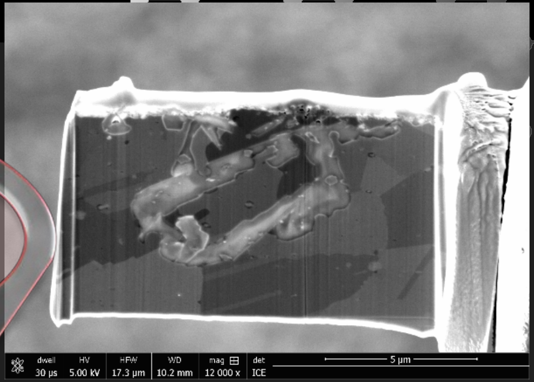


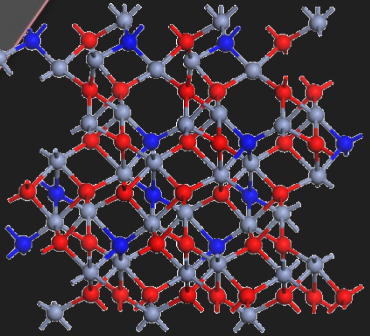
Access to metastable transients such as metal oxy-nitrides







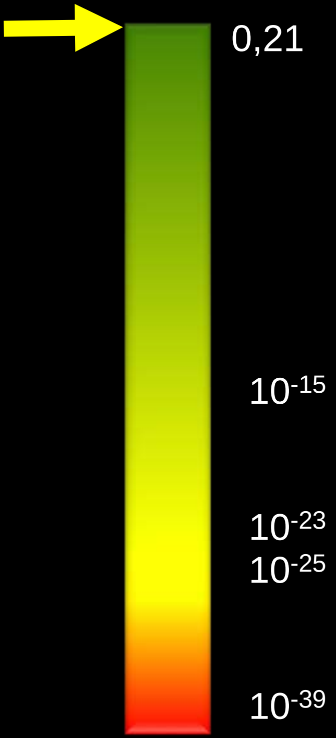




Conceptual understanding of the corrosion mechanism

Nitridation

Oxygen partial pressure (bar)



Application of N_2-5%H_2 with ~35 ppm H_2O as impurity

iron oxide is not stable

In this regime chromia, alumina, yttria and zirconia are stable

Questions we have addressed:

- stability of oxides under nitriding conditions, synergetic effects — HTC/KME 2015
- possible nucleation sites for chromia on an alumina forming alloy – identification by marker experiments — HTC/KME 2016
- the impact of surface texture on the onset of nitridation — HTC/KME 2017
- the effect of yttria and zirconia on alumina growth — HTC/KME 2018
- role of hydrogen on surface features

Carburization

Oxygen partial pressure (bar)

0,21

Application of Ar-5%CH_4–45%H_2 with a pO2 ~ 10^{-30} as impurity

10^{-15} iron oxide and chromia are not stable

10^{-23}

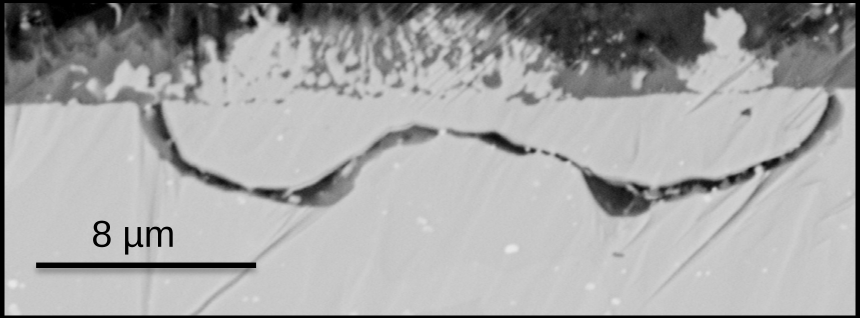
10^{-25}

10^{-39} In this regime, alumina, yttria and zirconia are stable

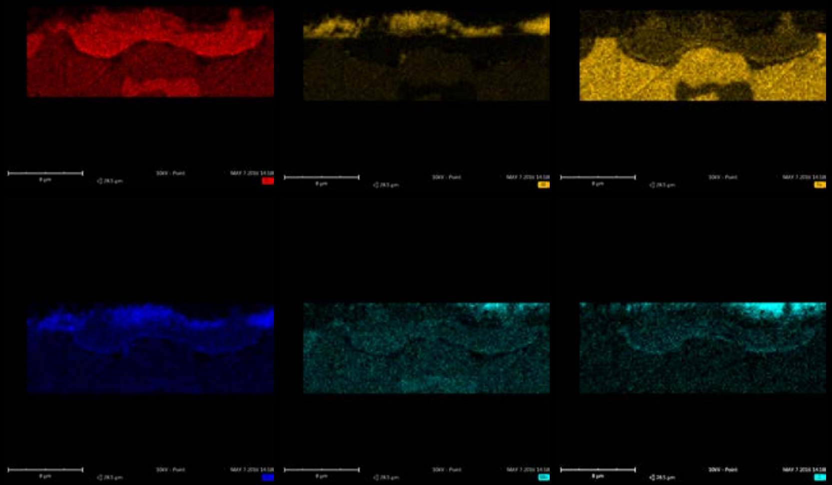
Questions we have addressed:

- Possibility to carburize an alumina former — HTC/KME 2016/17
- specific features of carburized alumina former — HTC/KME 2017/18

Carburization



APMT 24h Ar-45%H2-5%CH4, 900°C



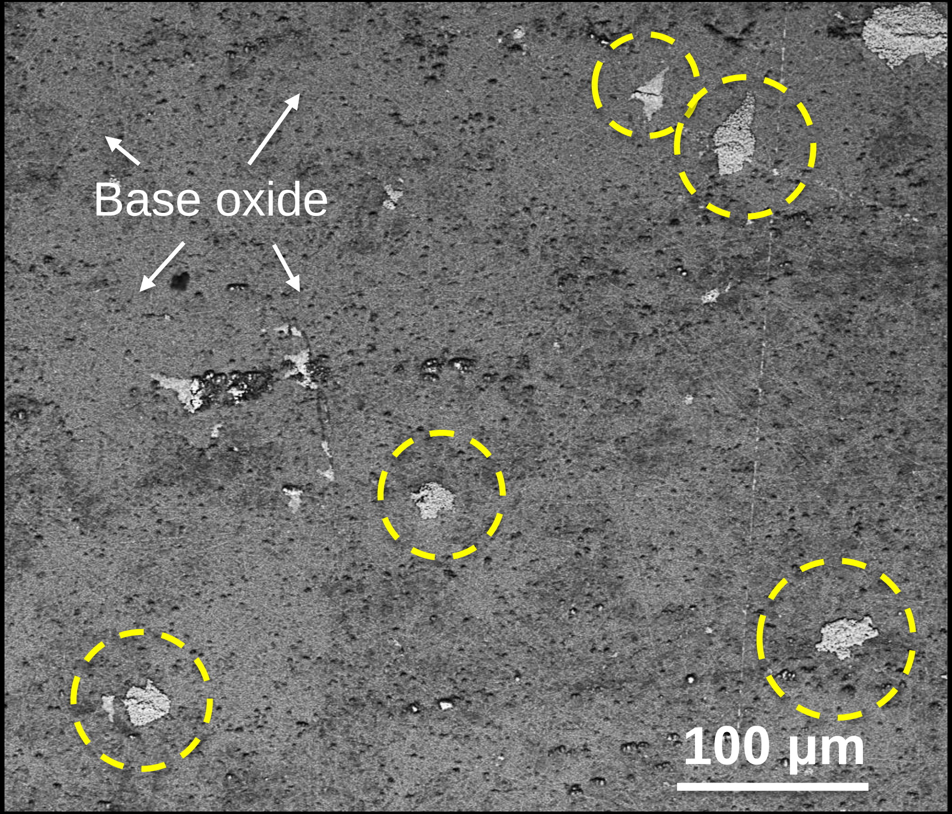
Cr, Al, Fe

O, Mo, C

Nitridation

Alloy: Kanthal APMT

Temperature: 900°C
Environment: 95%N_2 + 5%H_2
Exposure time: 1 week

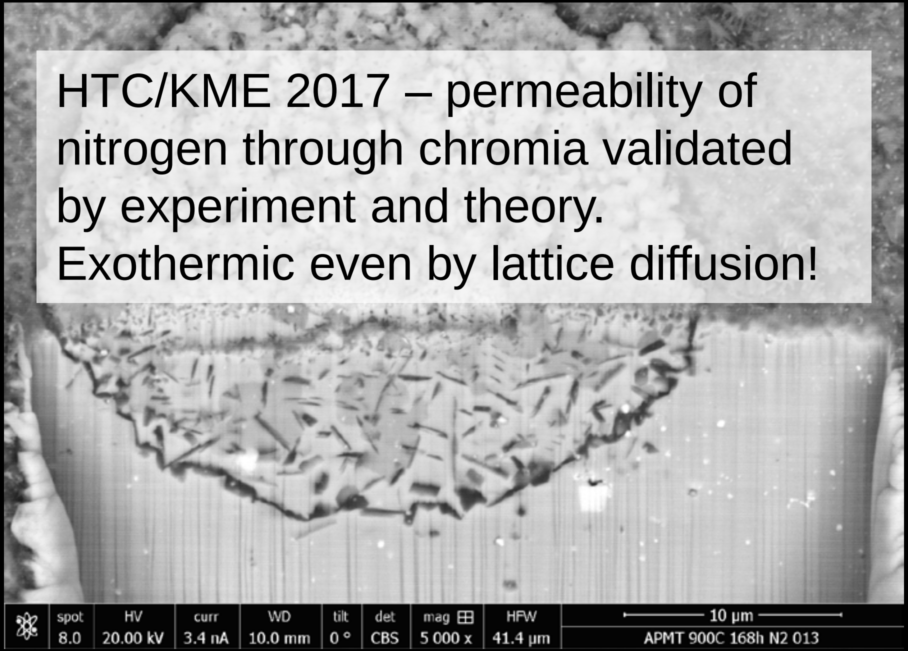


APMT
N_2-5%H_2
900°C
168h

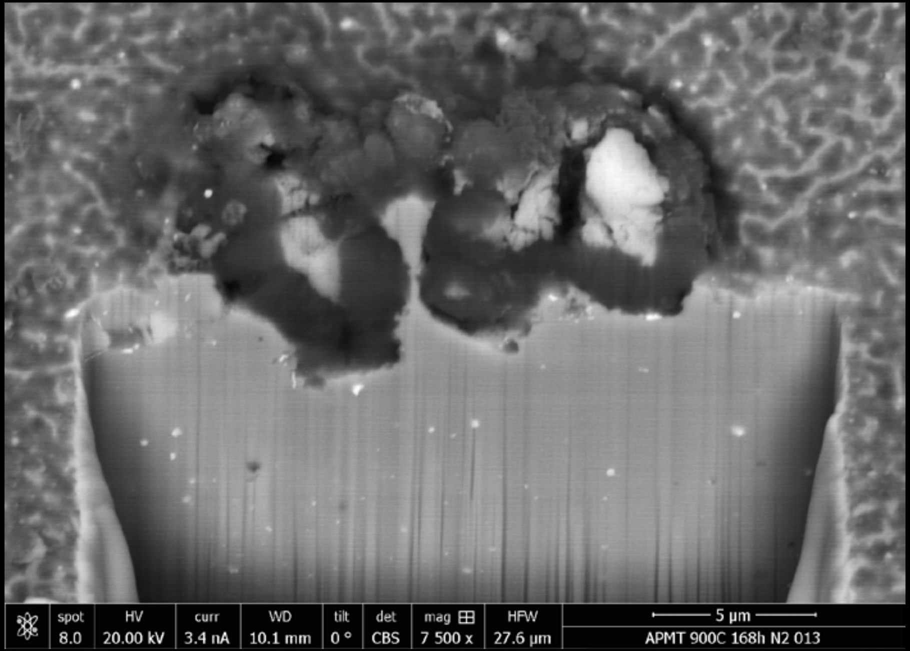
On the same sample, we found two outstanding features:

Local nitridation through chromia domains in the alumina scale

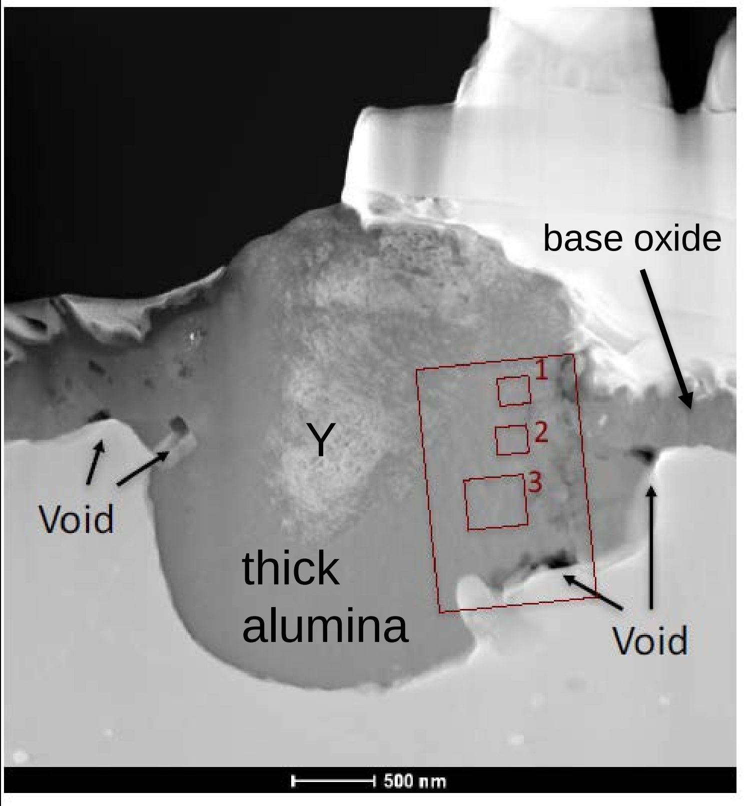
HTC/KME 2017 – permeability of nitrogen through chromia validated by experiment and theory. Exothermic even by lattice diffusion!



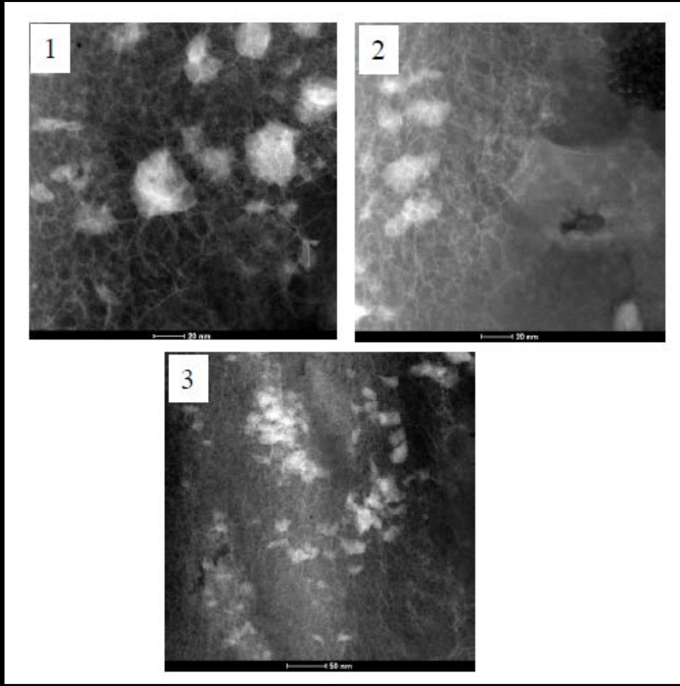
Very fast growth of alumina in the vicinity of reactive element particles!



A thick and rapidly growing alumina



TEM image



APMT
N_2-5%H_2
900°C

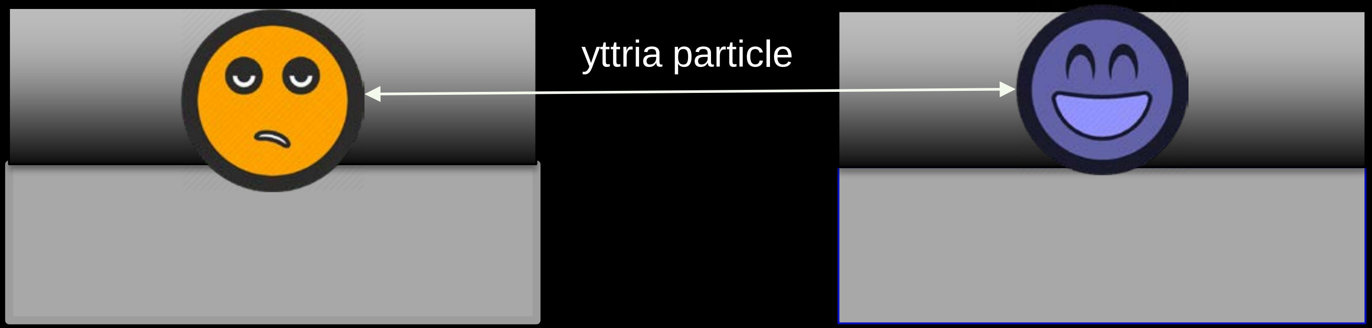
To illustrate what yttrium can do in a growing alumina scale we would like to take you on a conveyer belt tour…

no H_2O

H_2O

dispersed yttria particles remain inactive in perfectly dry environments

yttria mobility is greatly enhanced by hydroxylated interfaces formed with as little as few ppms of water in the environment

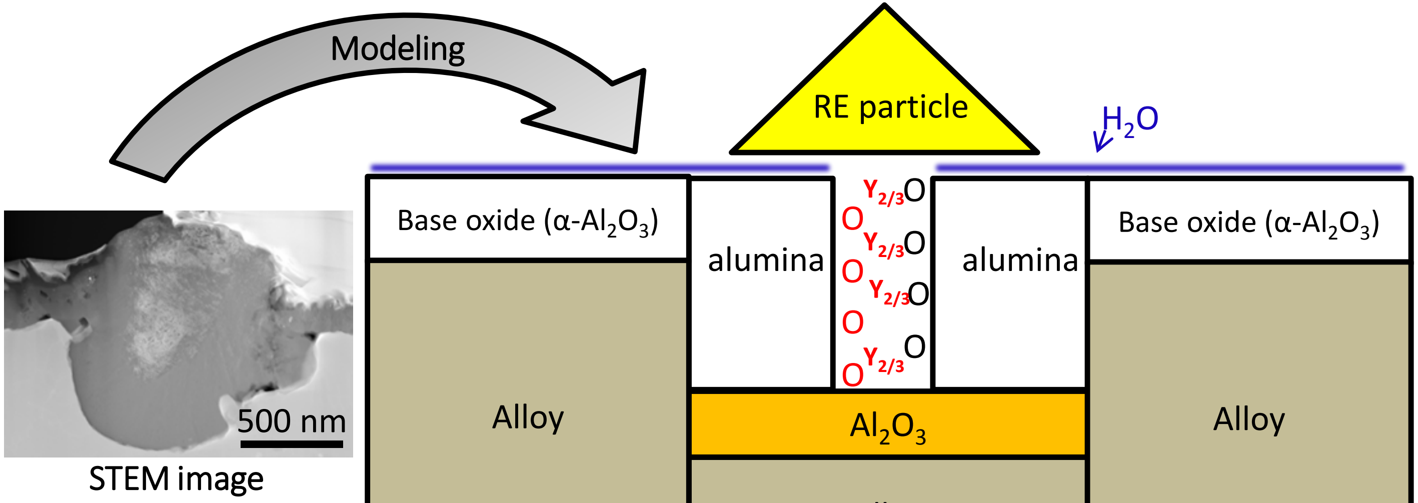


only very slow solid state diffusion is possible

rapid oxygen vacancy mediated transport along interfaces towards an inner cathode at the metal/oxide interface

The "conveyer belt" mechanism

A novel concept (emerging from experiment + DFT calculations + modeling)



The "conveyer belt" mechanism

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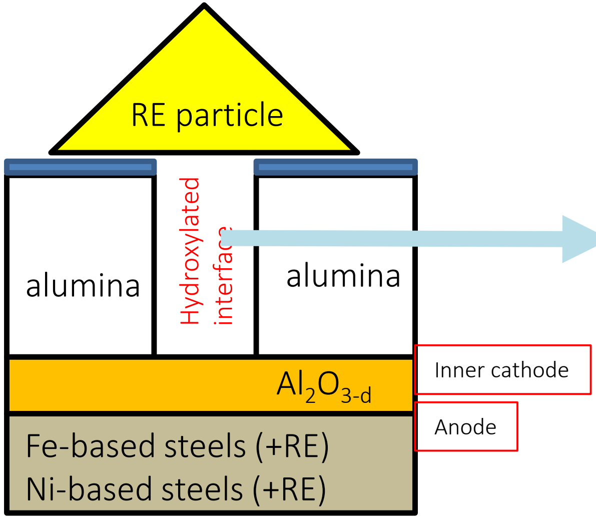
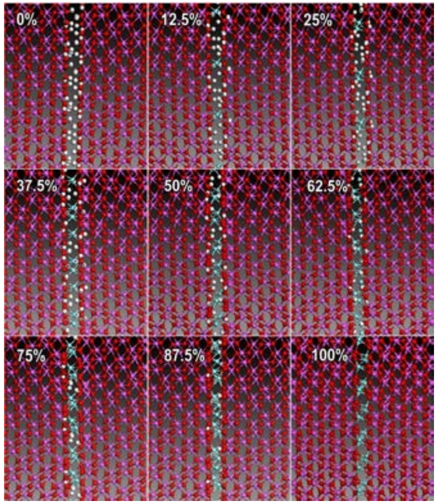


Supplementary Sec. 9



The "conveyer belt" mechanism

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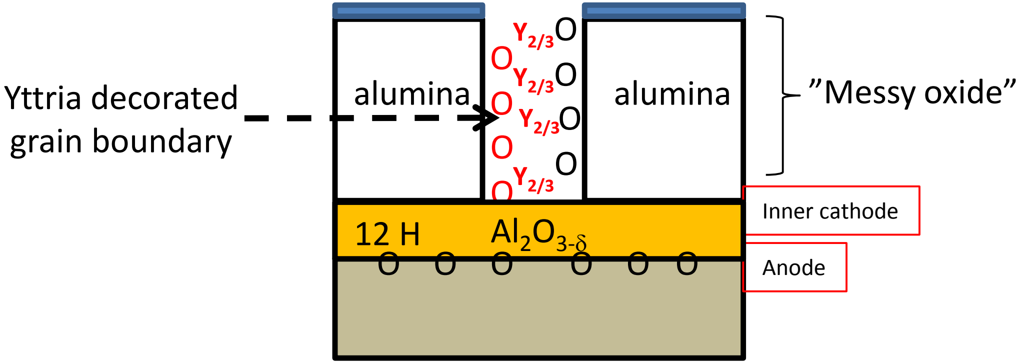
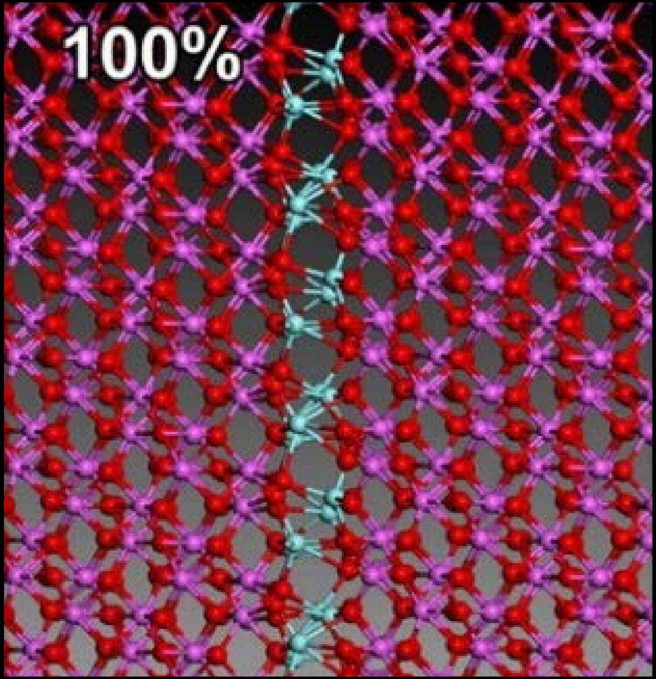
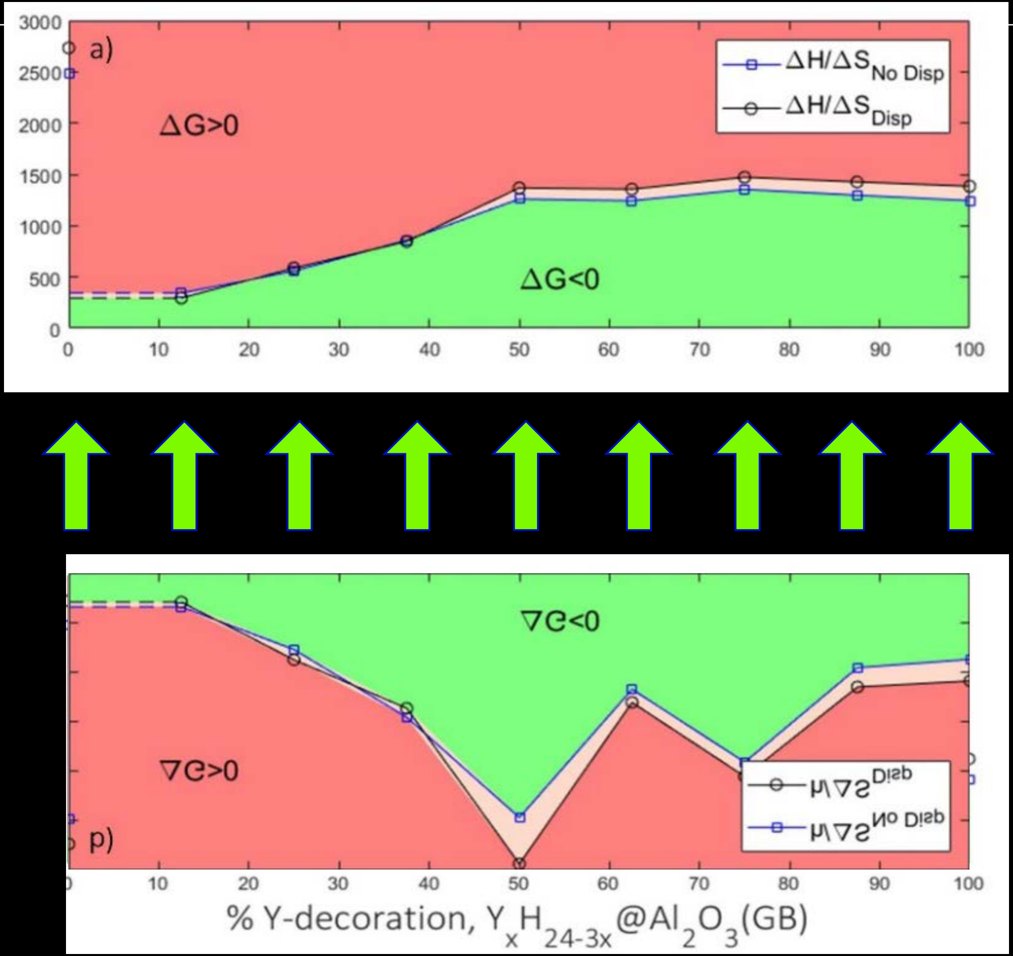



100%


a)
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90
100
ΔG>0
ΔG<0
ΔH/ΔS No Disp
ΔH/ΔS Disp
0
10
20
30
40
50
60
70
80
90
100
% Y-decoration, Y_xH_{24-3x}@Al_2O_3(GB)

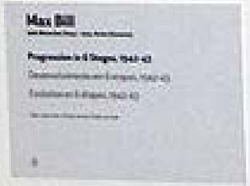
The last four years' research in the project industrial processes has resolved some of the long standing riddles in high temperature corrosion and allows new concepts to emerge.

- How nitrogen permeates alumina scale?

Through of chromia "window"

- Role of water?
- Role of RE?

Two riddles – one answer



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