CHALMERS
UNIVERSITY OF TECHNOLOGY

Critical corrosion phenomena in combustion of biomass and waste in combined heat and power boilers

A. Persdotter, A. Olivas, A. Talus, I. Hanif, J-E. Svensson, J. Liske, J. ***Eklund, J. Photer,*** L-G. Johansson, L. Paz, R. Norling, S. Andersson, S. Bigdeli, ***T. Jonsson***, V. Asokan

Project aim:

carry out research on high temperature corrosion during ***combustion*** *of* ***biomass and waste*** *in order to* ***help solve a number of corrosion problems*** *which restrict the development of* ***more energy efficient processes*** *and technologies.*

increasing the ***predictability*** *of corrosion attacks and* ***component life.***

Energy policy targets for Sweden

100 percent renewable electricity production by 2040	No emissions of greenhouse gases by 2045	50 percent more efficient use of energy in 2030, compared to 2005

Three pillars for Sweden's energy policy

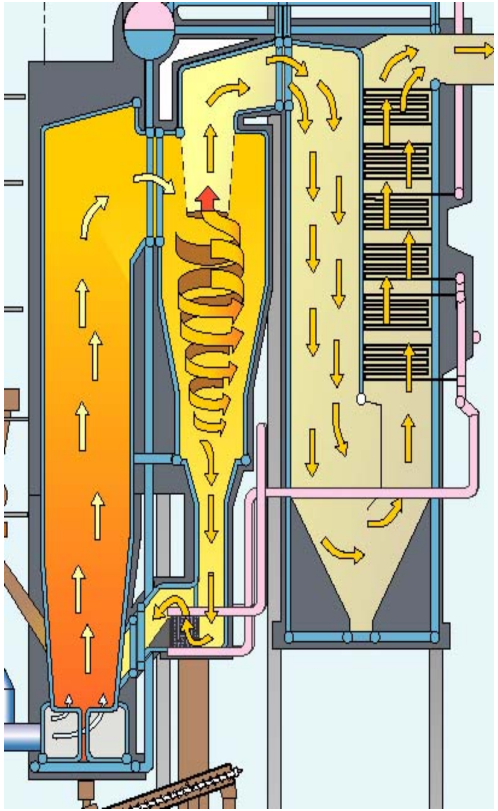
Swedish Energy Agency

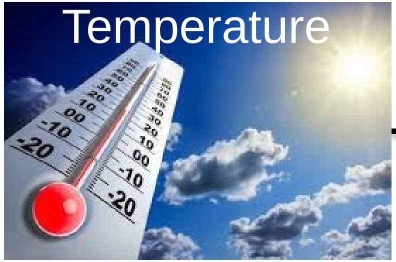
The future role of Bioenergy

More total Biomass utilization

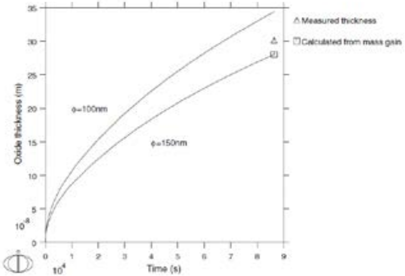
- Base load power
- Local small scale CHP
- Important complement to variable electricity sources

Swedish Energy Agency

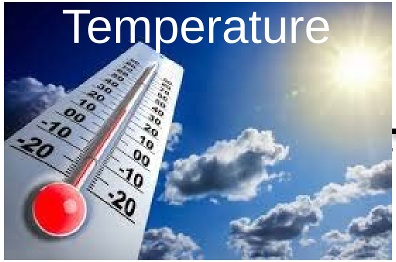




Corrosion rate



Life time of component



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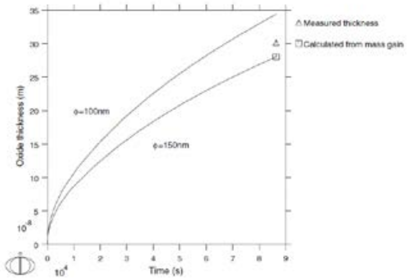
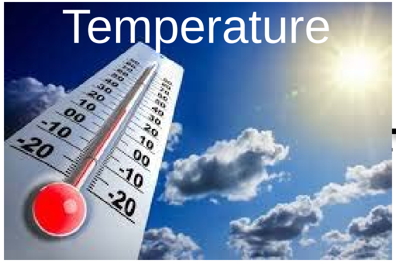
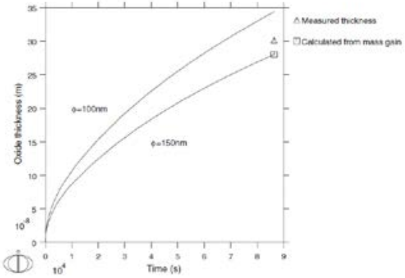
Corrosion rate



Life time of component

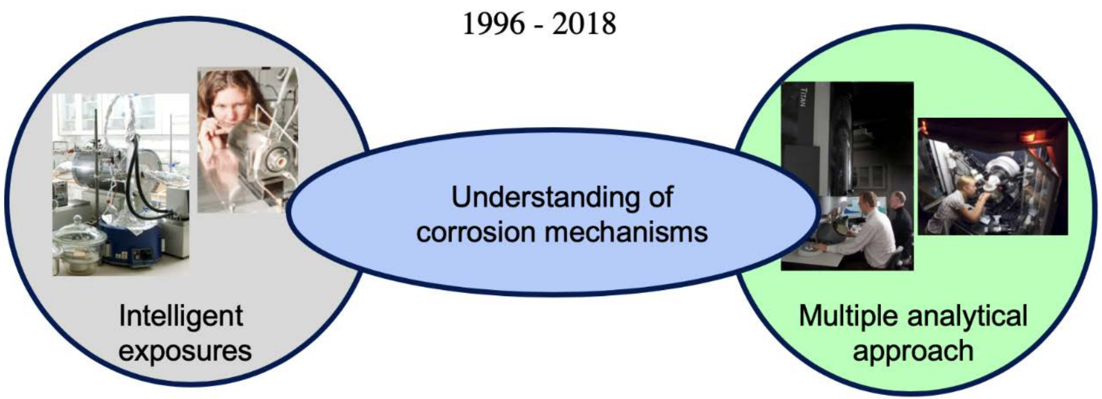


Corrosion rate

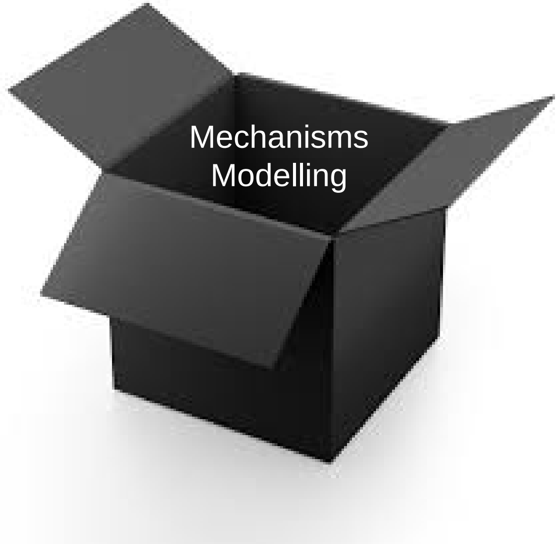


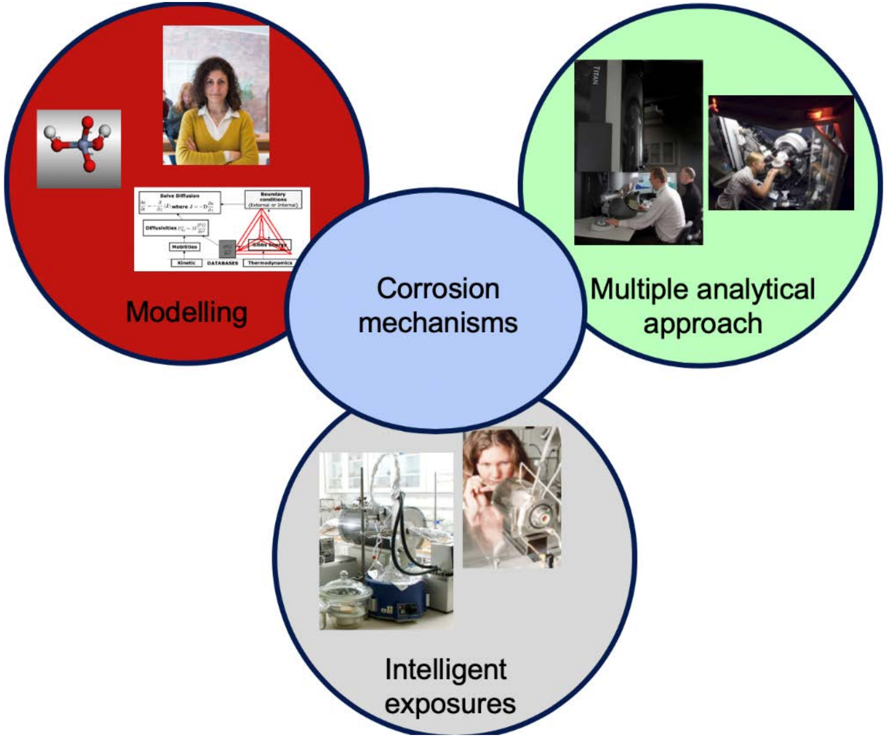
Life time of component


Mechanisms

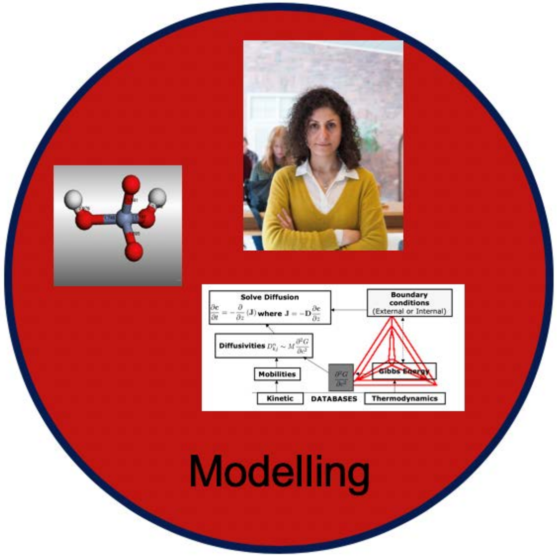

1996 - 2018
Intelligent exposures
Understanding of corrosion mechanisms
Multiple analytical approach

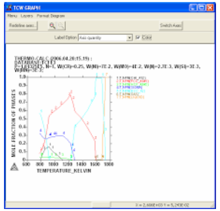
New approach!





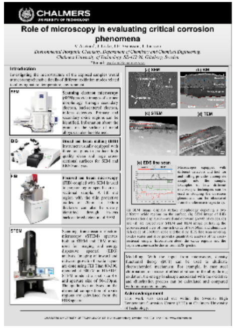
New approach!



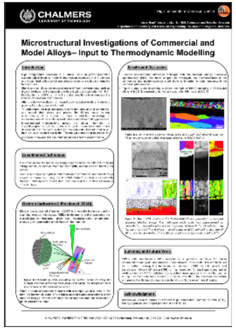


Sedi

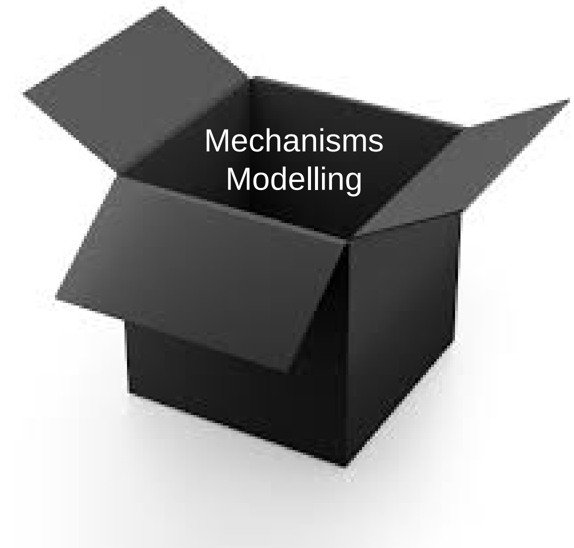
- Thermodynamic modelling
- Model alloys – systematic studies of different oxidation modes
- Microscopy – mechanisms AND input to modelling



Vijay

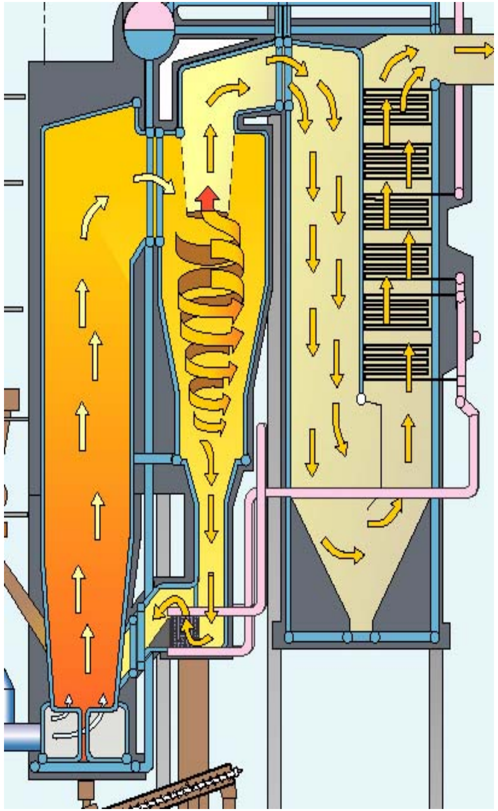


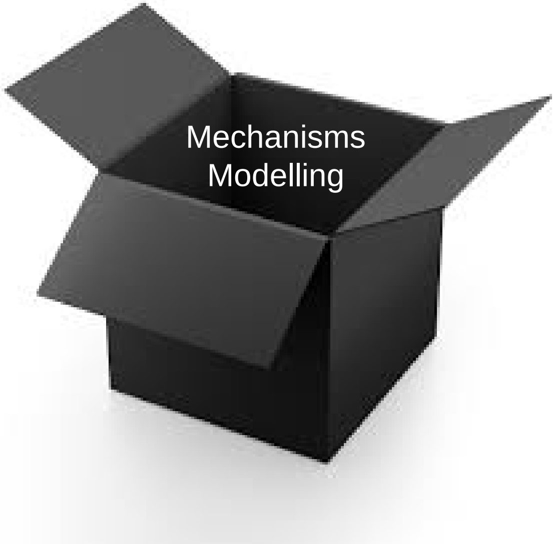
Imran



Temperature

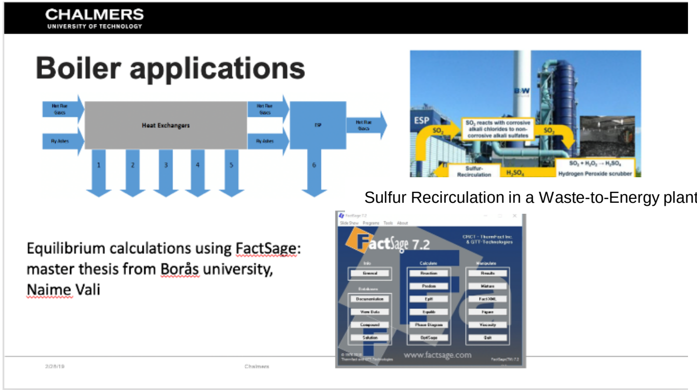
Model environment

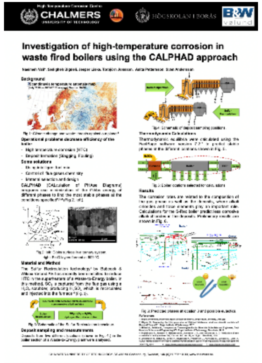


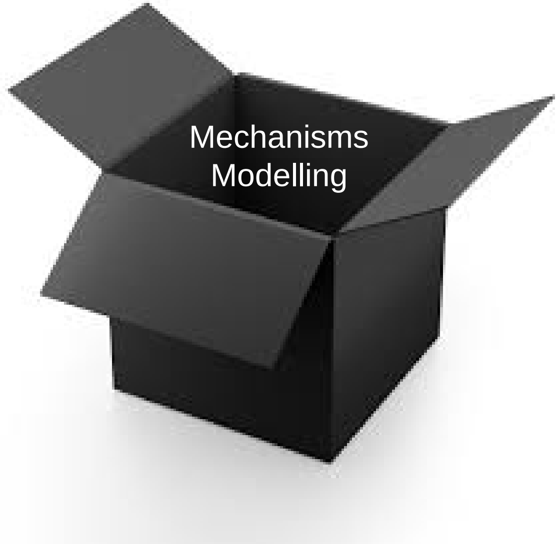


Temperature

Model environment



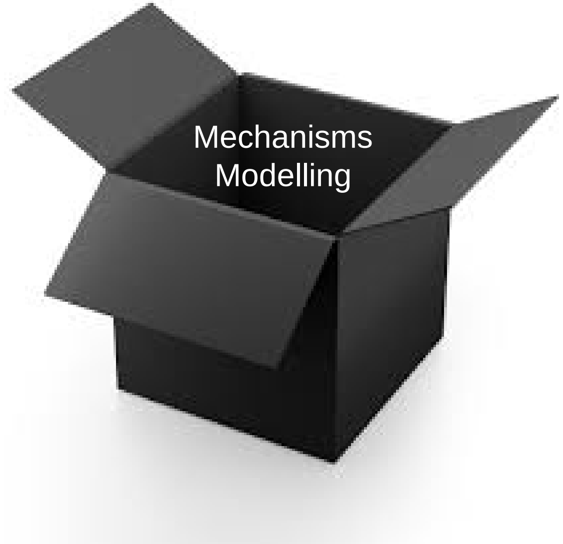




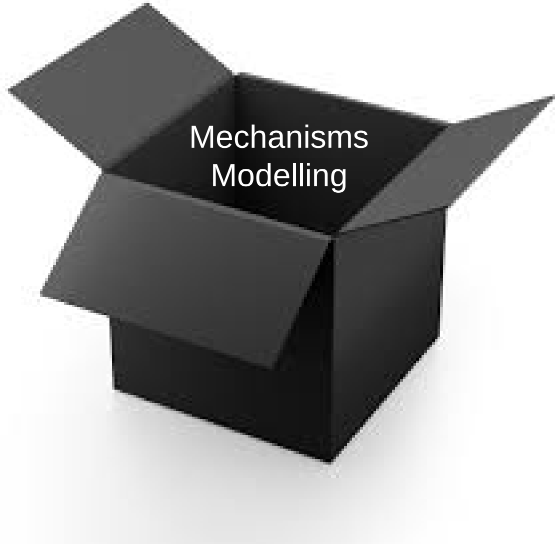
Temperature

Environment

Material



Temperature Environment	Low alloyed steels	Iron oxide
	Stainless steels	Chromium oxide
	FeCrAl alloys	Alumina



Temperature

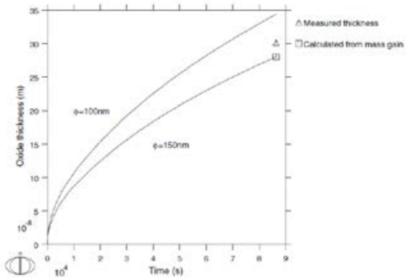
Environment

Material

Oxidation mode

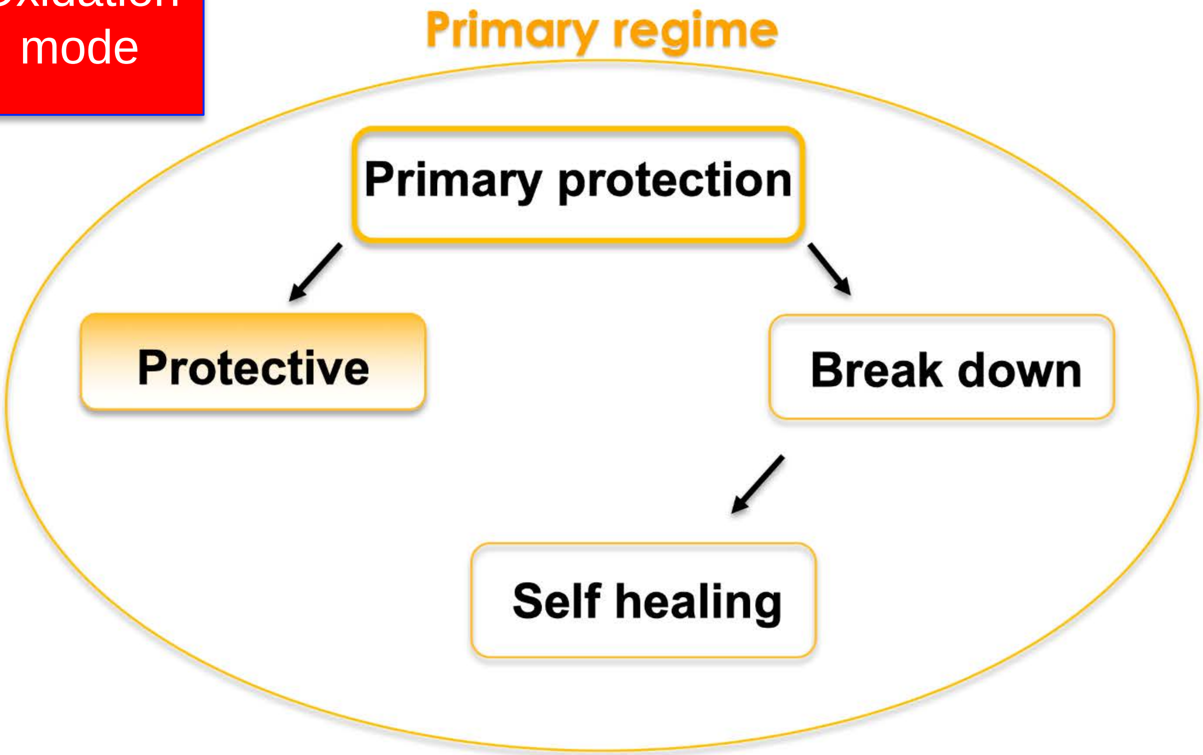
→

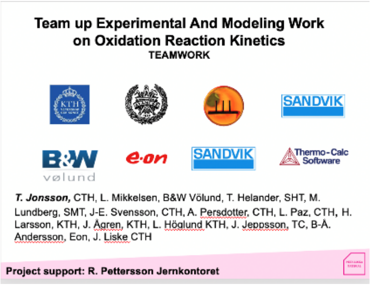
Corrosion rate



Life time of component

Oxidation mode

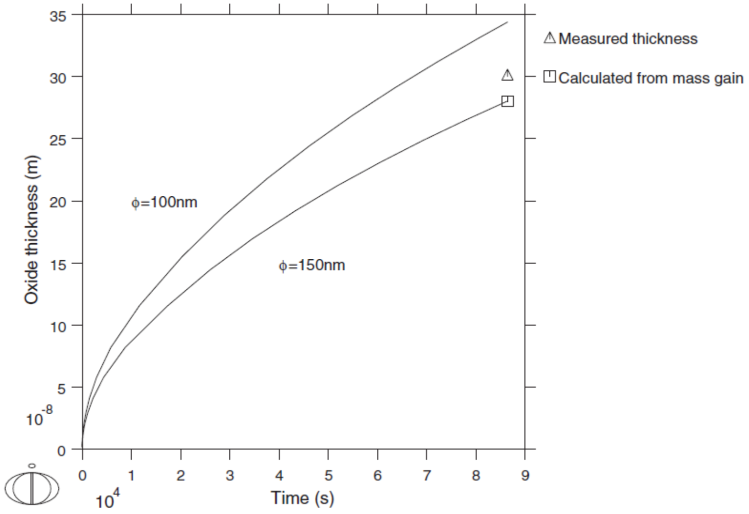



Team up Experimental And Modeling Work on Oxidation Reaction Kinetics
TEAMWORK

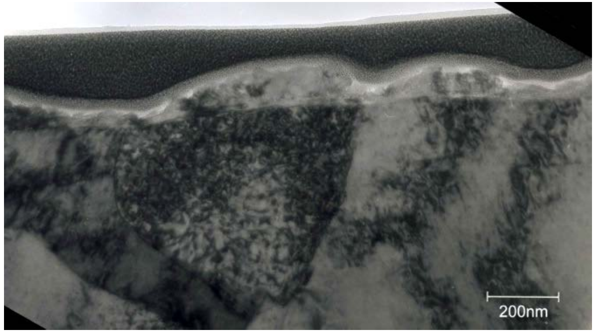
T. Jonsson, CTH, L. Mikkelsen, B&W Völund, T. Helander, SHT, M. Lundberg, SMT, J-E. Svensson, CTH, A. Persdotter, CTH, L. Paz, CTH, H. Larsson, KTH, J. Ågren, KTH, L. Höglund KTH, J. Jeppsson, TC, B-Å. Andersson, Eon, J. Liske CTH

Project support: R. Pettersson Jernkontoret

Primary protection:
Stainless steels – FeCrAl alloys



Cr oxidation at 600 °C



Ref: Jonsson, T., et al. 2013.

References:
Hallström, S., et al., 2013.
Pujilaksono, B., et al., 2011.

Primary regime

Primary protection

« Tertiary » regime

Protective

?

Break down

Secondary regime

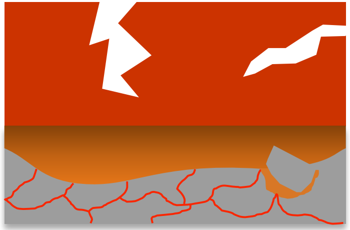
?

Self healing ?

Secondary protection

Protective

Break down



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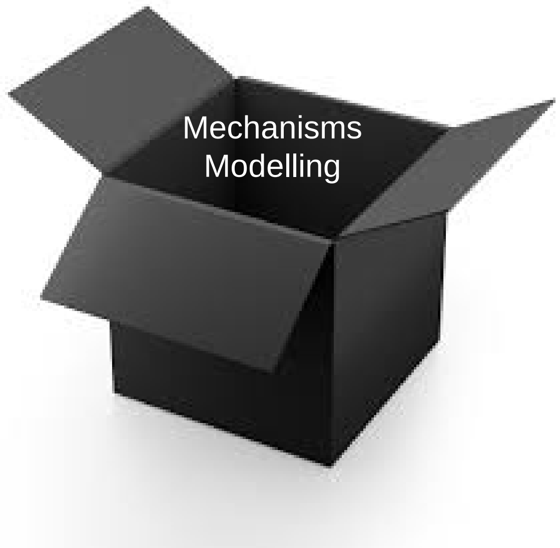


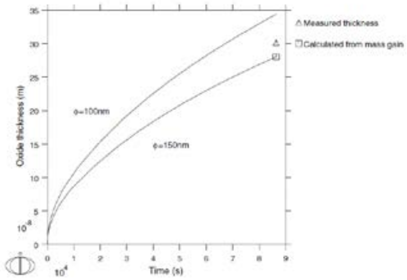
Temperature

Environment

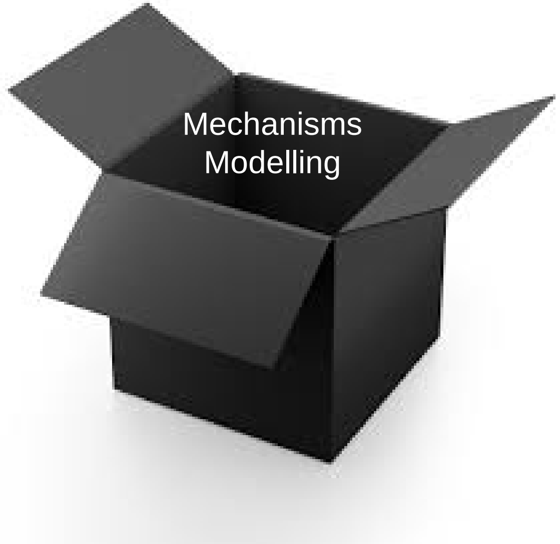
Material

Oxidation mode

Corrosion rate



Life time of component



Temperature

Environment

Material

√ Primary

√? Secondary

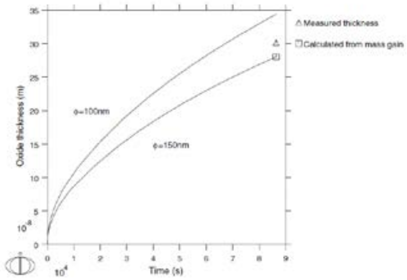
√? Tertiary

?

?

→

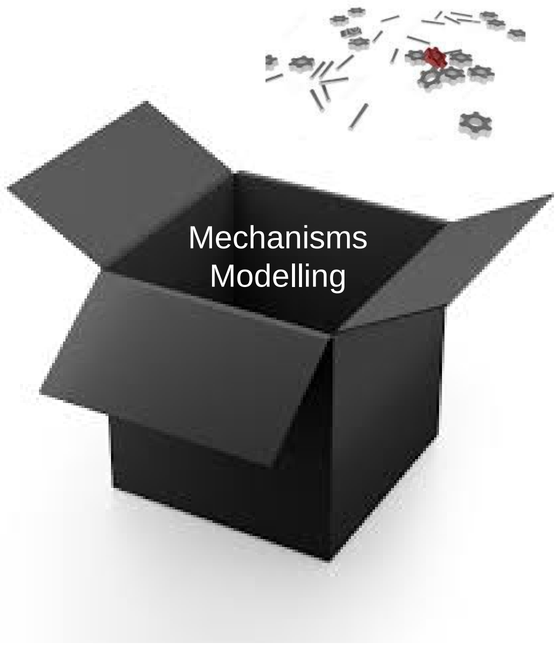
Corrosion rate



Life time of component

How to model high temperature corrosion
The effect of crack formation
The effect of alloying elements
KCl on the effect of secondary protection & GB’s

Sedi Bigdeli
Amanda Persdotter
Johan Eklund
Julien Photer



√
Primary

√?
Secondary

√?
Tertiary

?

?

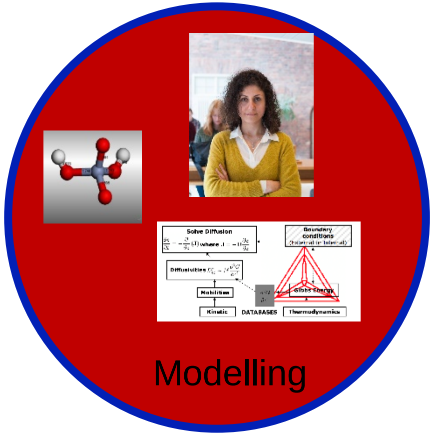
Calphad: CALculation of PHase Diagrams

Calphad software minimize the total Gibbs energy for the system under the defined conditions to find the equilibrium.

They collects thermodynamic information from databases which contain Gibbs energy for each phase.

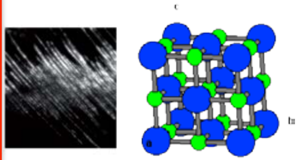
There are different Calphad-based software:
Thermo-Calc/Dictra/TC-prisma, Factsage, Pandat, etc.

Background - examples

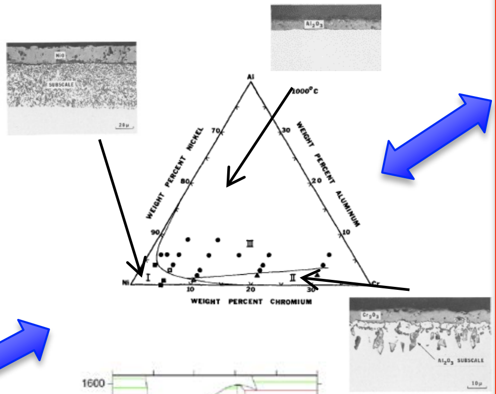


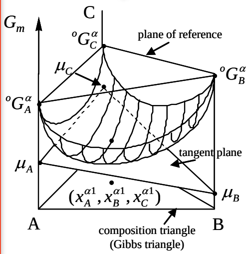
Calphad calculations can be used for both ***analysis*** of the problem/results and ***predict***/design materials properties!

Work towards a lifetime prediction model

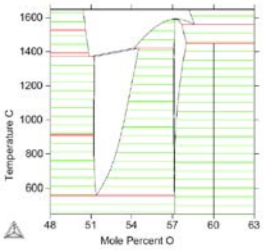


Atomistic simulations & experimental data

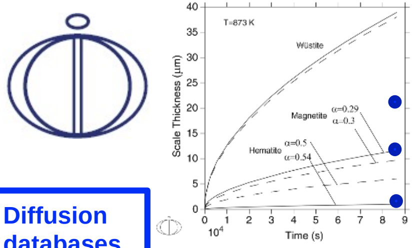




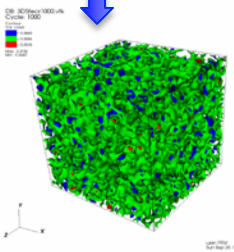
Phenomenological models - Calphad



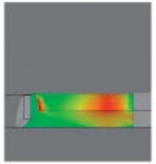
Thermodynamic databases



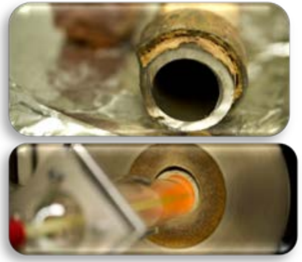
Diffusion databases

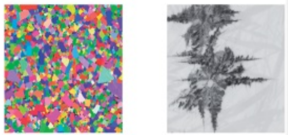


Phase-field simulation



Finite element simulations



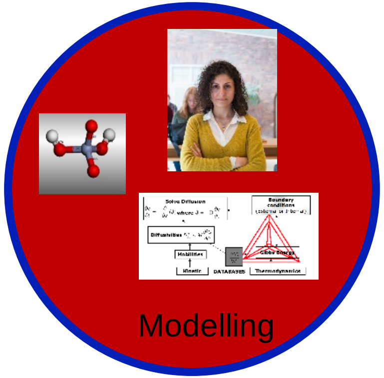


Lab exposures & microscopy

Plant

Developed tools in Teamwork project

We created a strong computational platform for thermodynamic/kinetic modelling of high temperature oxidation.

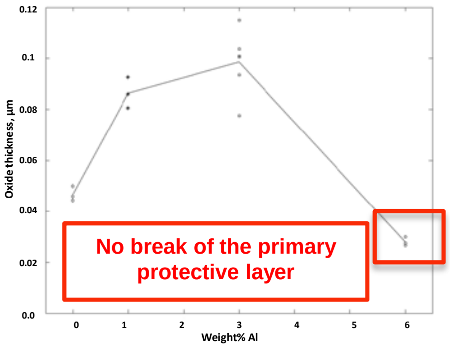


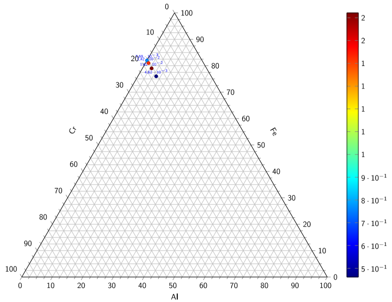
Our current tools can be used in different ways:

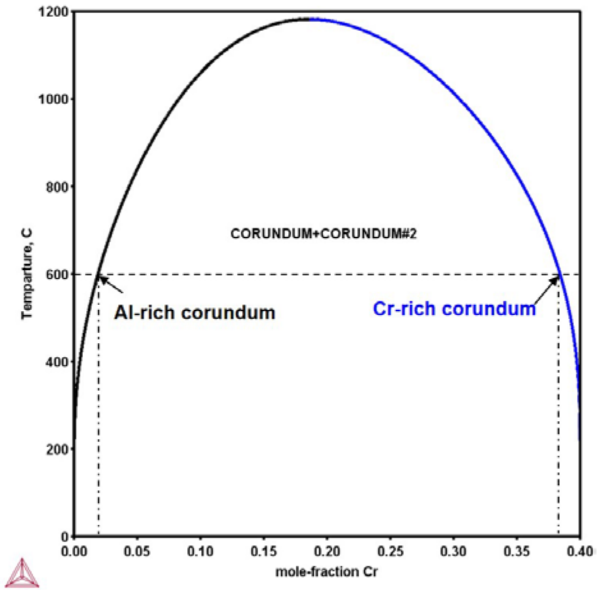
Equilibrium calculations to understand microstructure

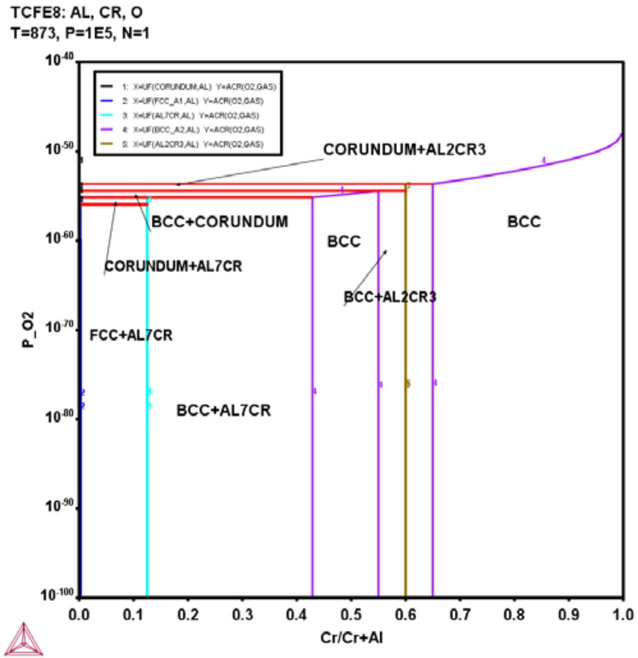
Example: understating the nature of primary protective layer in FeCrAl model alloys using Thermo-Calc

Equilibrium calculation in Cr-Al-O system





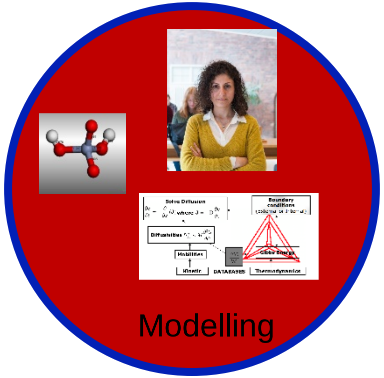




Developed tools in Teamwork project

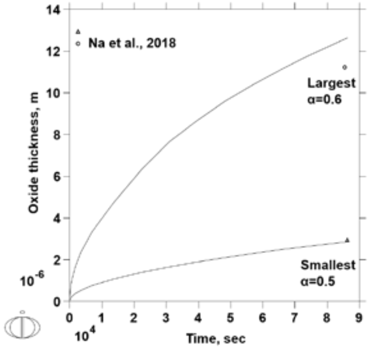
We created a strong computational platform for thermodynamic/kinetic modelling of high temperature oxidation.

Example: calculate and predict the oxide thickness of primary and secondary protective layers using Dictra

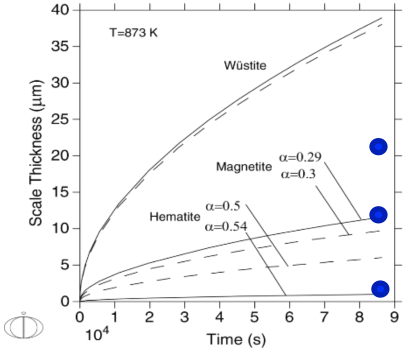


Our current tools can be used in different ways:

Diffusion simulations to predict the phase transformation's kinetic and products,

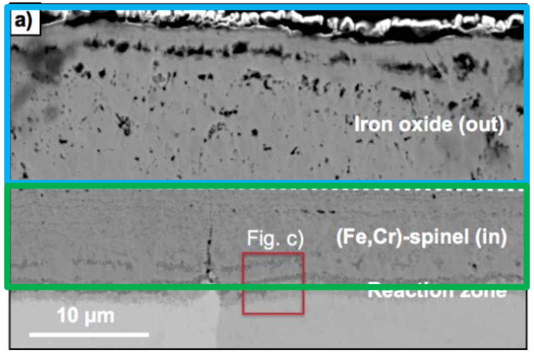


Primary protection



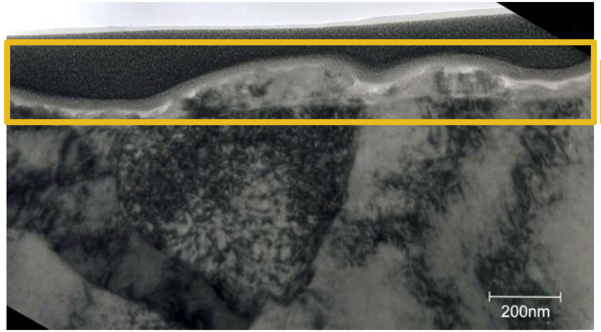
Secondary protection

Modelling strategy - Primary and secondary protection FeCrAl alloys

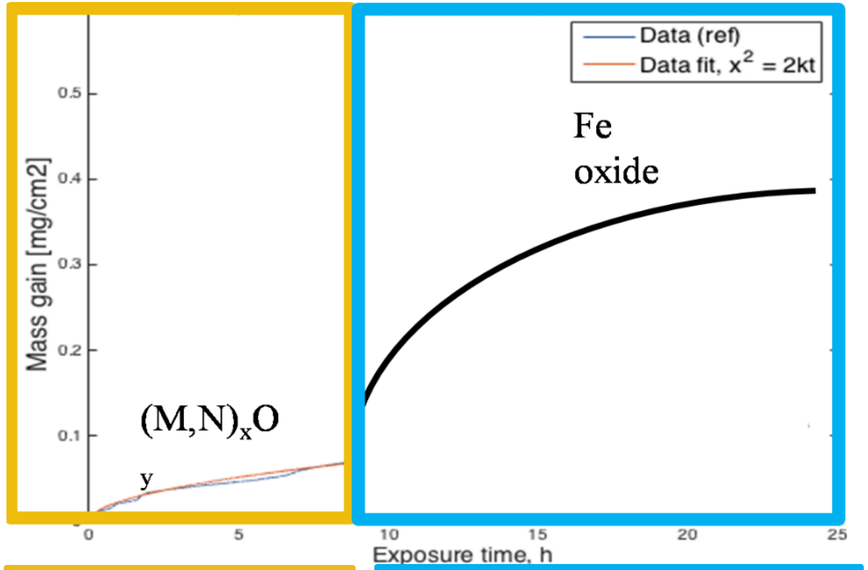


Secondary protection
Fe oxidation

Secondary protection
Inward spinel



Primary protection

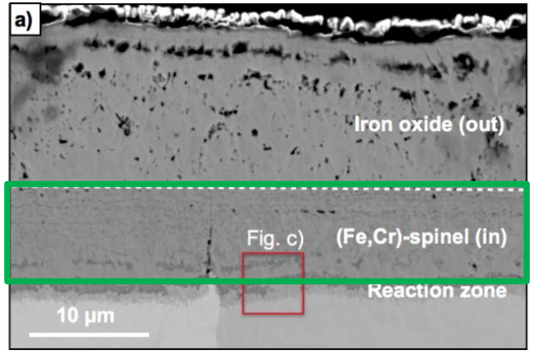


Primary protection

Secondary protection

Ref: Jonsson, T., et al. 2013.

Secondary protection in FeCrAl alloys



Inward spinel

Developed tools in Teamwork project

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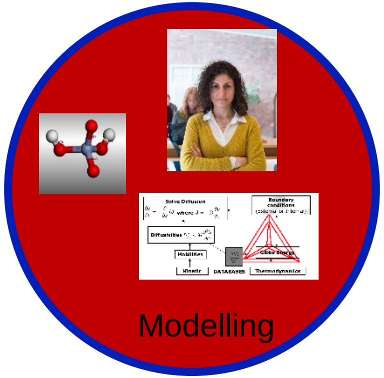
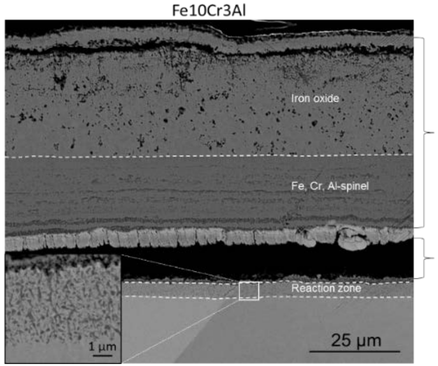


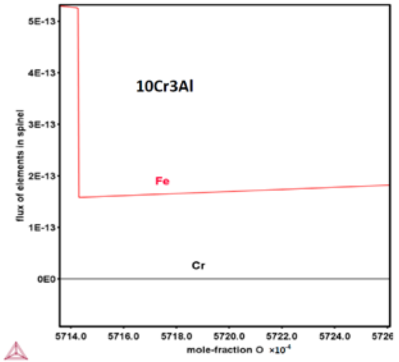
Our current tools can be used in different ways:

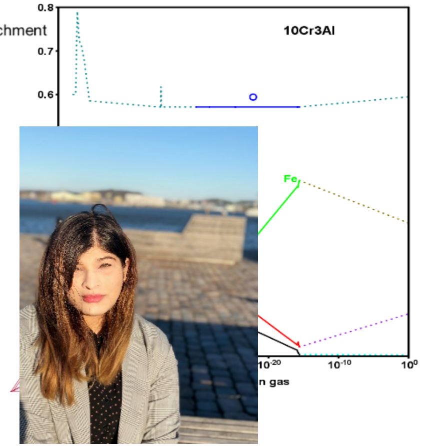
Example: calculate possible phases and flux of different species to explain the inward spinel formation in secondary protection using Thermo-Calc

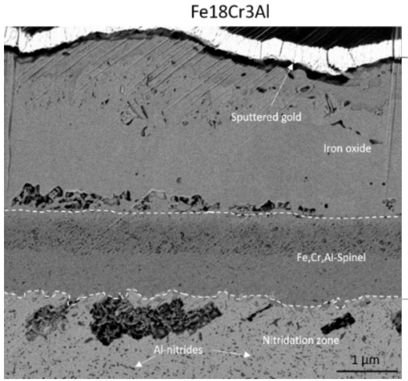
Equilibrium calculations to predict possible phases and explain the process,

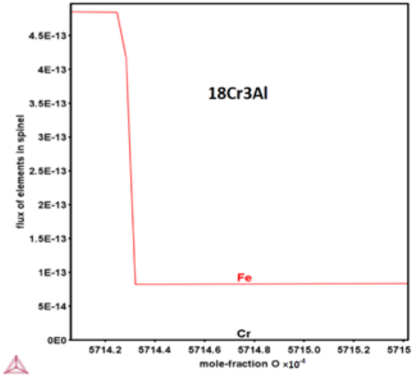
Equilibrium calculations for inward spinel

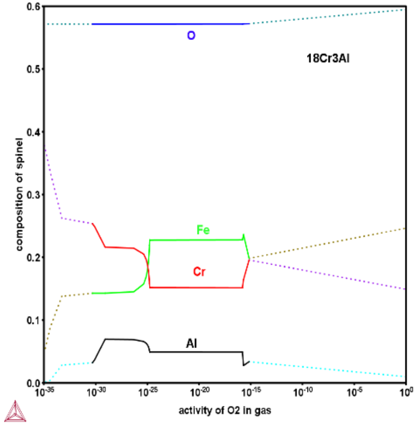








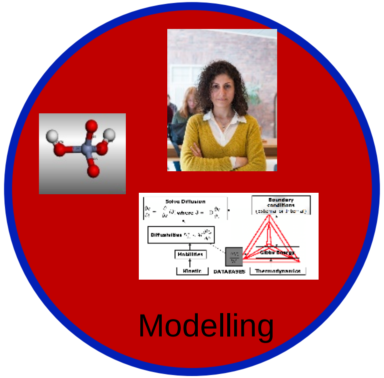




Equilibrium calculations for all model alloys:
master thesis Kiran Mayee;
Poster today!

Developed tools in Teamwork project

We created a strong computational platform for thermodynamic/kinetic modelling of high temperature oxidation.

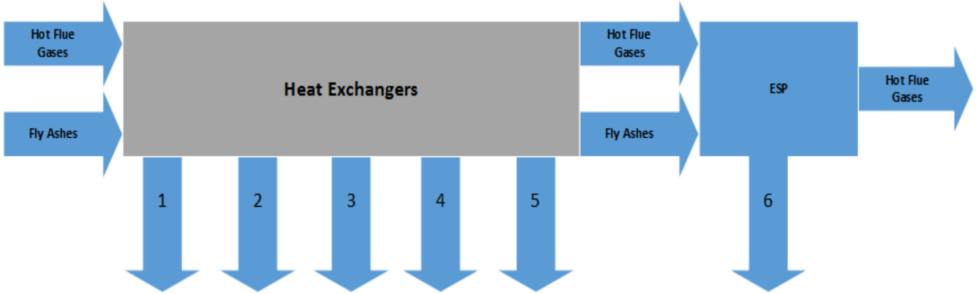


Our current tools can be used in different ways:

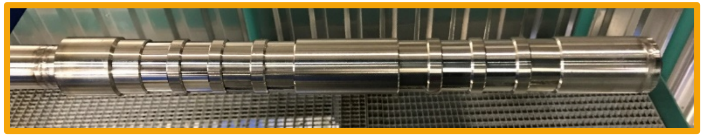
Example: calculate possible phases formed during real processes in boilers using FactSage

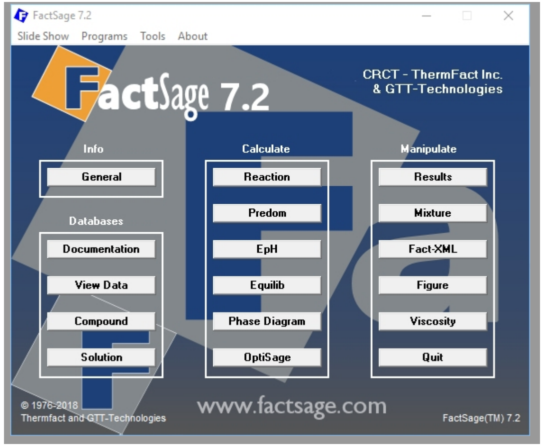
Equilibrium calculations to predict possible phases and explain the process,

Boiler applications



sulphur recirculation in a bio plant





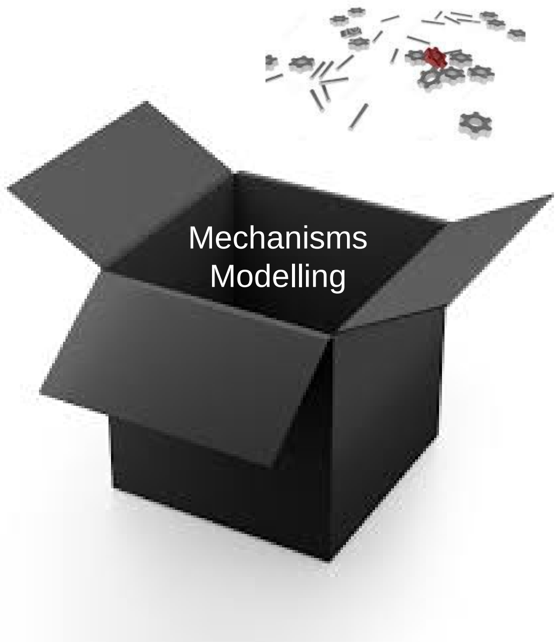
Equilibrium calculations using FactSage: master thesis from Borås university, Naime Vali, poster today!

Conclusions

- We can use computational thermodynamics to predict and understand the oxidation.
- We can also use our experimental knowledge to improve efficiency of our modelling.

We can build a strong bridge between experiment and modelling for the complicated phenomenon of multicomponent oxidation to design new materials and work towards predicting service life!

How to model high temperature corrosion — *Sedi Bigdeli*
The effect of crack formation — ***Amanda Persdotter***
The effect of alloying elements — *Johan Eklund*
KCl on the effect of secondary protection & GB's — *Julien Photer*



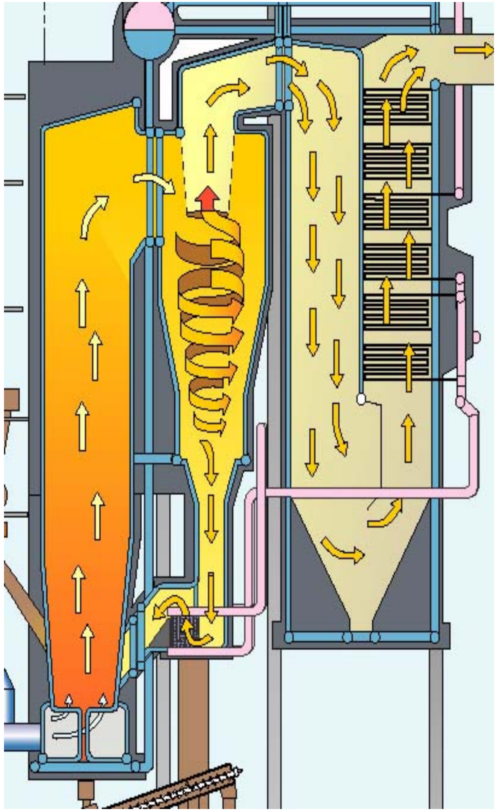
Primary ✓

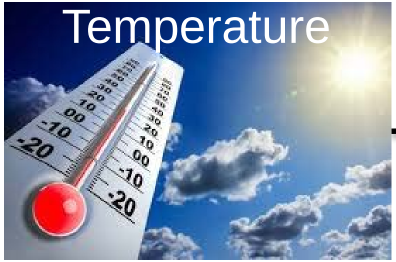
Secondary ✓?

Tertiary ✓?

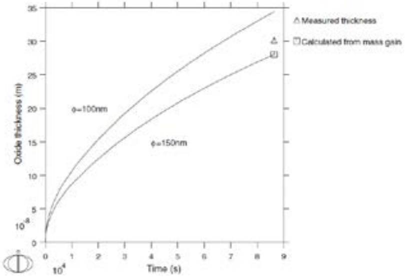
?

?

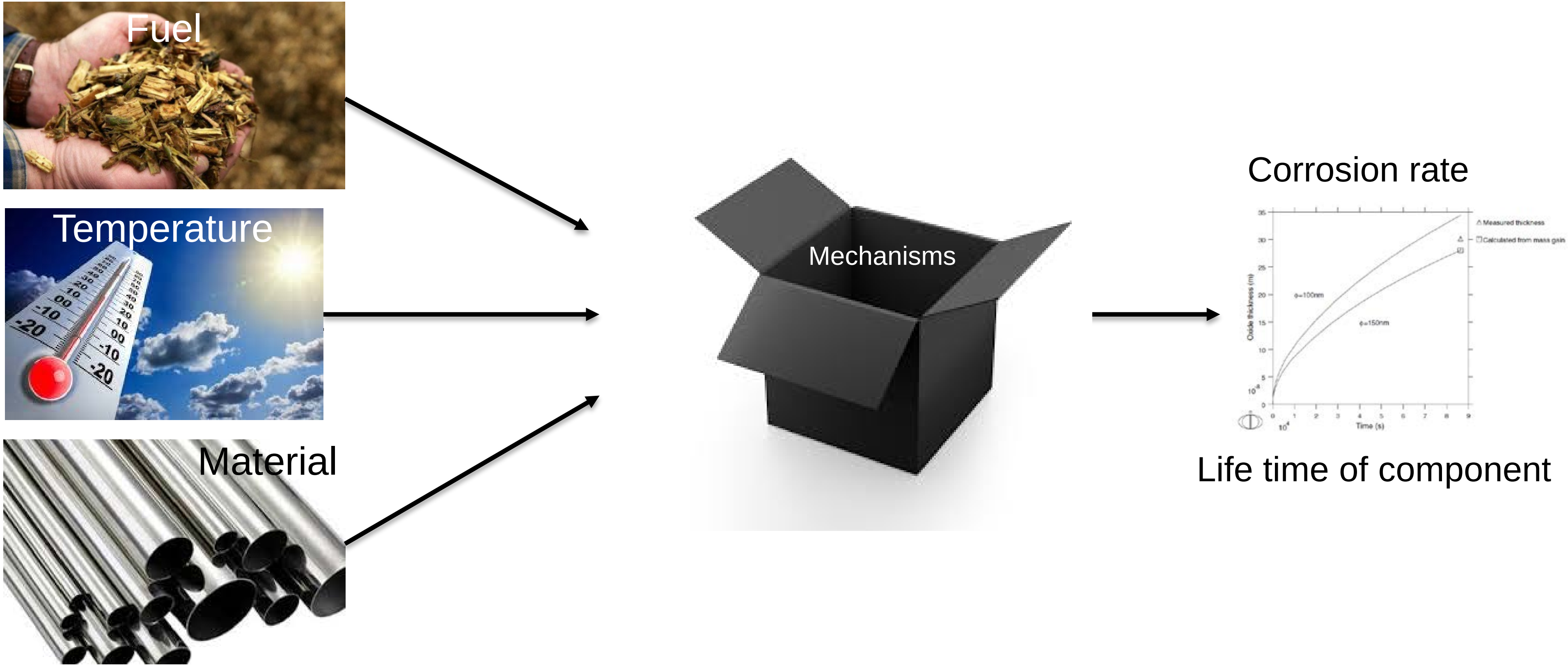




Corrosion rate



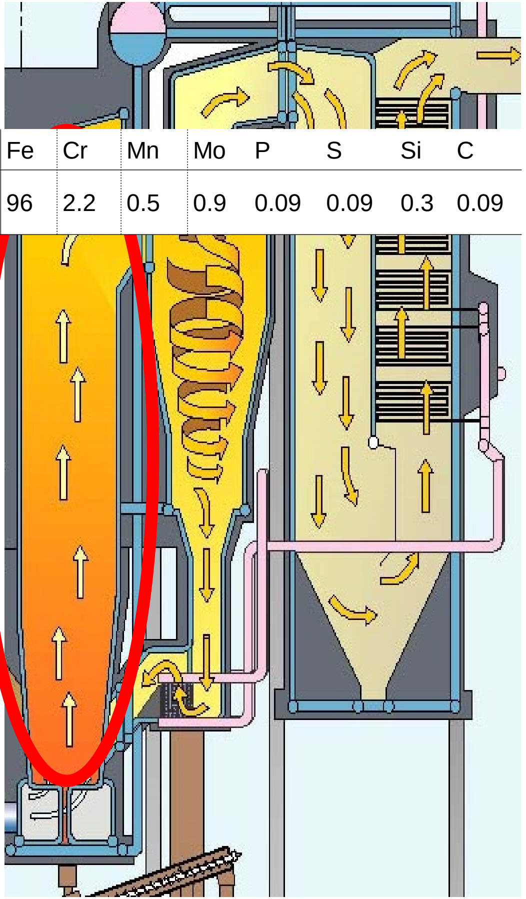
Life time of component


Fuel
Temperature
Material
Mechanisms
Corrosion rate
Measured thickness
Calculated from mass gain
Time (s)
Life time of component

Waterwall corrosion

Conditions:

- Low alloyed steels: **Fe-2.25Cr-1Mo (T22)**
- Relatively low temperatures (< **400 °C**)
- High levels of:
  - chlorine (**KCl**, HCl)
  - alkali (K, Na)
  - heavy metals (Pb, Zn)

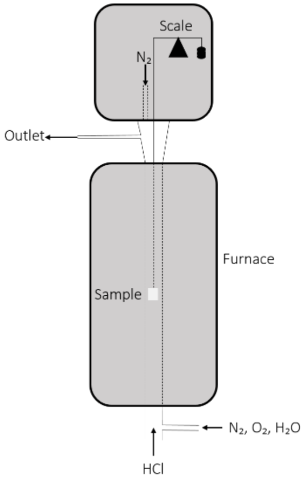


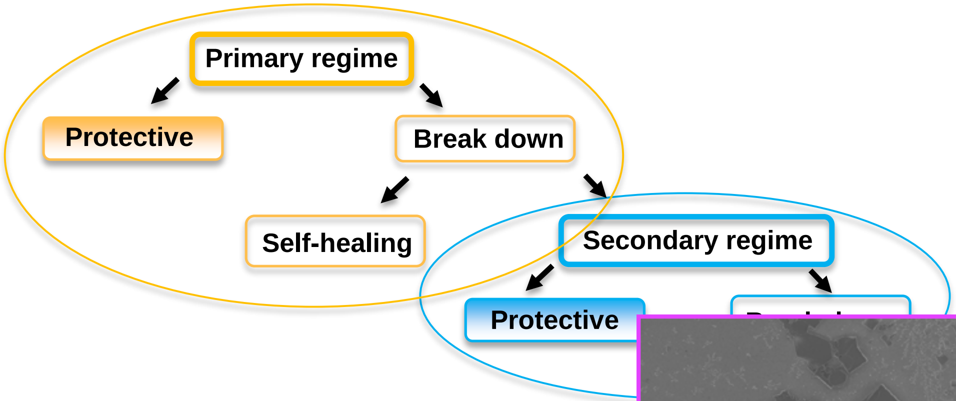
T22	Fe	Cr	Mn	Mo	P	S	Si	C
at%	96	2.2	0.5	0.9	0.09	0.09	0.3	0.09

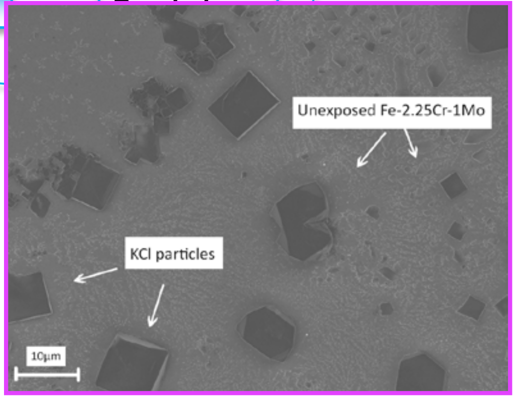
How is this studied?

Mass gain study

- TGA (kinetics)
- Initiation(24 hours)





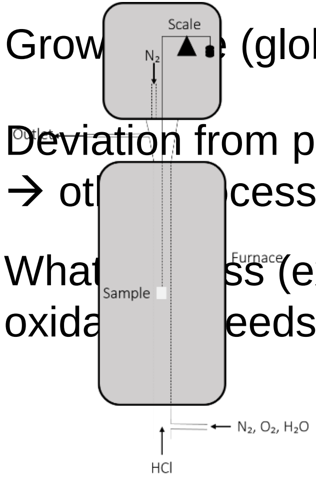


Primary (Ref.): 5% O_2 + 20% H_2O + N_2

Secondary (KCl): Ref. + 0.1 mg/cm^2 KCl(s)

Mass gain study

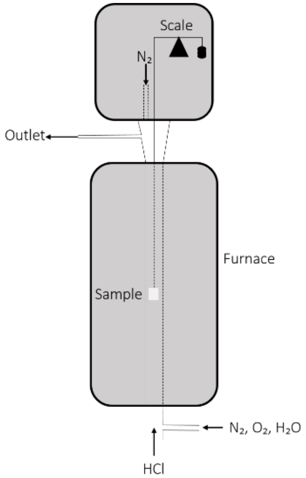
- Parabolic growth
  → diffusion controlled
- Grow e (global k_p?)
- Deviation from parabolic
  → ot cesses (local k_p)
- What ss (except for
  oxida eeds to be modelled?



How is this studied?

Mass gain study

- TGA (kinetics)
- Initiation(24 hours)



Microstructural investigation

BIB

FIB

XRD

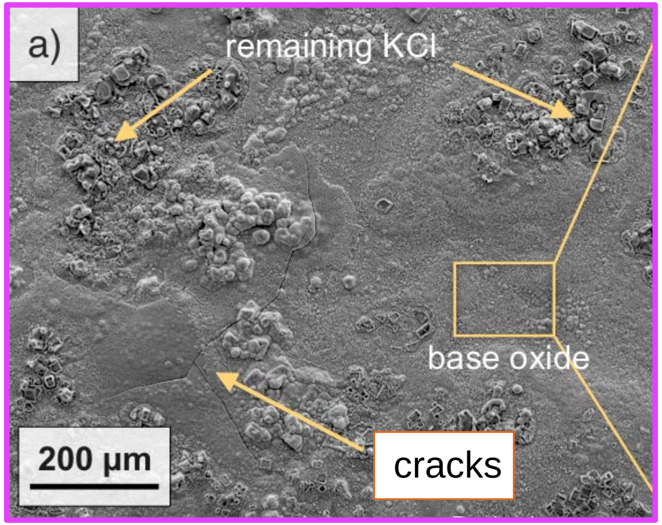
TKD

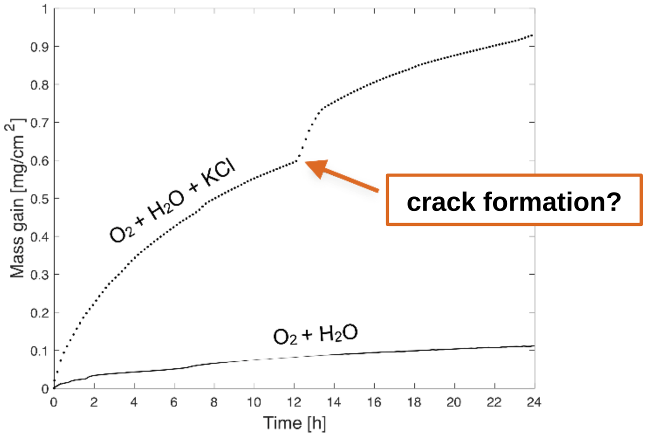
EDX

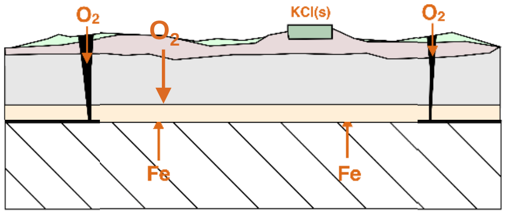
SEM

TEM

What causes the transition?

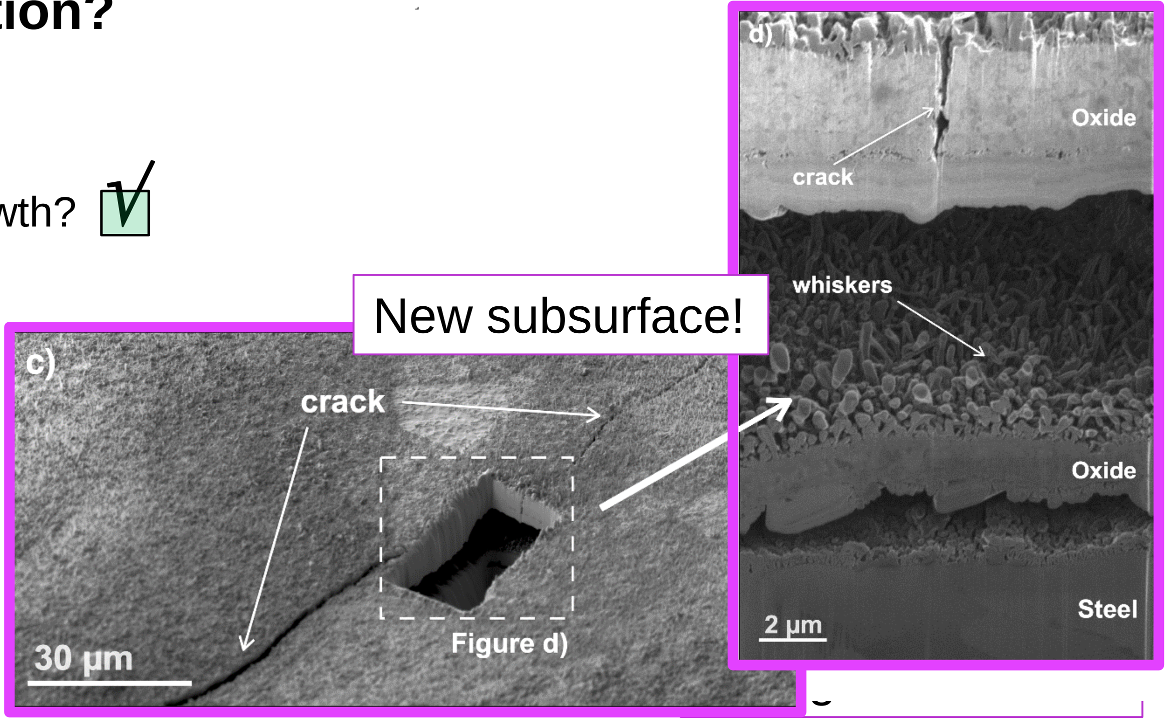






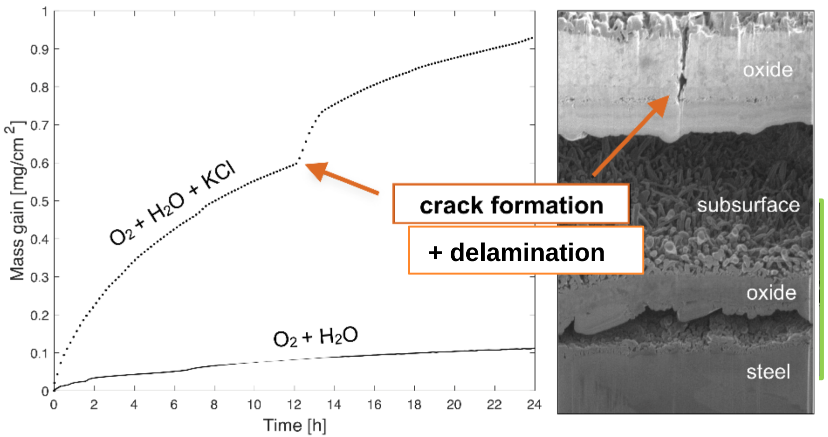
What causes the transition?

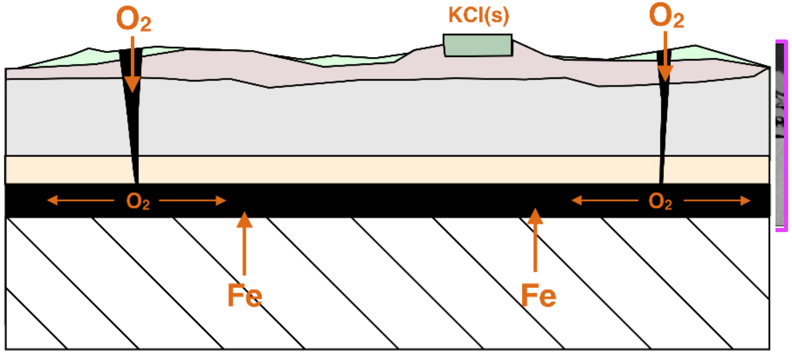
- Cracks form during oxide growth? ✓
- Local corrosion attack? ✗
- Delamination / lateral cracks

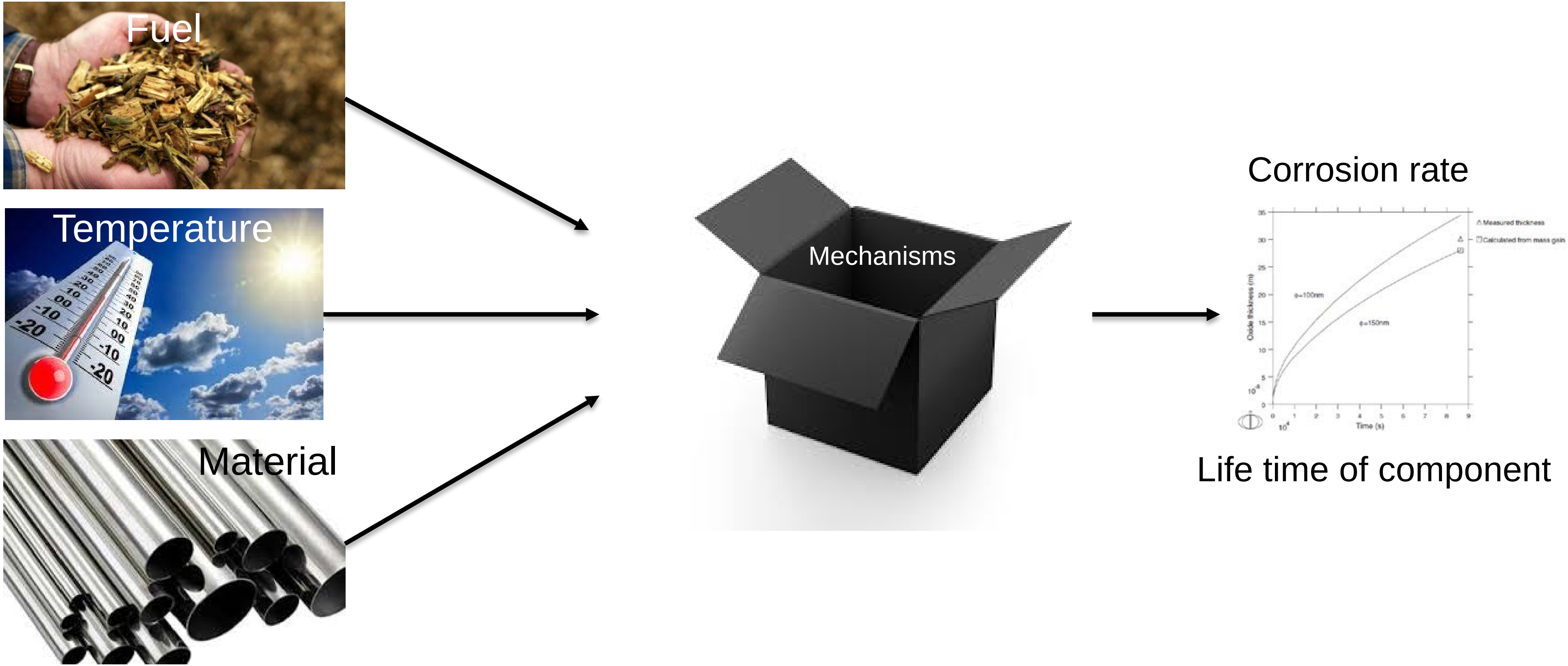


What causes the transition?

- Cracks form during oxide growth? √
- Local corrosion attack? X
- Delamination / lateral cracks
  - Global? √
  - During oxide growth? √






Fuel
Temperature
Material
Mechanisms
Corrosion rate
Time (s)
Life time of component

How to model high temperature corrosion
The effect of crack formation
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KCl on the effect of secondary protection & GB's

Sedi Bigdeli
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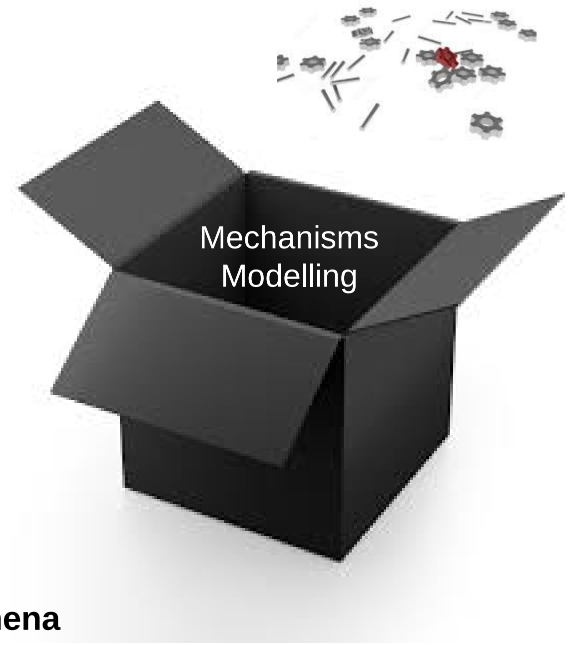


Primary ✓

Secondary ✓?

Tertiary ✓?

?

?

Collaboration between projects:
HTC1a – Critical Corrosion Phenomena
TEAMWORK
KME 709, 711, 720

Challenges with FeCrAl alloys

Temperature

Applications

1400°C

1200°C

1000°C

800°C

600°C

400°C

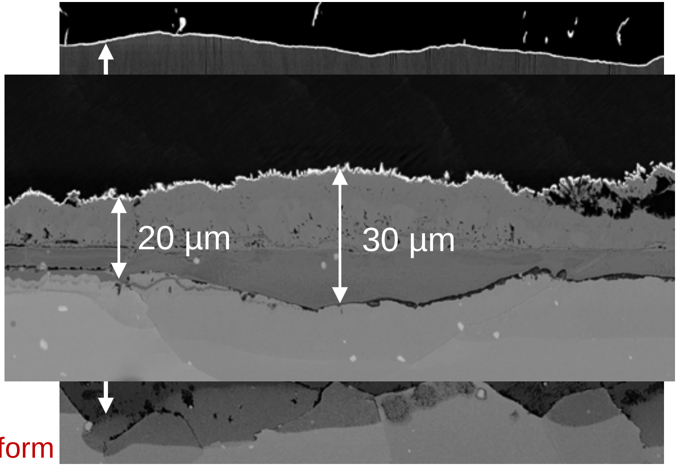
Heating elements

Boilers?

An α-alumina scale forms at temperatures above ~900 °C that protects the alloy

Secondary protection

Primary protection



At lower Temperatures

- Metastable forms of alumina may form
- Not as protective as α-alumina

Research strategy

Model FeCrAl alloys – tailor made for biomass and waste fired boilers

- Investigate effect of Cr content
  - Secondary protection
- Investigate effect of Al content
  - Secondary protection
- Investigate effect of minor additions of other elements (RE, Si, etc.)
  - Secondary Protection

Experimental procedure

- Polished samples exposed in TGA system
  - 600 °C
  - 48 hours
  - K_2CO_3 deposited on surface to **break primary protection**

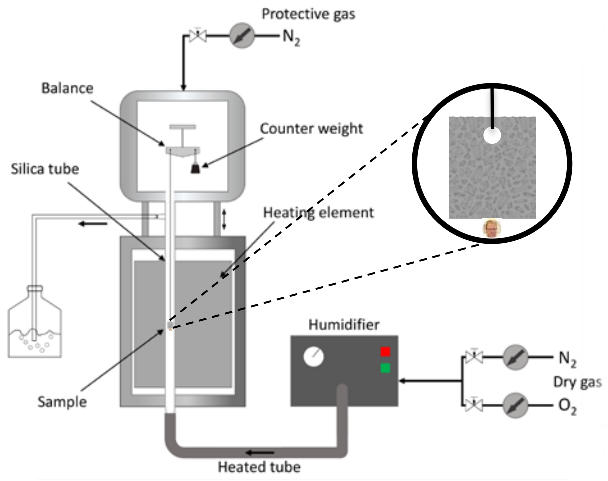
- Cross sections of exposed samples prepared (BIB) and analyzed using Scanning Electron Microscopy (SEM)

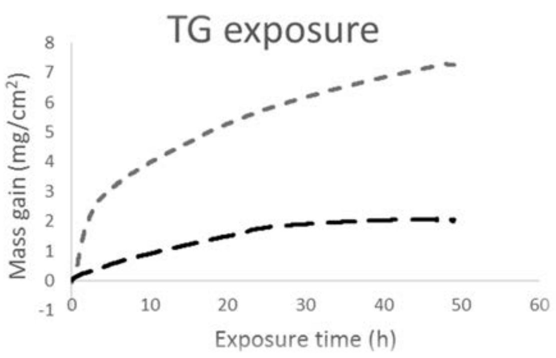
Al-effect

Alloy	Fe	Cr (wt-%)	Al (wt-%)
Fe18Cr	Bal.	18	0
Fe18Cr**1Al**	Bal.	18	1
Fe18Cr**3Al**	Bal.	18	3
Fe18Cr**6Al**	Bal.	18	6

Cr-effect

Alloy	Fe	Cr (wt-%)	Al (wt-%)
Fe**5Cr**3Al	Bal.	5	3
Fe**10Cr**3Al	Bal.	10	3
Fe**18Cr**3Al	Bal.	18	3
Fe**25Cr**3Al	Bal.	25	3



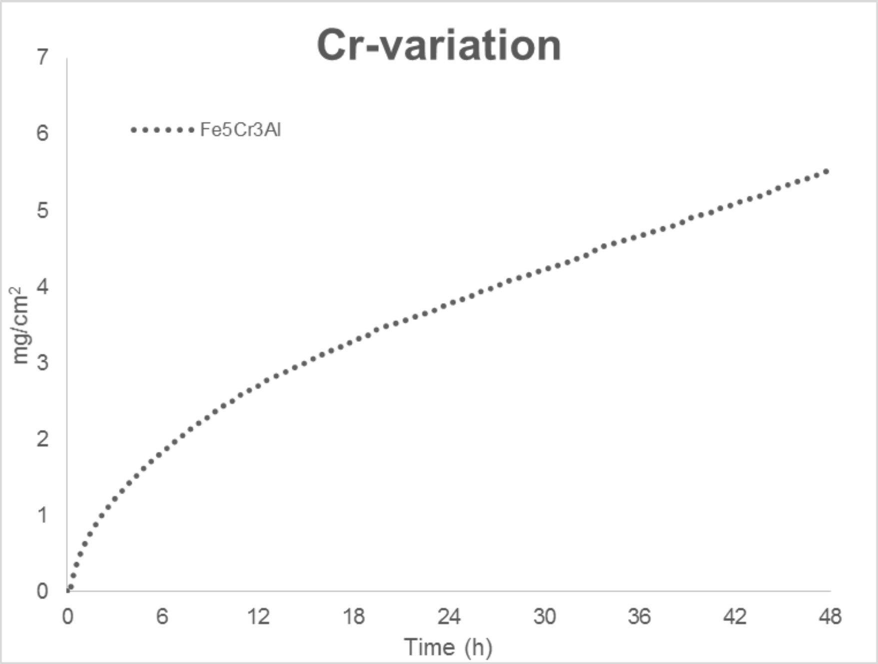


Research strategy

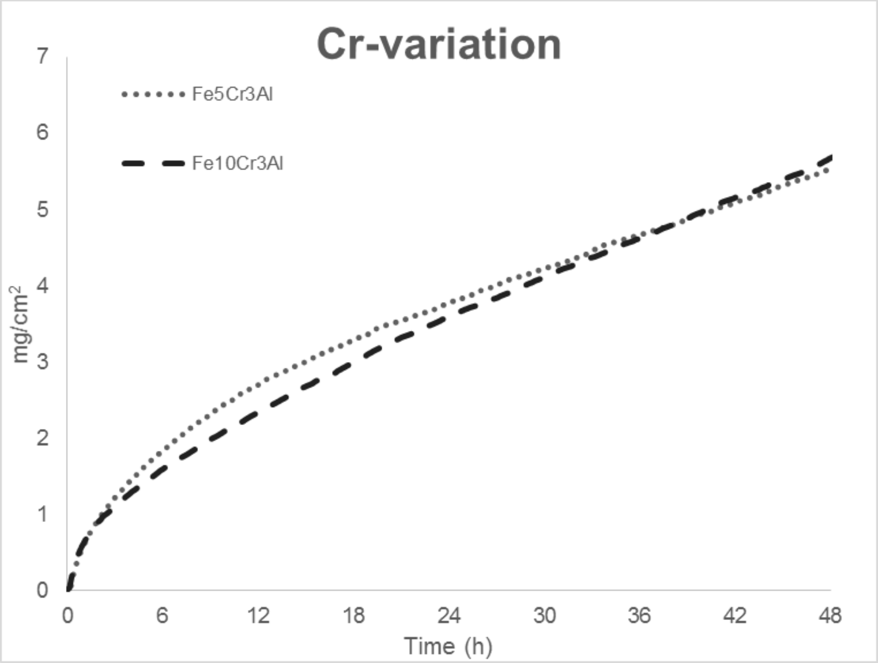
Model FeCrAl alloys – tailor made for biomass and waste fired boilers

- Investigate effect of Al content
  - Secondary protection
- Investigate effect of Cr content
  - Secondary protection
- Investigate effect of minor additions of other elements (RE, Si, etc.)
  - Secondary Protection

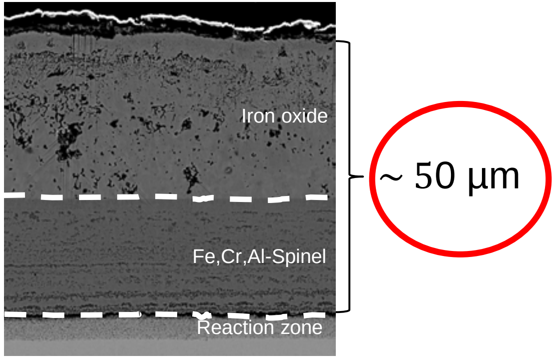
Kinetics – Cr-effect



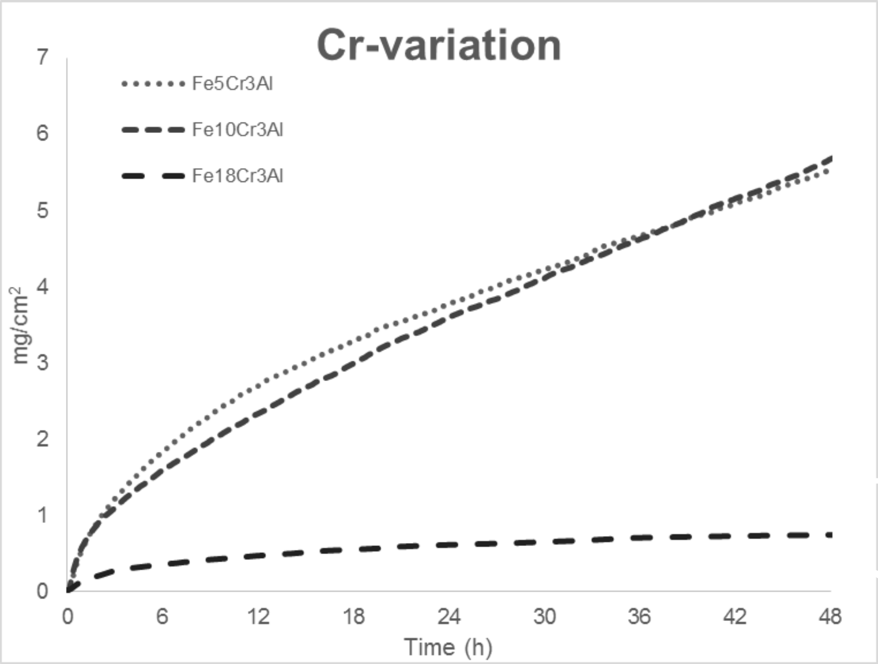
Kinetics – Cr-effect



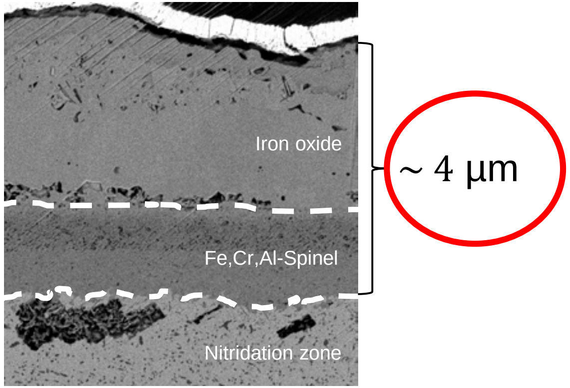
- No difference in growth rate upon adding 5 or 10 wt% Cr



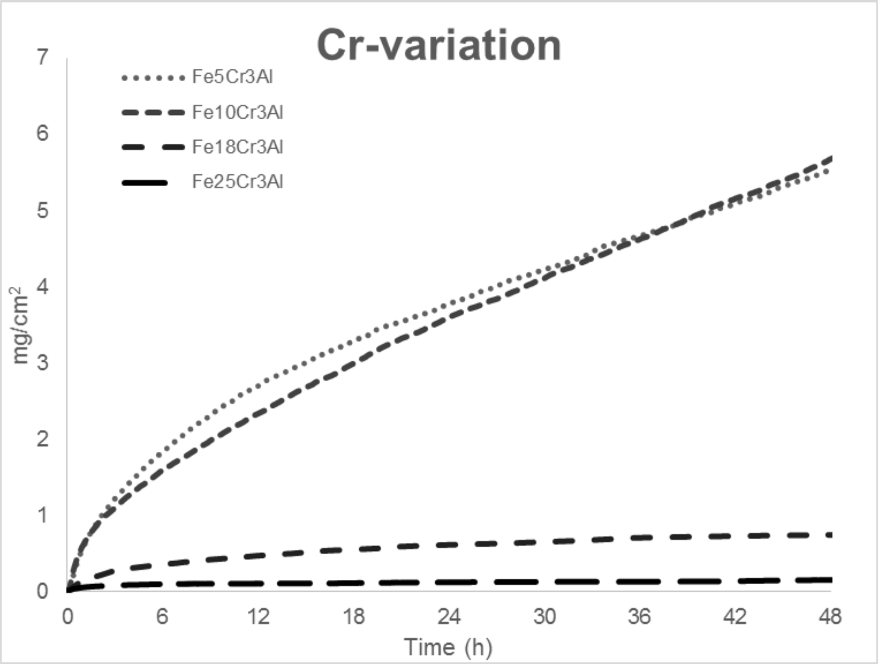
Kinetics – Cr-effect



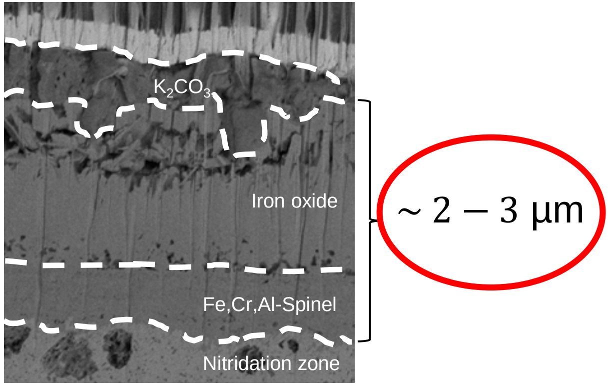
- No difference in growth rate upon adding 5 or 10 wt% Cr
- Addition of 18 wt% Cr results in a drastic reduction in growth rate
  - Critical Cr-content between 10 and 18 wt%



Kinetics – Cr-effect

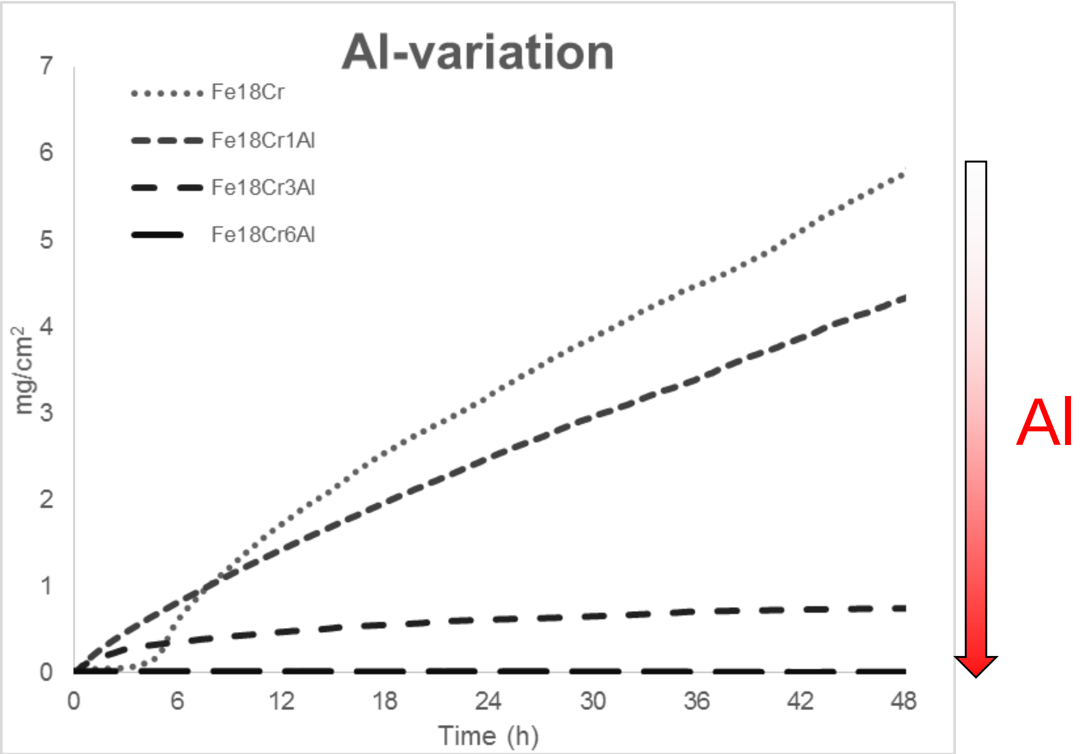


- No difference in growth rate upon adding 5 or 10 wt% Cr
- Addition of 18 wt% Cr results in a drastic reduction in growth rate
    - Critical Cr-content between 10 and 18 wt%
- Further reduction in growth rate with 25% Cr



Kinetics – Al-effect

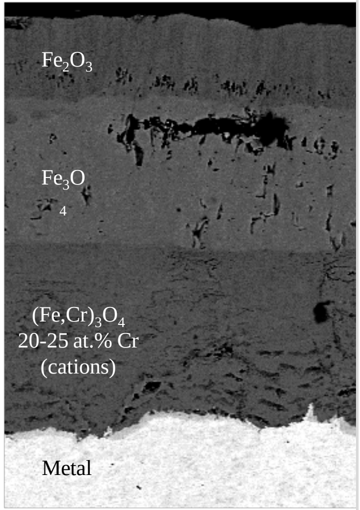
- **Addition of Al significantly reduces the growth rate of the iron-rich oxide**
  - **Improves secondary protection**

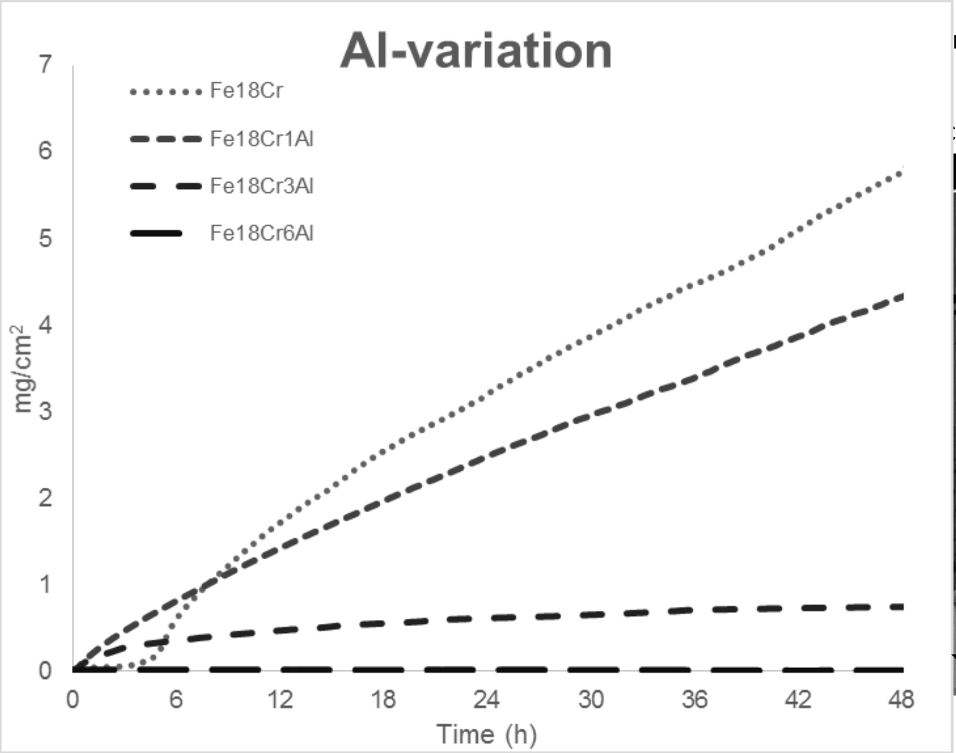


Combined Cr- and Al-effect

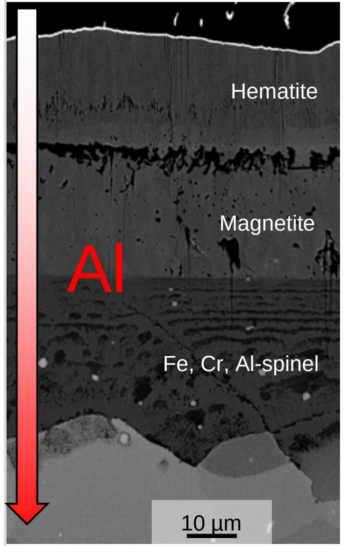
It has earlier been s … rotection) at 600 °C

Fe10



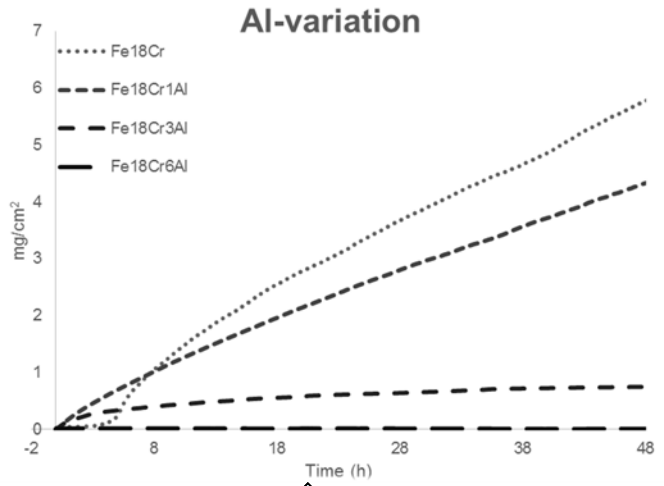


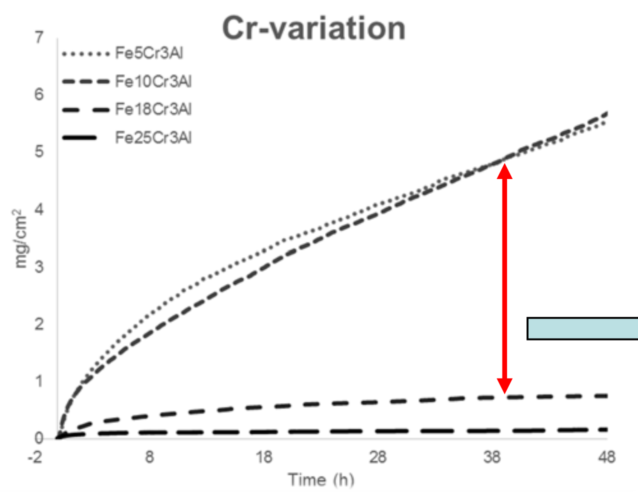
r4Al



Combined Cr- and Al-effect

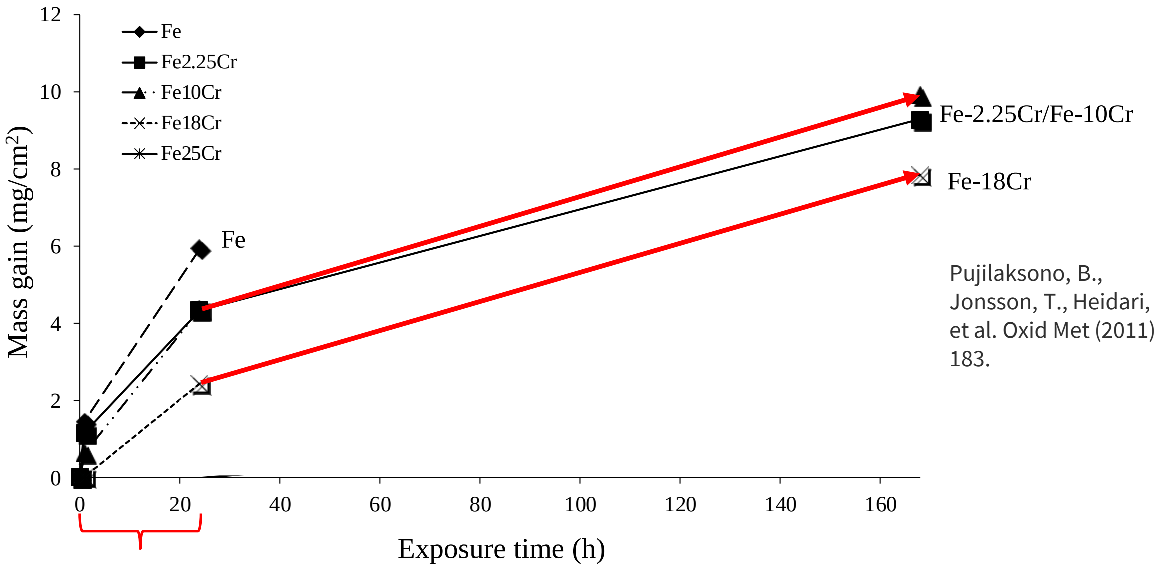
When reaching the critical Cr-content, Al addition has a large effect





Critical Cr-content between 10-18 wt%

The influence of Cr on the secondary protection in FeCr alloys – $O_2 + H_2O$ at 600 °C



Pujilaksono, B., Jonsson, T., Heidari, H. et al. Oxid Met (2011) 75: 183.

- Increased incubation time
- Minor or no influence on secondary protection

Synergistic effects between elements in FeCrAl alloys

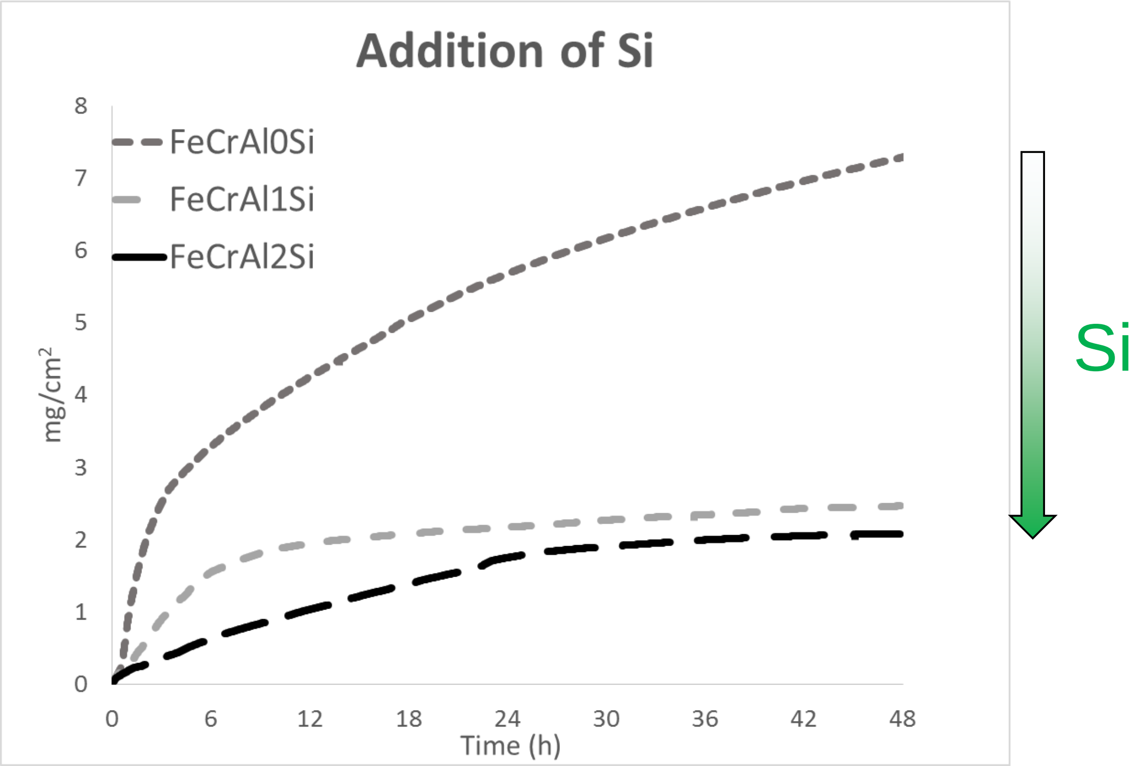
Research strategy

Model FeCrAl alloys – tailor made for biomass and waste fired boilers

- Investigate effect of Cr content
  - Secondary protection
- Investigate effect of Al content
  - Secondary protection
- Investigate effect of minor additions of other elements (RE, Si, etc.)
  - Secondary protection

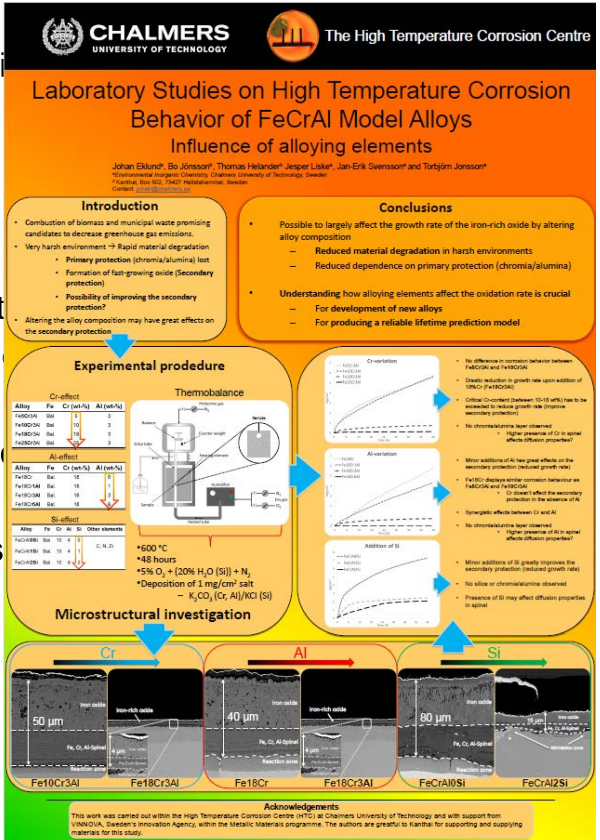
Effect of Silicon

- **Minor Si-addition greatly reduce oxide growth rate**
  - **Improves secondary protection**



Summary

- Possible to largely affect the growth rate of the iron-rich oxide by alteri
  - Reduced material degradation in harsh environments
  - Reduced dependence on primary protection (chromia/alumina)
- Synergistic effects between Cr and Al
  - Critical Cr content has to be exceeded to achieve beneficial effect
  - Minor or no effect of Cr-addition on the secondary protection in th
- Minor Si-additions has great influence on the growth rate of the iron-ri
- **Understanding how alloying elements affect the oxidation rate is reliable lifetime prediction model**



How to model high temperature corrosion	*Sedi Bigdeli*
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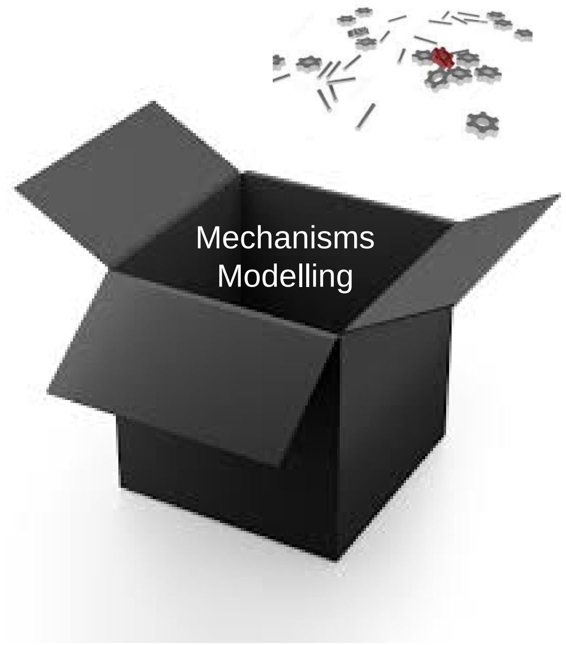
The effect of alloying elements	*Johan Eklund*
KCl on the effect of secondary protection & GB’s	***Julien Phother***



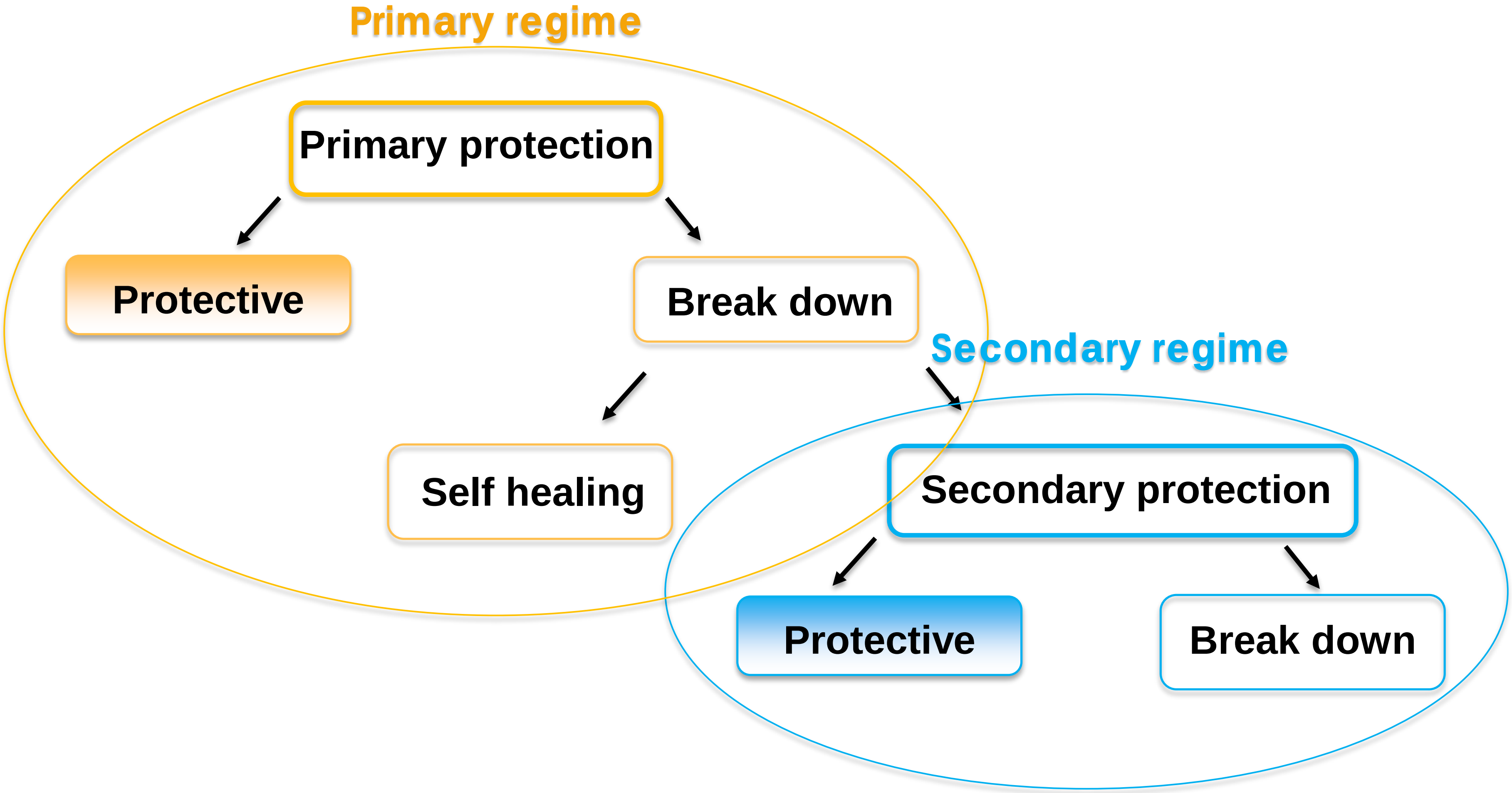
Primary ✓

Secondary ✓?

Tertiary ✓?

?

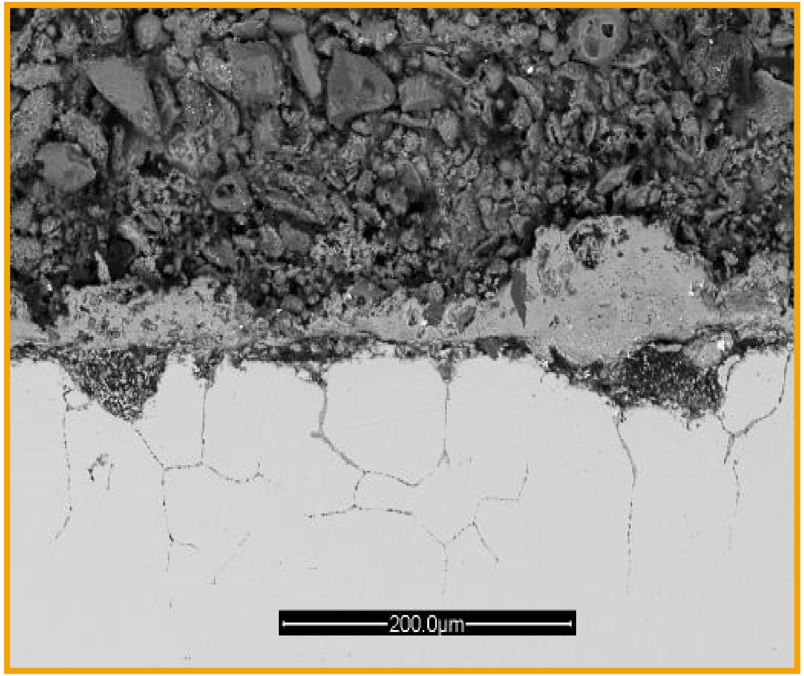
?


Primary regime
Primary protection
Protective
Break down
Self healing
Secondary regime
Secondary protection
Protective
Break down

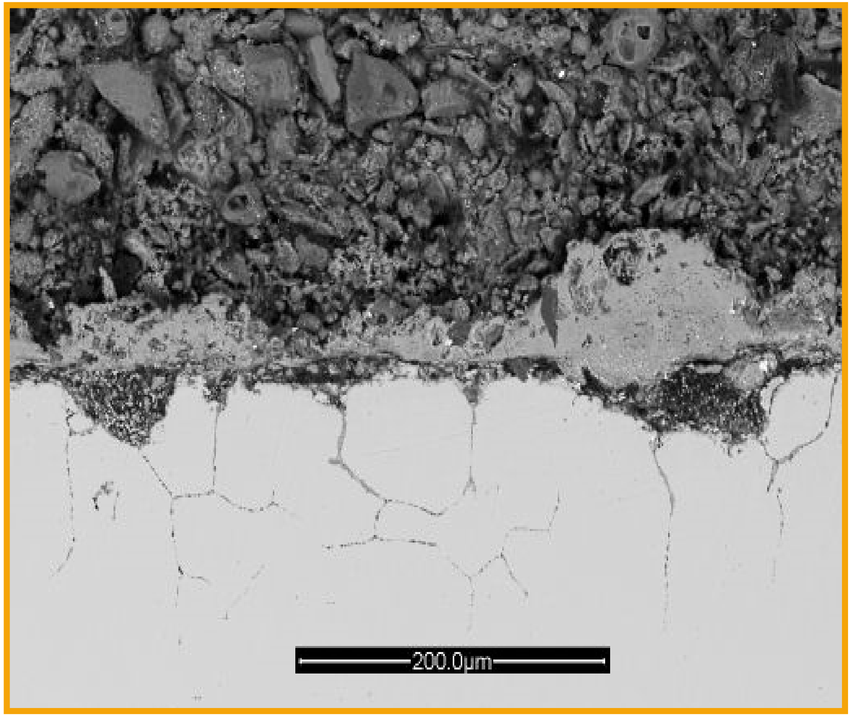
Secondary protection

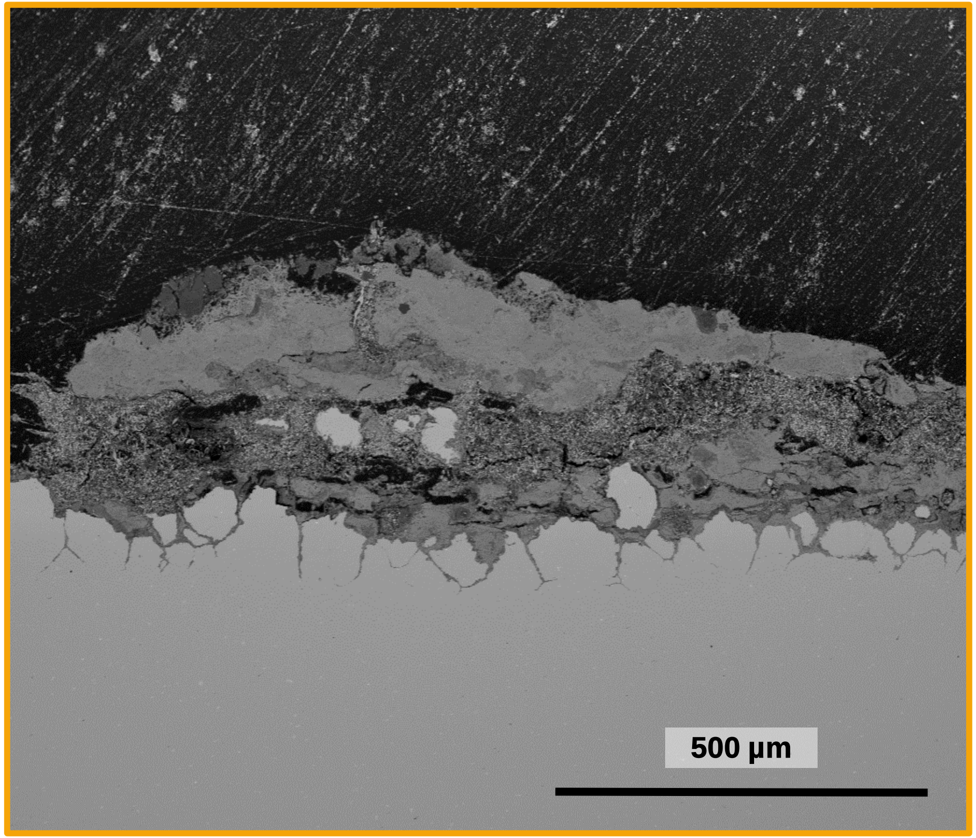
304L - 600 °C - SRF boiler

Flue gas temperature ~750 °C
Concentration KCl+NaCl in flue gas: ~100 ppm

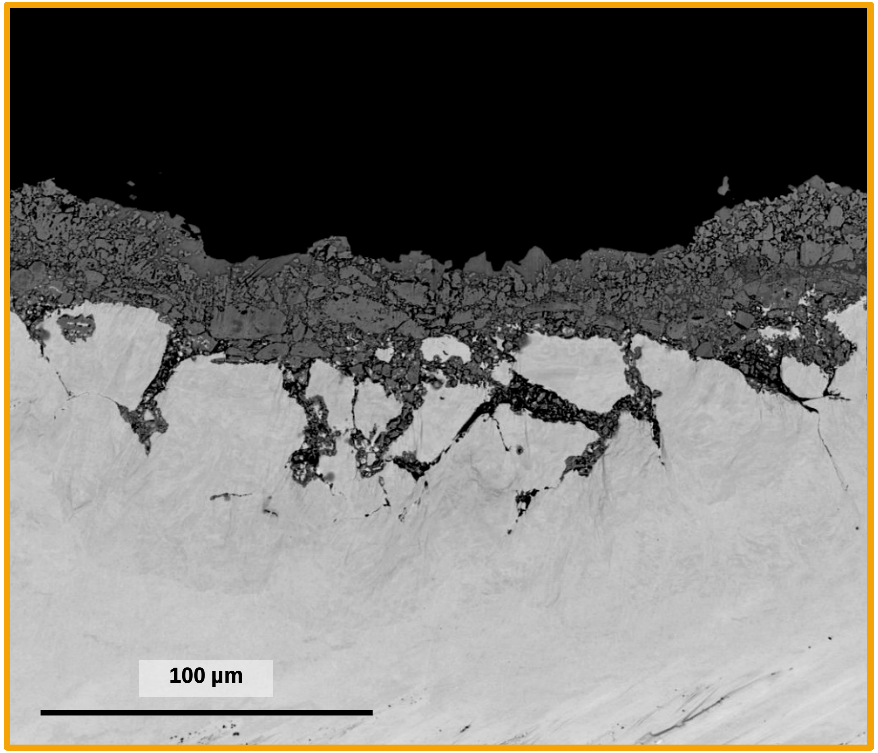


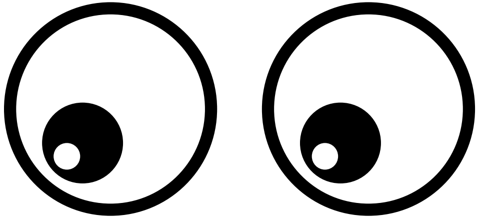
24 hours


200.0µm

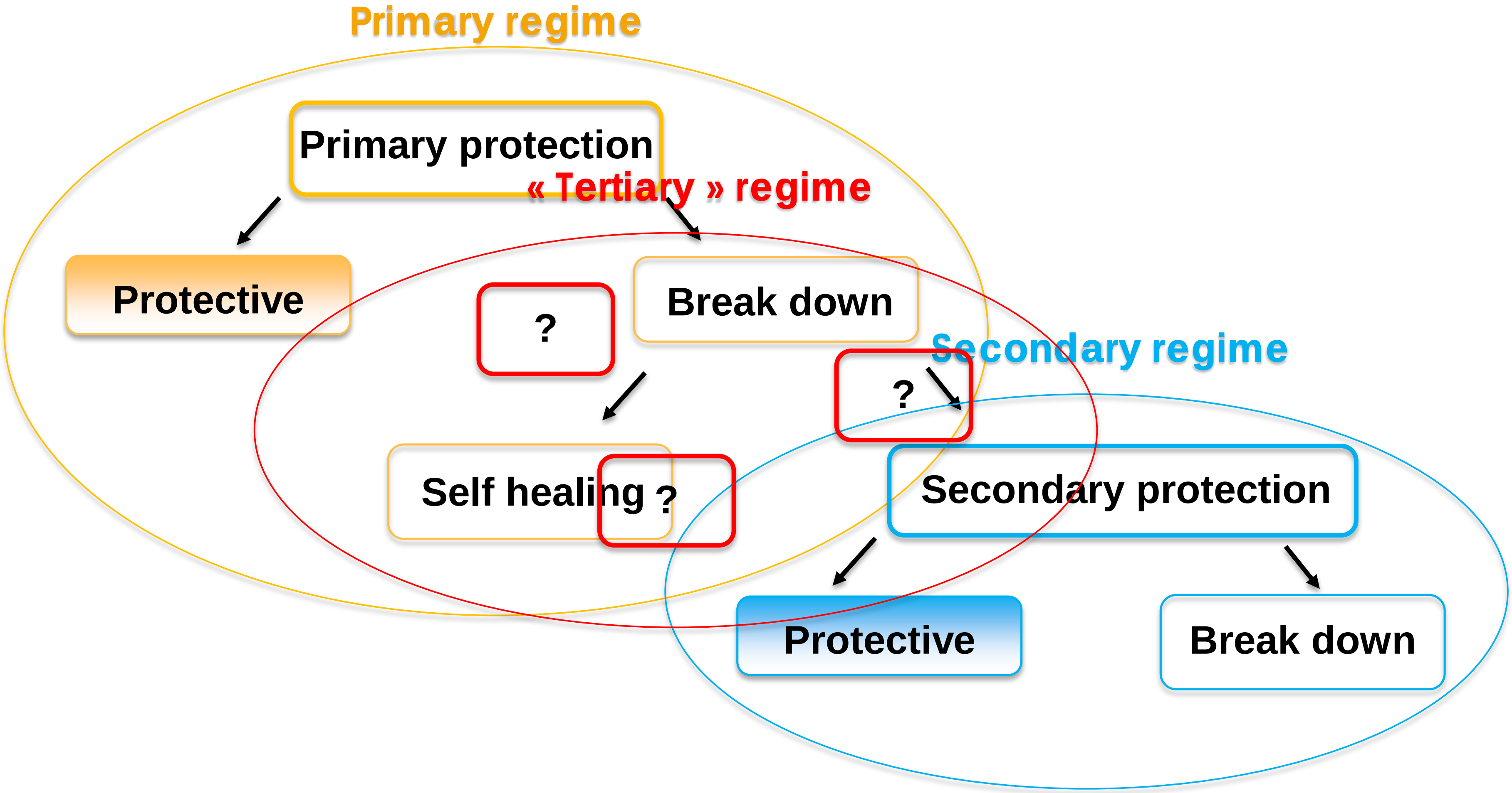

500 µm


KCl source


100 µm



Secondary protection → **???**


Primary regime
Primary protection
« Tertiary » regime
Protective
?
Break down
Secondary regime
?
Self healing ?
Secondary protection
Protective
Break down

Role of chlorine in accelerated corrosion

High temperature corrosion of low-alloyed and stainless steels: mechanistic study of cholrine-induced corrosion

Chlorination of iron and low-alloyed steel by KCl or HCl in the presence of O^{2-} New insights by atomistic modelling

24th of April – 10:00 am
Chalmers University of Technology
Chemistry and Chemical Engineering building
10:an

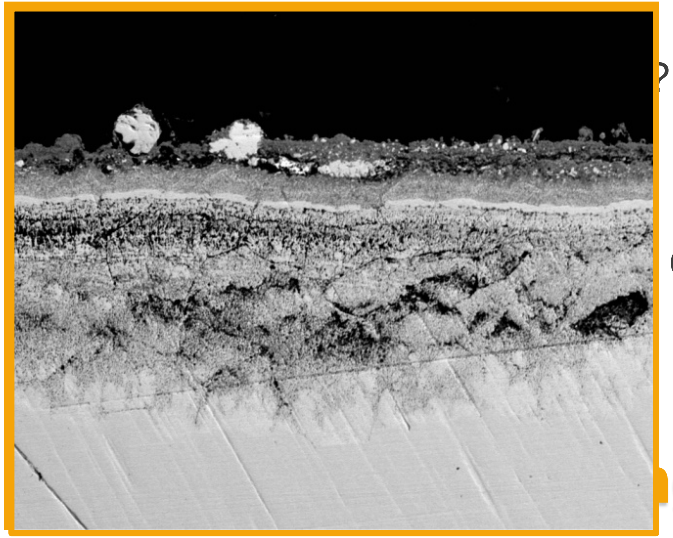
Mercedes Andrea Oliva Ogaz
Valentina Cantatore

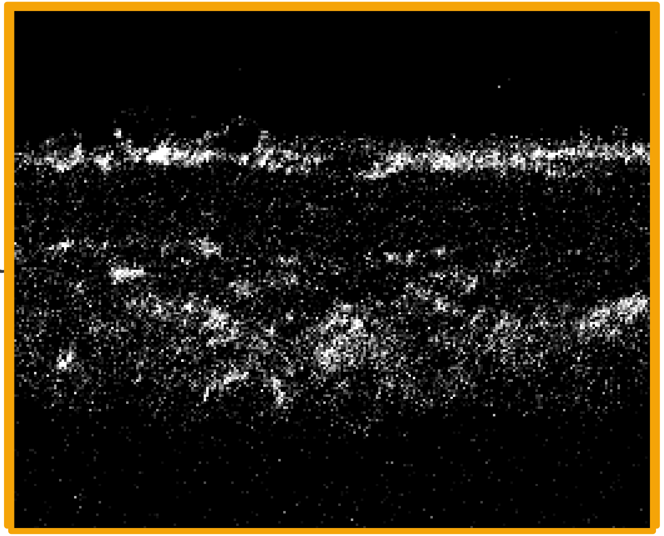
Where is it located ?

- Is it ?

distribu

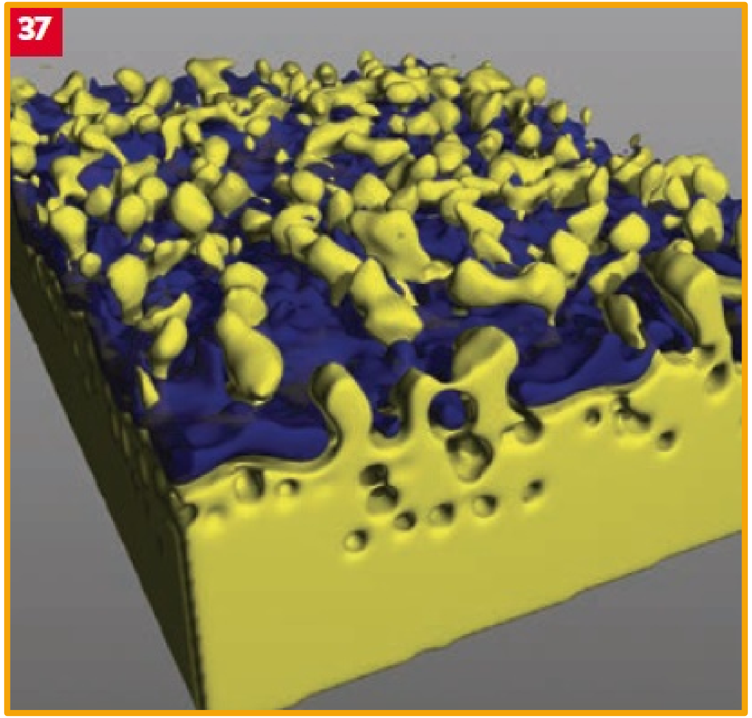
ng of





3D EDX reconstruction

https://www.tescan.com/en-us/technology/gaia3



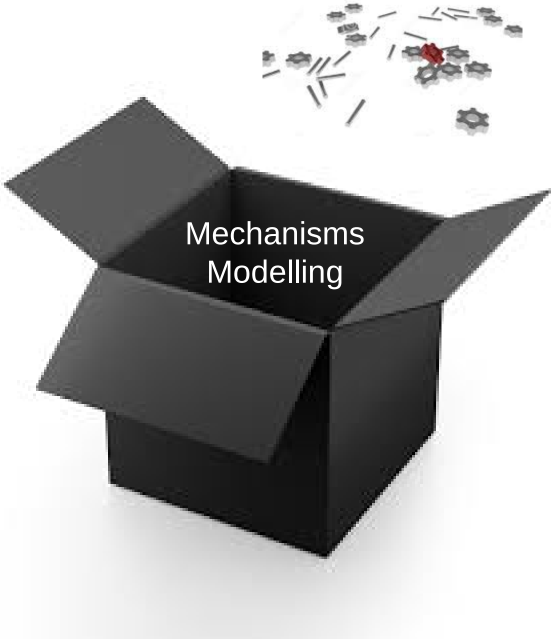
3D EDX reconstruction showing corrosion through Cr plating on steel

How to model high temperature corrosion — *Sedi Bigdeli*

The effect of crack formation — *Amanda Persdotter*

The effect of alloying elements — *Johan Eklund*

KCl on the effect of secondary protection & GB's — *Julien Photer*



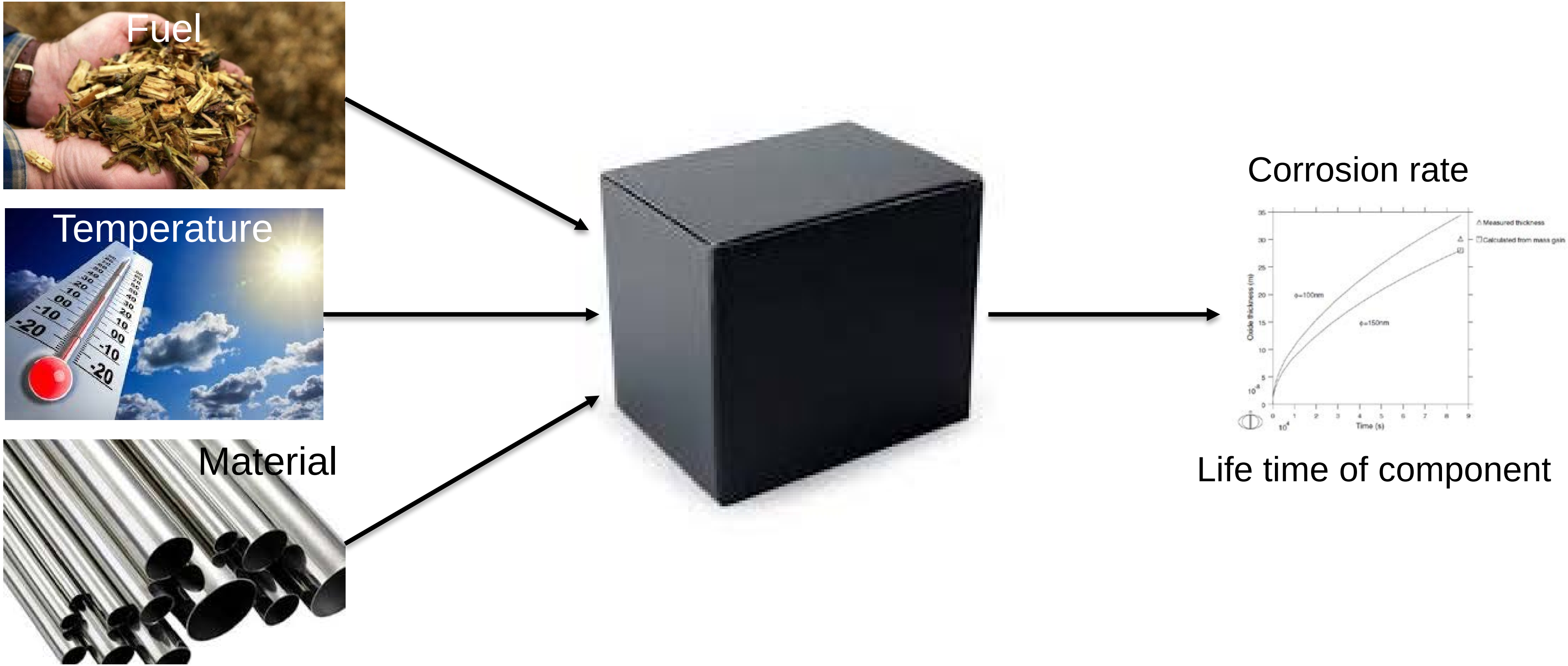
√ Primary

√? Secondary

√? Tertiary

?

?


Fuel
Temperature
Material
Corrosion rate
Life time of component

Energy policy targets for Sweden

100 percent renewable electricity production by 2040	No emissions of greenhouse gases by 2045	50 percent more efficient use of energy in 2030, compared to 2005

Three pillars for Sweden's energy policy

Swedish Energy Agency

*...sion during **combustion** of*
number of corrosion problems
...es.

*increasing the **predictability** of corr...*

The future role of Bioenergy

More total Biomass utilization

- Base load power
- Local small scale CHP
- Important complement to variable electricity sources

Swedish Energy Agency

SANDVIK
Sumitomo SHI FW
KANTHAL Part of Sandvik Group
Valmet

AVANCEZ

1829

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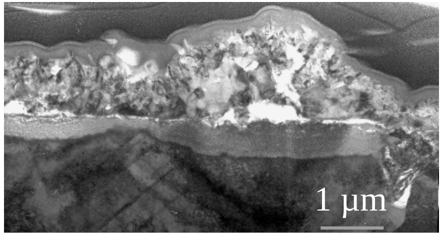
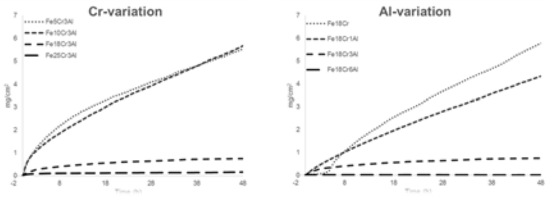
Future work

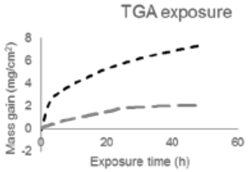
The High-Temperature Corrosion Center

- Improve the understanding of the mechanisms
  - Cr-, Al- and Si-effects in FeCrAl alloys
  - Synergistic effects in FeCrAl alloys





Microstructural analysis



Modeling:
Thermodynamic calculations
Kinetic simulations