HTC Project 2a

New corrosion resistant materials for challenging process environments – low oxygen activities and very high temperatures

Presented by LG. Johansson and C. Geers

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Project Organization

- *Project leader:* LG Johansson, Chalmers
- *Companies:* SANDVIK, KANTHAL® Part of Sandvik Group, Entech
- *Researchers in HTC :* LG Johansson, JE Svensson, M Halvarsson, I Panas, C Geers, M. Sattari I. Panas Loli Paz (all Chalmers) Post-Doc: N Mortazavi, Chalmers/Monash
- *PhD students:* V.Babic, T. Sand

Project plan

- **Project Goals:**
- Investigate the nitridation and carburization of high temperature alloys and the RE effect with the aim to formulate new strategies for developing alloys with superior ability to resist challenging environments and extreme temperatures
- **Materials:**
  - Alumina-forming alloys
  - Chromia-forming alloys

Background

- Materials that can withstand process environments at very high temperatures without failing due to corrosion are necessary in, e.g., steel production, in thermal treatment of metals and ceramics, and in the manufacture of batteries and electronics
- Developing new materials that can withstand higher temperatures and more corrosive environments enables large energy efficiency gains
- Also, new materials with superior ability to resist high temperature corrosion will enable novel energy efficient and environmentally friendly processes and technologies

Why are low a(O_2) environments challenging?

- All high temperature alloys rely on the formation of a thermally grown oxide scale (usually Cr_2O_3 or Al_2O_3) which protects the material from further reactions with the environment
- If the availability of oxygen carriers such as O_2 or H_2O is very low, the protective scale may fail to form or it will be unable to form again if damaged
- The resulting nitridation and/or carburization often limits the service life of components

Methodology

- Furnace exposures under carefully controlled conditions ($a(O_2)$, $P(H_2O)$, T, t) Polished coupons, triplicate samples, Corrosion rate measurements
- Post-analysis of exposed samples to evaluate corrosion morphology (SEM and TEM investigations on cross sections prepared by broad ion beam (BIB) milling and Focused Ion Beam Microscopy (FIB). SIMS, Auger and TEM provide information about crystal structure, chemical composition and image information down to a few nanometers.

Methodology

- The combination of furnace exposures and post-analysis gives rise to ideas concerning, e.g., why a protective alumina scale fails in a certain case
- The new ideas are tested by performing First principles calculations on selected processes in the sequence of events that lead to scale failure. The calculations helps us understand and pinpoint processes that are crucial for corrosion behaviour
- Kanthal and Sandvik are responsible for the alloy development work. They also provide the materals, including commercial alloys, experimental alloys and model alloys

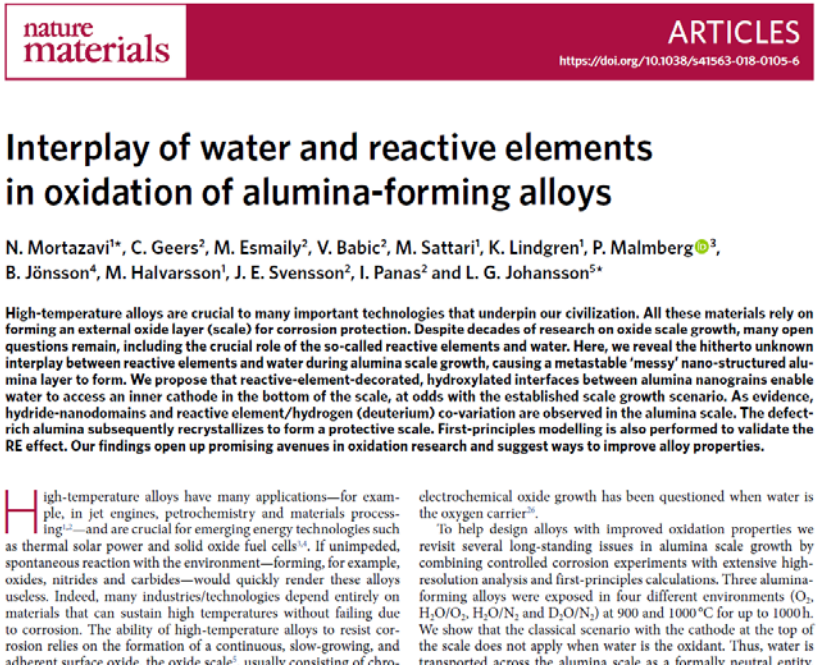
Why study the RE effect?

- All alloys designed for temperatures >800 °C contain small amounts of so called reactive elements (Y, Zr, Hf, Ce, et cetera). The RE additions greatly improve the protective properties of the oxide scale and have been used for >70years. However, after perhaps 4000 scientific papers on this subject there is still no consensus as to the mechanisms behind the “RE effect”!
- During the last contract period (2014 to 2017) HTC made important contributions to this field, revealing the interplay of water and RE element particles on a FeCrAl alloy. The work is highly relevant to nitridation in environments where water is the only oxygen carrier.

Some recent results on the RE-effect

A study of the early oxidation behaviour of alloy *Kanthal APMT in N_2 + H_2 with traces of H_2O at 900 ^oC* was published in 2018

Kanthal APMT is a powder processed FeCrAl(Y) alloy with excellent oxidation properties



nature materials
ARTICLES
https://doi.org/10.1038/s41563-018-0105-6

Interplay of water and reactive elements in oxidation of alumina-forming alloys

N. Mortazavi[1]*, C. Geers[2], M. Esmaily[2], V. Babic[2], M. Sattari[1], K. Lindgren[1], P. Malmberg[3], B. Jönsson[4], M. Halvarsson[1], J. E. Svensson[2], I. Panas[2] and L. G. Johansson[5]*

High-temperature alloys are crucial to many important technologies that underpin our civilization. All these materials rely on forming an external oxide layer (scale) for corrosion protection. Despite decades of research on oxide scale growth, many open questions remain, including the crucial role of the so-called reactive elements and water. Here, we reveal the hitherto unknown interplay between reactive elements and water during alumina scale growth, causing a metastable 'messy' nano-structured alumina layer to form. We propose that reactive-element-decorated, hydroxylated interfaces between alumina nanograins enable water to access an inner cathode in the bottom of the scale, at odds with the established scale growth scenario. As evidence, hydride-nanodomains and reactive element/hydrogen (deuterium) co-variation are observed in the alumina scale. The defect-rich alumina subsequently recrystallizes to form a protective scale. First-principles modelling is also performed to validate the RE effect. Our findings open up promising avenues in oxidation research and suggest ways to improve alloy properties.

High-temperature alloys have many applications—for example, in jet engines, petrochemistry and materials processing[1,2]—and are crucial for emerging energy technologies such as thermal solar power and solid oxide fuel cells[3,4]. If unimpeded, spontaneous reaction with the environment—forming, for example, oxides, nitrides and carbides—would quickly render these alloys useless. Indeed, many industries/technologies depend entirely on materials that can sustain high temperatures without failing due to corrosion. The ability of high-temperature alloys to resist corrosion relies on the formation of a continuous, slow-growing, and adherent surface oxide, the oxide scale[5], usually consisting of chro-

electrochemical oxide growth has been questioned when water is the oxygen carrier[26].

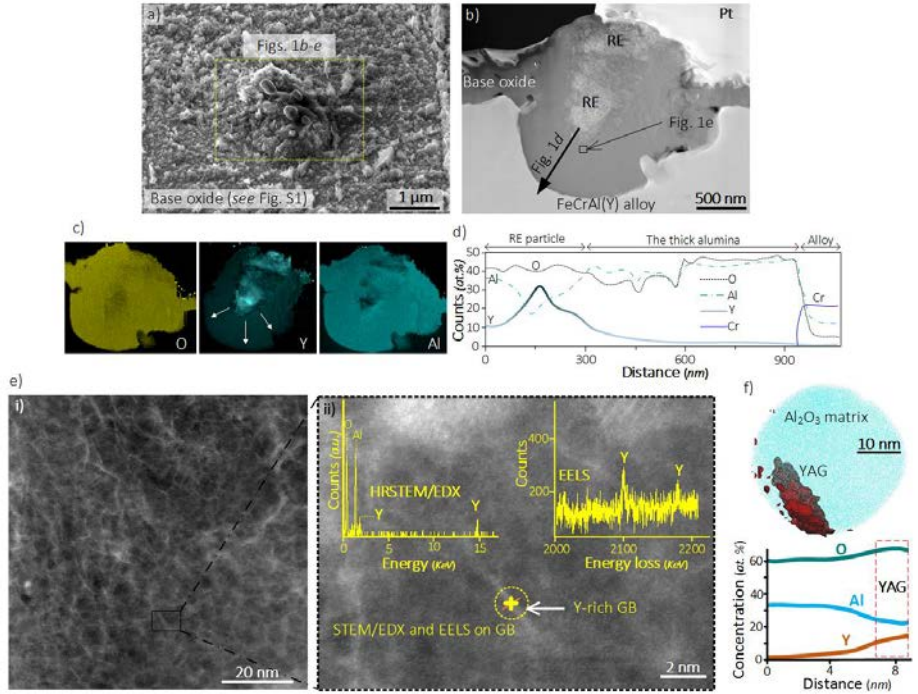
To help design alloys with improved oxidation properties we revisit several long-standing issues in alumina scale growth by combining controlled corrosion experiments with extensive high-resolution analysis and first-principles calculations. Three alumina-forming alloys were exposed in four different environments (O_2, H_2O/O_2, H_2O/N_2 and D_2O/N_2) at 900 and 1000 °C for up to 1000 h. We show that the classical scenario with the cathode at the top of the scale does not apply when water is the oxidant. Thus, water is transported across the alumina scale as a formally neutral entity

The RE element additions in the alloy are mainly present as 5 to 500 nm particles.

The image highlights an Y rich particle at the alloy surface which has become incorporated into the Al_2O_3 scale, forming an oxide nodule.

While the centre of the nodule consists of Y_2O_3, the periphery consists of nanocrystalline, metastable alumina.

The nano-grain boundaries are enriched in Y^{3+}.

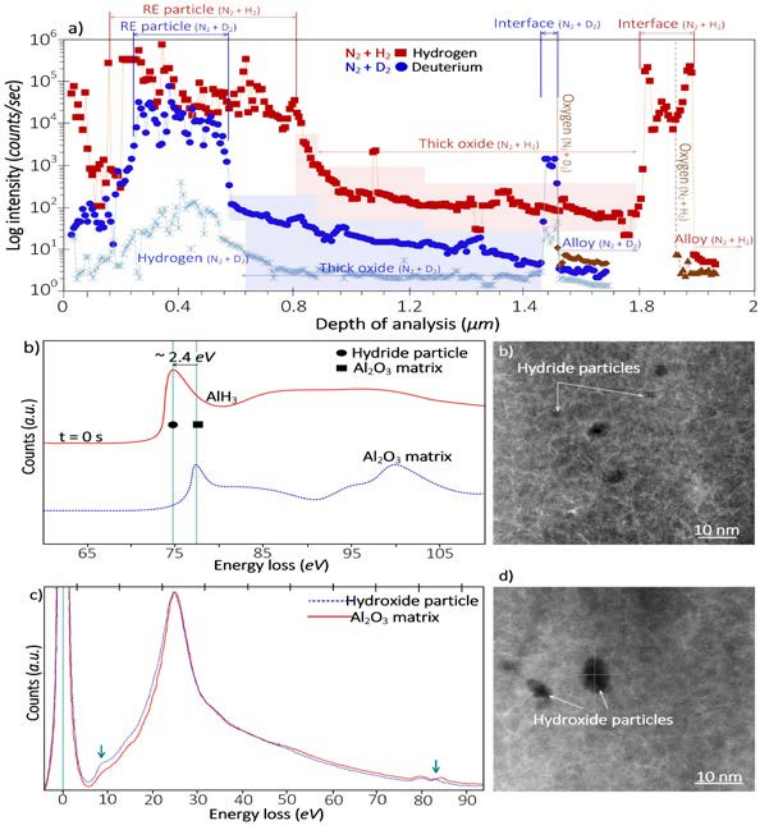


Concentration gradients
show that Y^{3+} is transported towards
the scale /alloy interface, across the ”messy”
alumina.

The only source of the oxygen neessary
for growing Al_2O_3 is H_2O

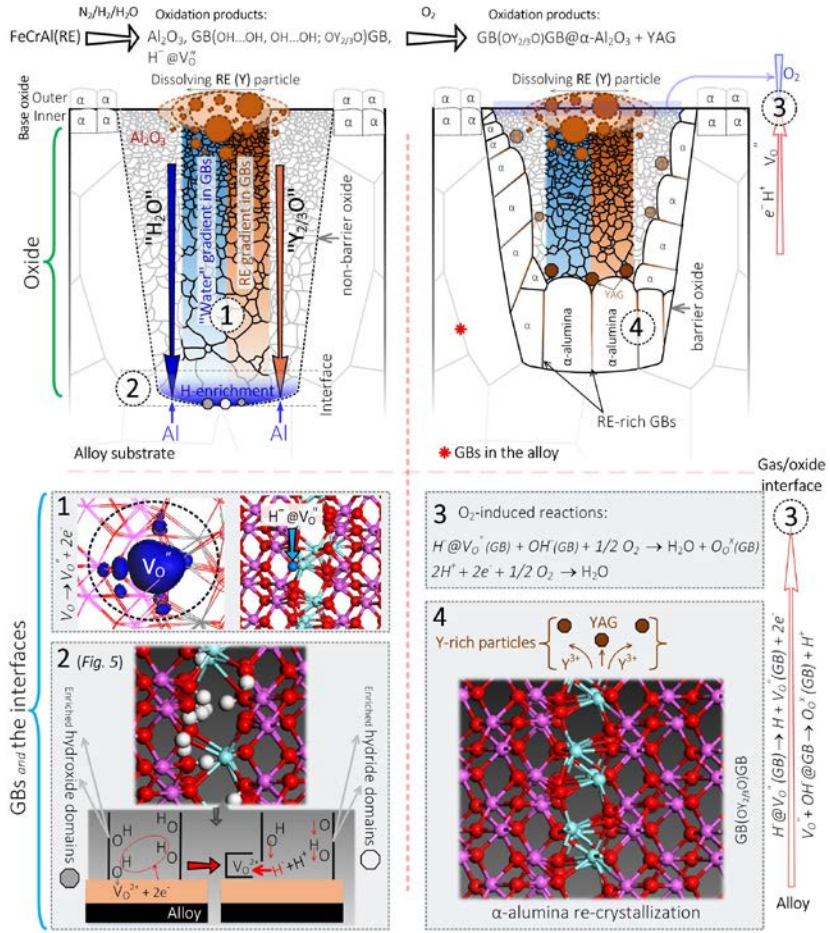
H(D) gradients measured by
SIMS show that ”water”
is *also transported across* the ”messy” alumina

Evidence for both H^+ and H^- in alumina



Using First – Principles calculations, we discovered a process by which H_2O and Y_2O_3 are *jointly transported* along the nanograin boundaries in the messy alumina.

Reaction between Al in the alloy and alumina creates oxygen ion vacancies in alumina that play a key part in the transport



Summary

What else…

Nitridation of FeCrAl

Oxid Met (2017) 87:321–332
DOI 10.1007/s11085-016-9703-3

ORIGINAL PAPER

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3rd element effect

RSC Advances

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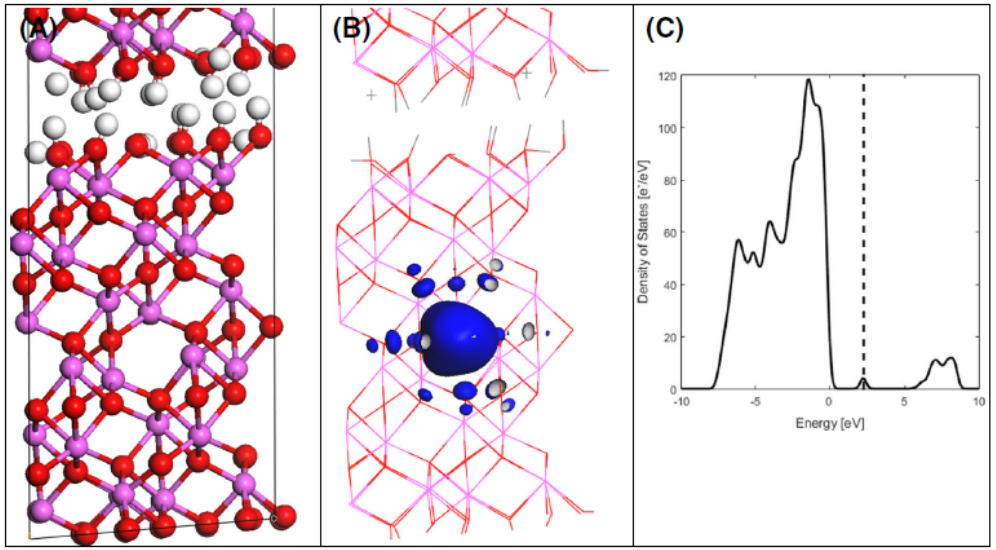
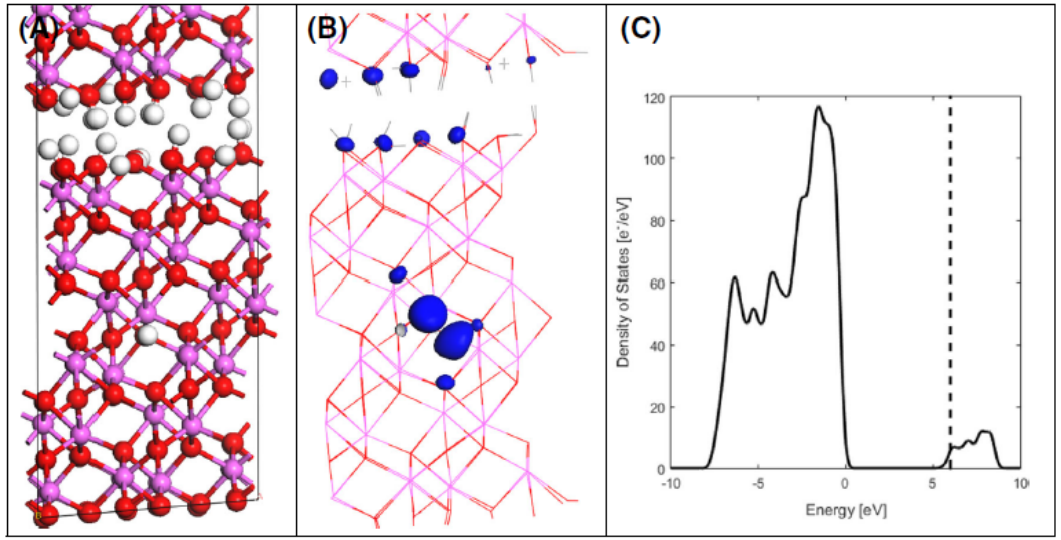
Received: 6 February 2018 / Published online: 28 August 2018

Theoretical study of hydrogen in Al2O3

What to do with the released hydrogen from the oxidation of aluminium by water



Oxygen vacancy in Al2O3 in the vicinity of a hydroxilated interphase creates accessible states at the Fermi level of alumina



Hydrogen can be deposited into the vacancy as hydride

$$\begin{cases} H_2O(g) + (OH)_{11}H@Al_2O_3(V_O)_2(slab) \rightarrow (OH)_{12}@Al_2O_3(H@V_O)_2(slab) \\ H_2O(g) + H^{\bullet}_{O,surface} + OH^{\bullet}_{O,surface} + 2V^{x}_{O} \rightarrow 2OH^{\bullet}_{O,surface} + 2H^{\prime}_{O} \end{cases} \quad \Delta E = -0.26\ eV$$

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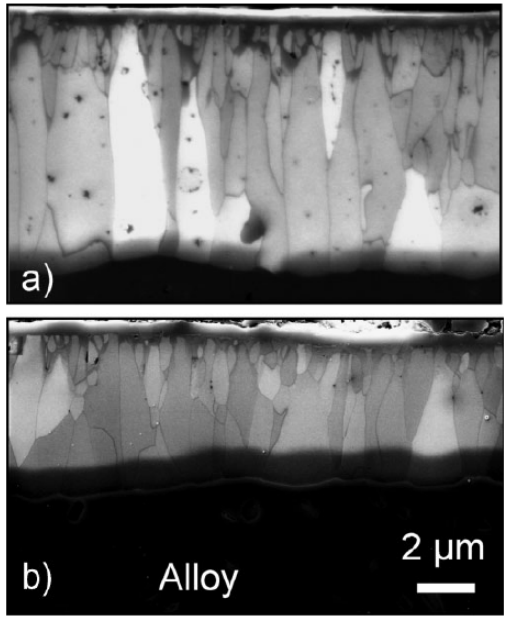
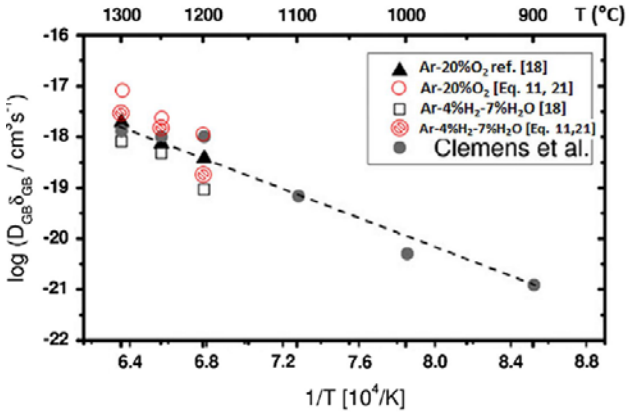
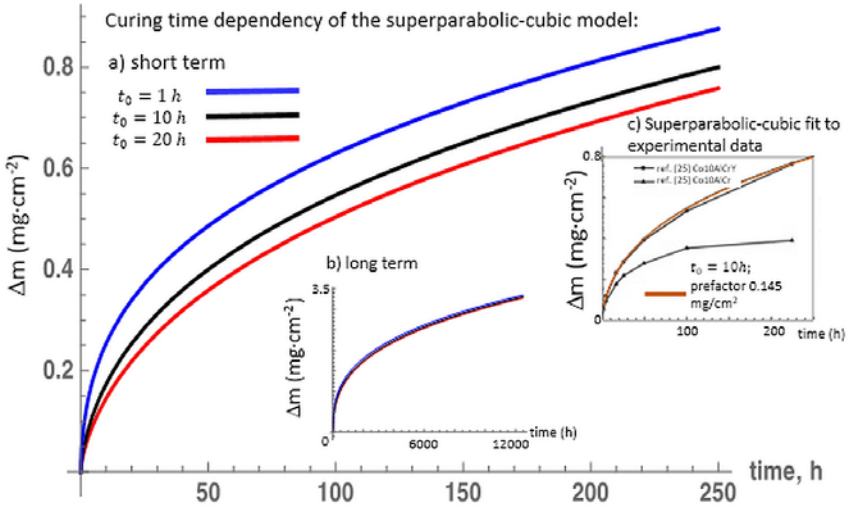
Grain boundary transport –
How is oxide growth changing with time dependent changing grain boundary density



Young, Naumenko, Niewolak, Wessel, Singheiser, and Quadakkers
Materials and Corrosion **2010**, 61, No. 10

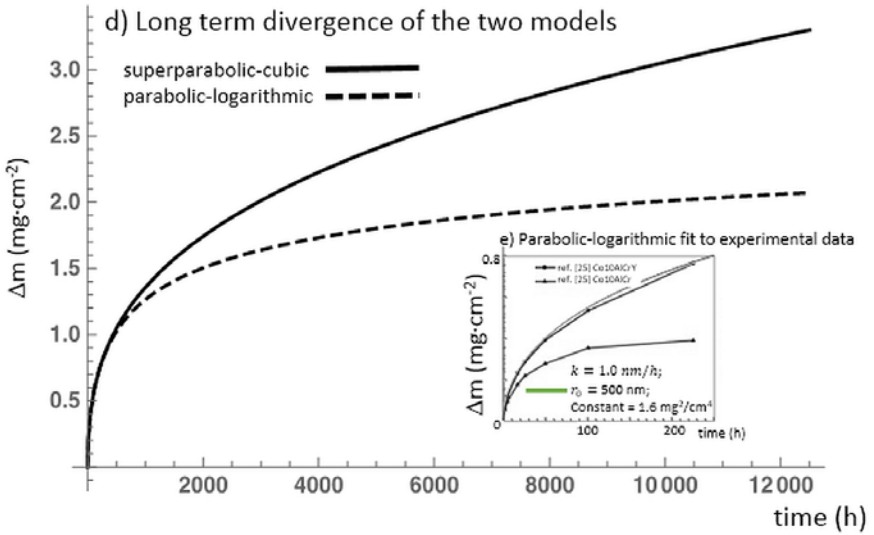


Reading and analysis of mass gain data with two mathematical models



Superparabolic – cubic model

$$X \approx k(grains\ coarsening)$$



Superparabolic – cubic model vs.
Parabolic-logarithmic model

$$X \neq k(grains\ coarsening)$$

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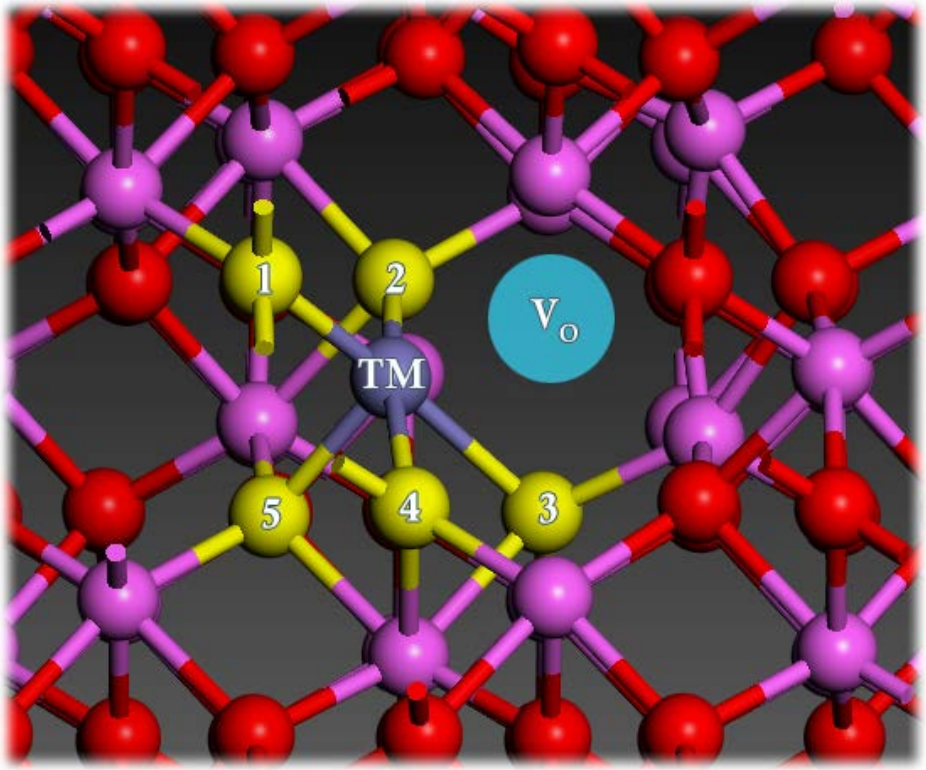
Third element effect – Crucial for the formation of a well protective α-alumina scale

- The impact of transition metal (TM) ions (Sc, Ti, V, Cr, Mn, Fe, Co, Ni) on:
  - the oxygen vacancy diffusion
  - electron transport in a-alumina was studied by employing DFT



- Electron mobility during oxidation along grain boundary vacancies is not limiting
- Oxygen vacancy diffusion is rate limiting during oxide growth
- 3d elements such as iron or chromium show different affinities to vacancies
- A high affinity to neutral vacancies can accumulate defects from the nucleating alumina at TM
- α-alumina formation can allocate its vacancies while growing at TM

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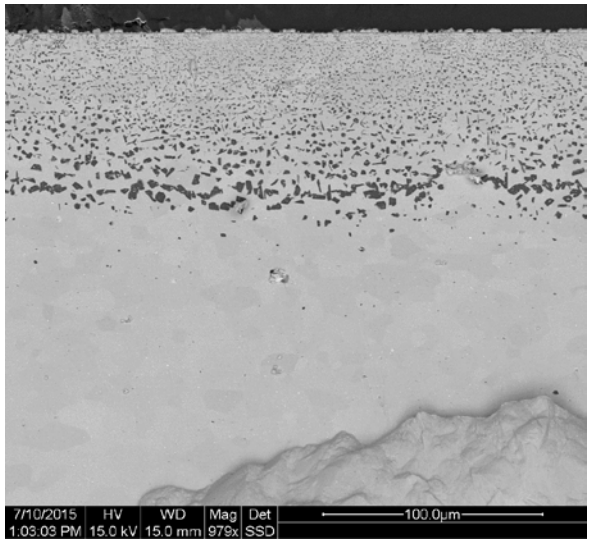
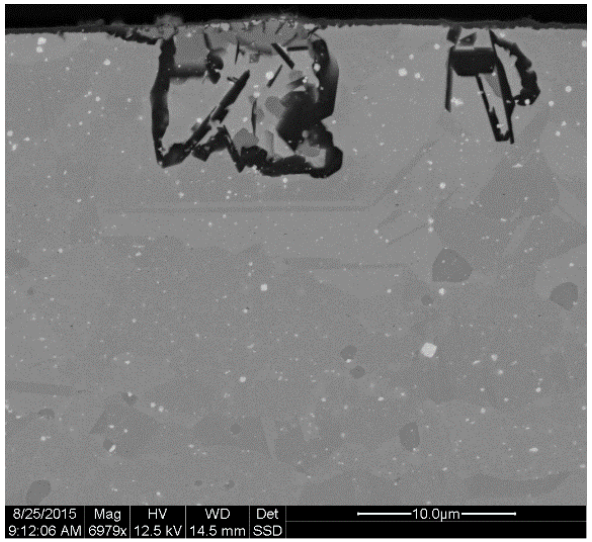
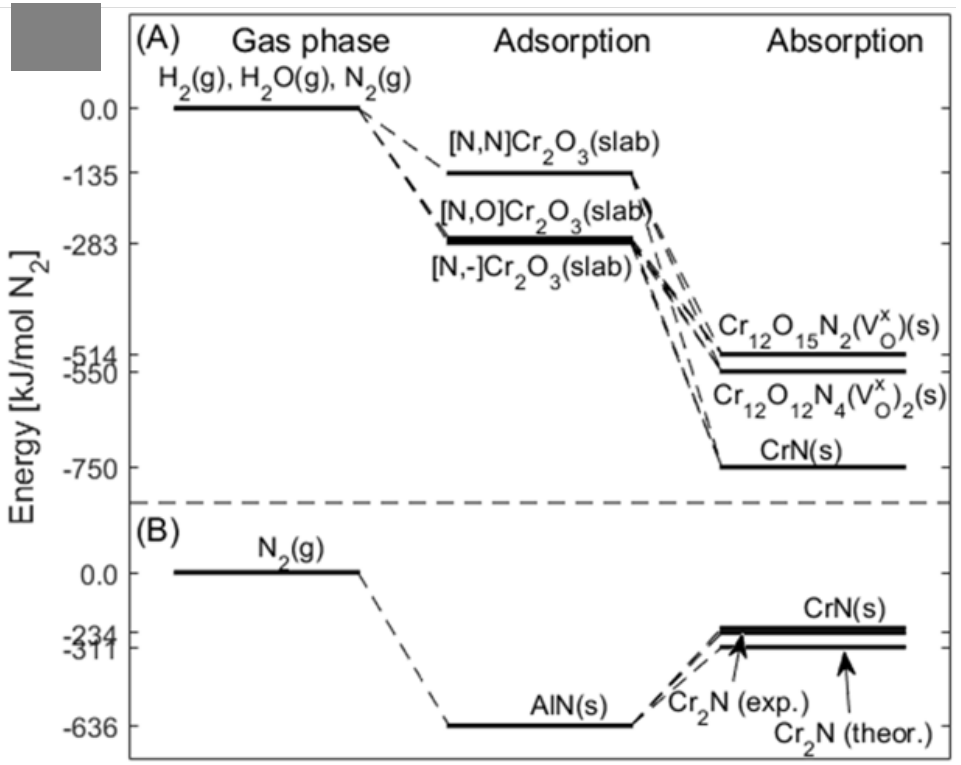
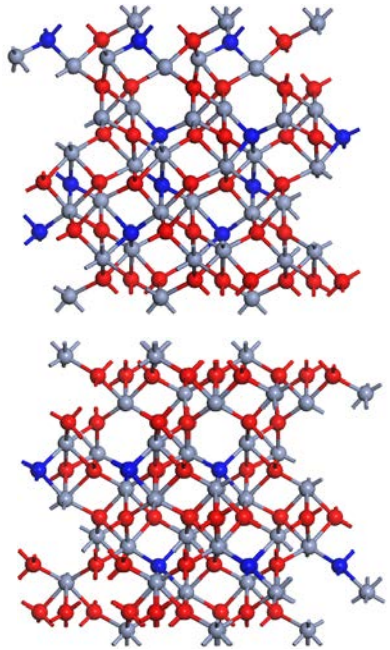




Nitridation in low pO2 environments on FeCrAls and FeNiCrAls

- Chromia renders surface defects in a continuous alumina scale:
- Chromia is nitrogen transparent under these conditions.





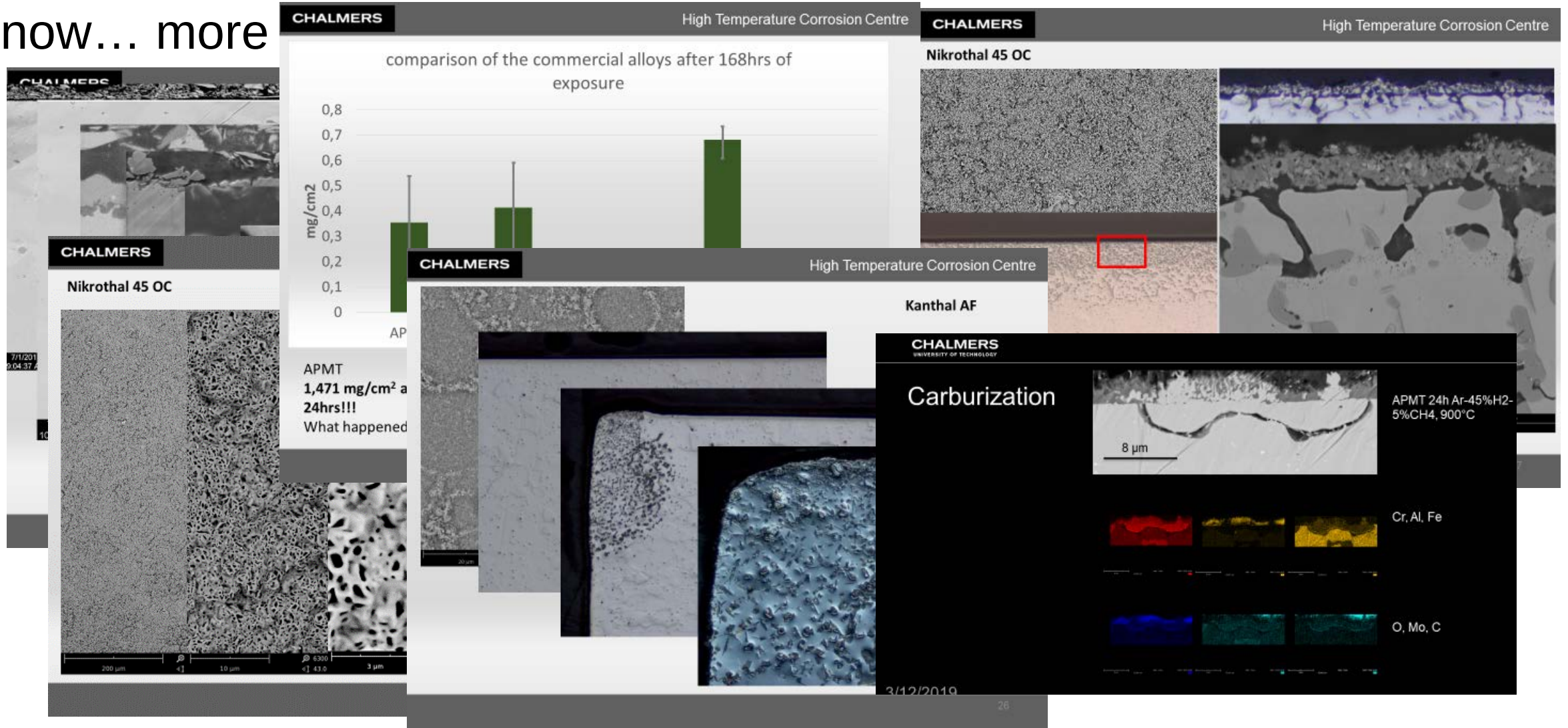
Acknowledgement for the Theoretical work via first principle (DFT):

Prof. Itai Panas

Ph.D. candidate Vedad Babic

!!! Ph.D. Thesis Defense – 29th May 2019, Chalmers !!!

Project output is not yet finished and needs to be put into context of the found models and mechanisms (three manuscripts are in the pipeline now… more



Ongoing laboratory work will constantly improve our understanding

Loli Paz and Tommy Sand 2019 -

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

Exposure settings

Materials

Alumina formers:
- Kanthal APMT
- Kanthal AF
- Nikrothal PM58
- Alloy 197
- Alloy 198

Chromia formers:
- 253MA (21Cr, 11Ni, Si, Ce)
- 310 (25Cr, 20Ni)
- San31 HT (20Cr, 30Ni)
- 353MA (25Cr, 35Ni, Si, Ce)
- San70 (16Cr, 70Ni)

Temperatures

800°C
900°C
1100°C

Time

1 week
4 weeks

Thank you for your kind attention

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