Understanding the mechanism of fast corrosion initiation caused by KCl on waterwalls and superheated materials in waste and bio-fired power plants

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Background

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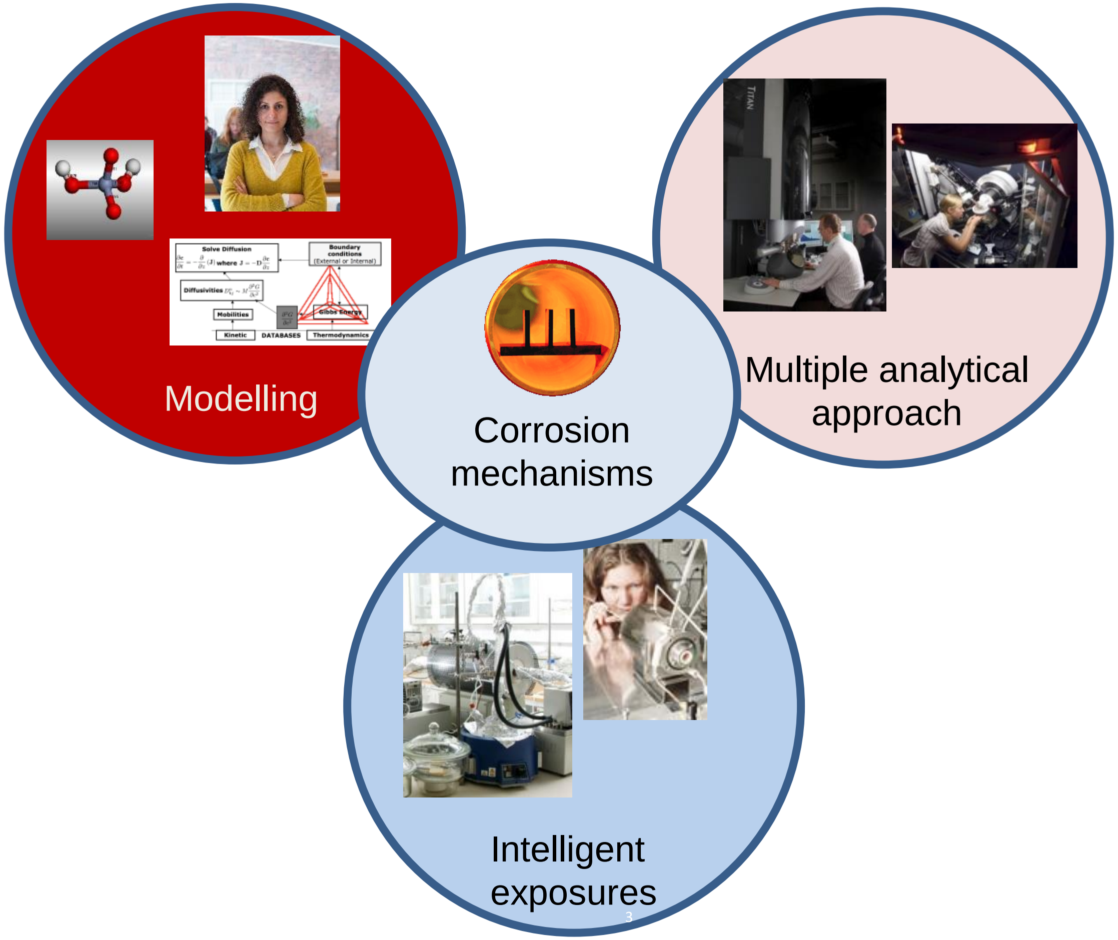
KTH Royal institute of technology

High Tempterature Corrosion Center

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

Courtesy Torbjörn Jonsson



Modelling

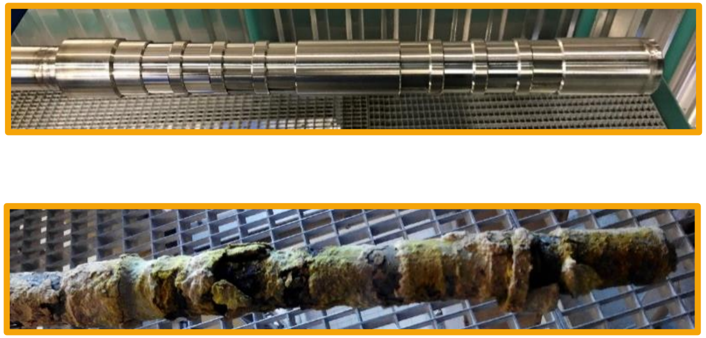
Corrosion mechanisms

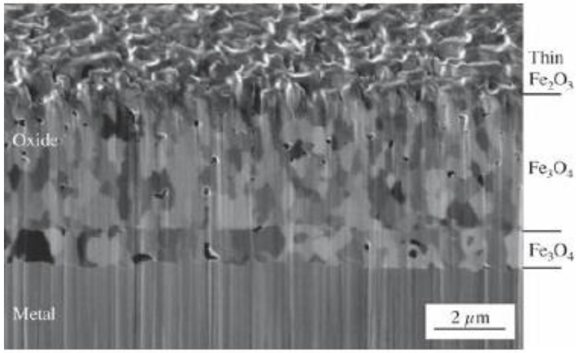
Multiple analytical approach

Intelligent exposures

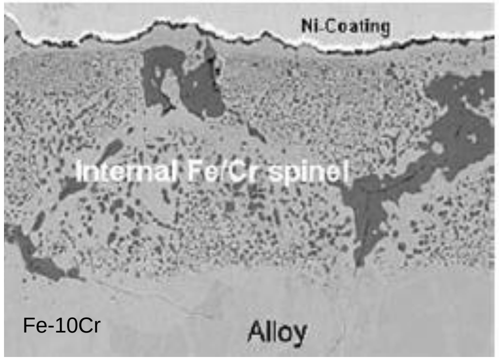
HTC industrial problem: corrosion

- ***Corrosion is an important degradation mechanism*** that limits the life time for steels and superalloys in applications at high temperatures and harsh environments.
- Oxidation leads to formation of exterior oxide scales and/or internal oxide particles dispersed in the metal matrix.



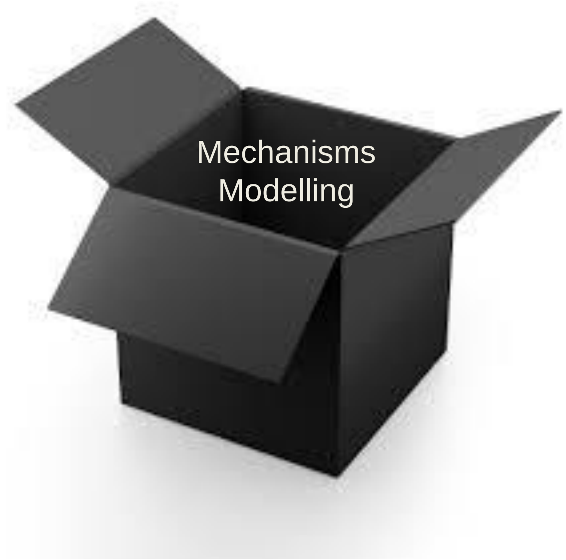


Jonsson et al. 2006

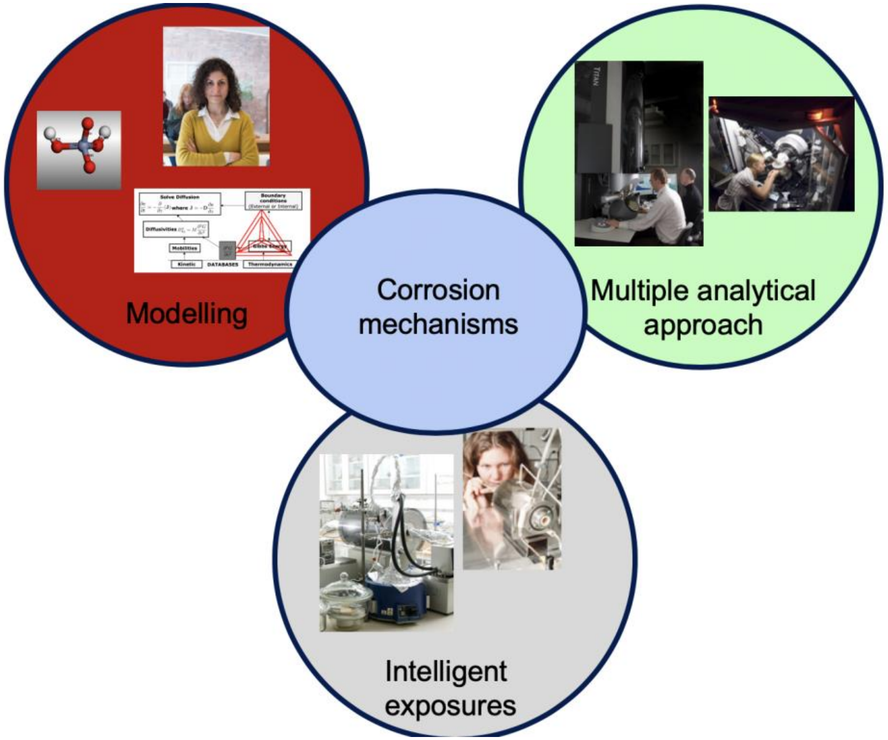


Essuman et al. 2008

Courtesy of John Ågren and Julien Phother Simon

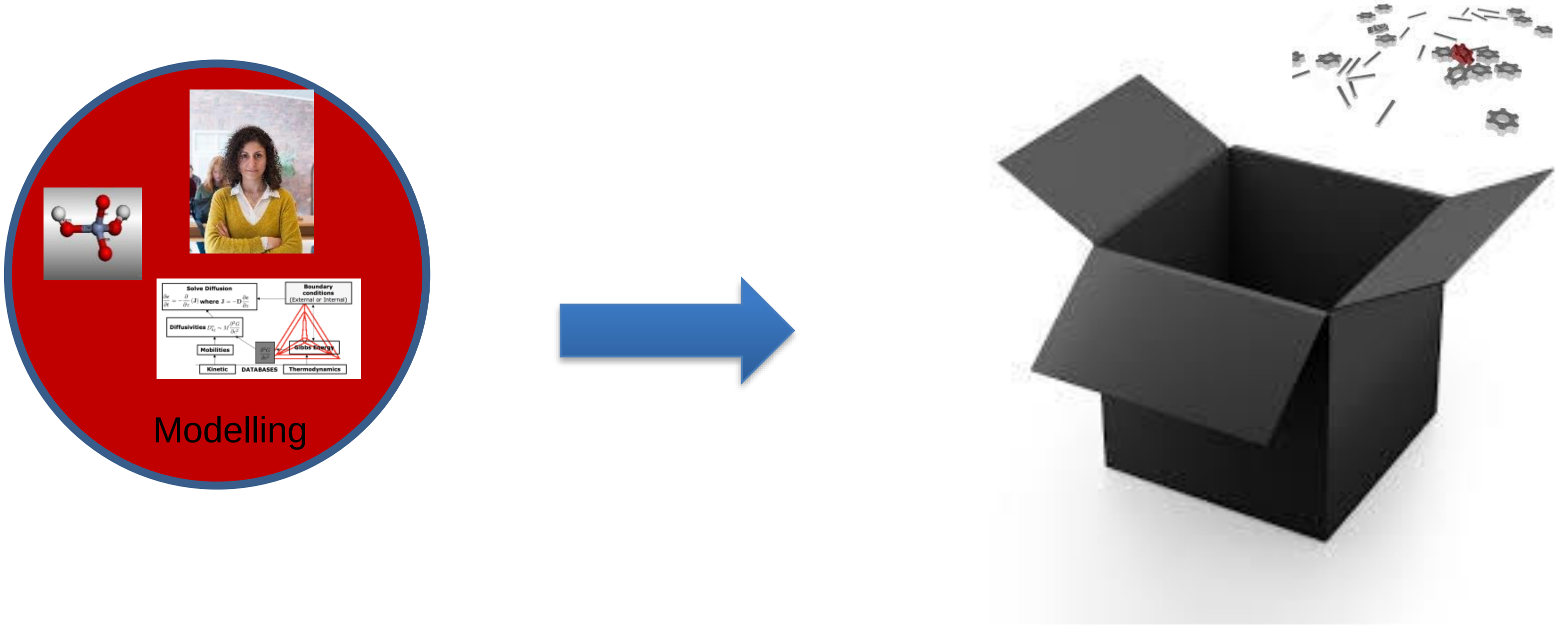


New approach!

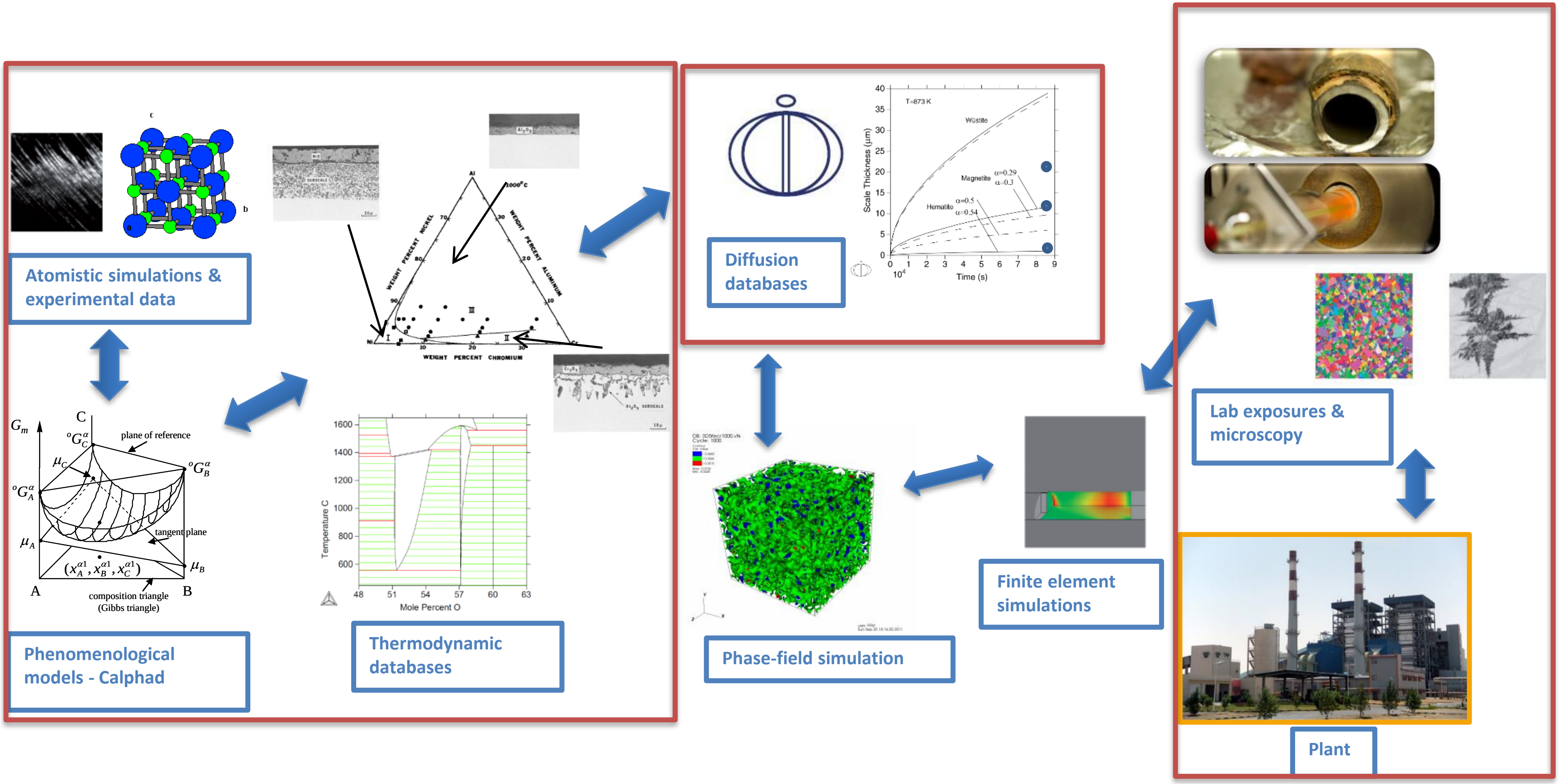


Project aim to implement computational thermodynamics

- ***Work towards a lifetime prediction model***
- Understand the corrosion mechanisms and microstructure observations by theoretical calculations



Work towards a lifetime prediction model



Atomistic simulations & experimental data

Phenomenological models - Calphad

Thermodynamic databases

Diffusion databases

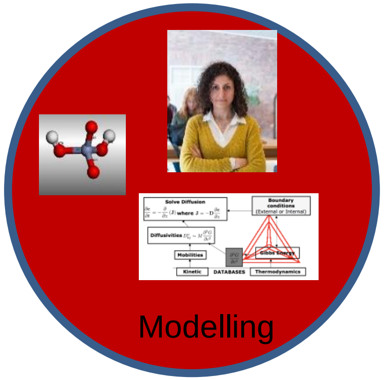
Phase-field simulation

Finite element simulations

Lab exposures & microscopy

Plant

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



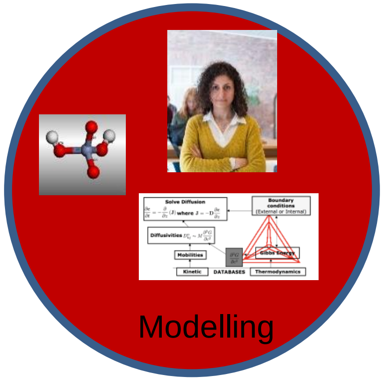
Our current tools can be used in different ways:

- Equilibrium calculations to understand microstructure,
- Diffusion simulations to predict the phase transformation's kinetic and products,
- Equilibrium calculations to predict possible phases and explain the process,
- ….

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

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

Example: calculate possible phases formed during lab exposure



Our current tools can be used in different ways:

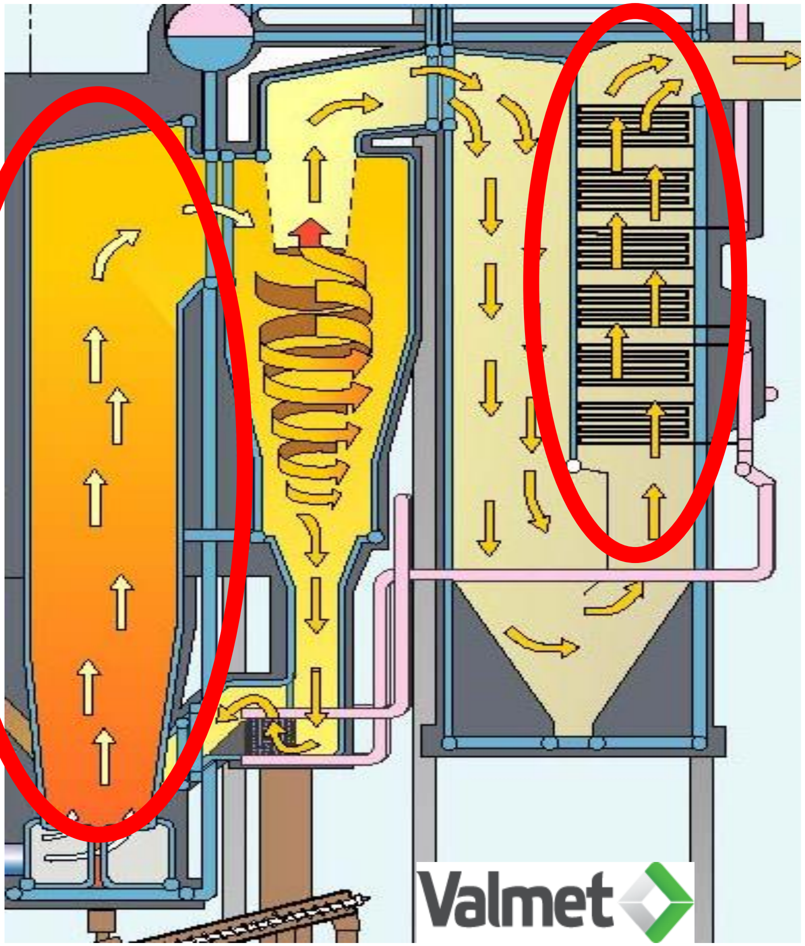
Equilibrium calculations to predict possible phases and explain the process,

Waste and biomass as alternative fuels

- Does not give a net contribution of CO_2 to the atmosphere when combusted
- Good availability
- Problems related to fossil fuels a diminished

There are however problems with Waste and Bio-mass

CFB boiler



Corrosive species → high corrosion rates on heat exchange materials

Lower steam temperature decreases the electrical efficiency

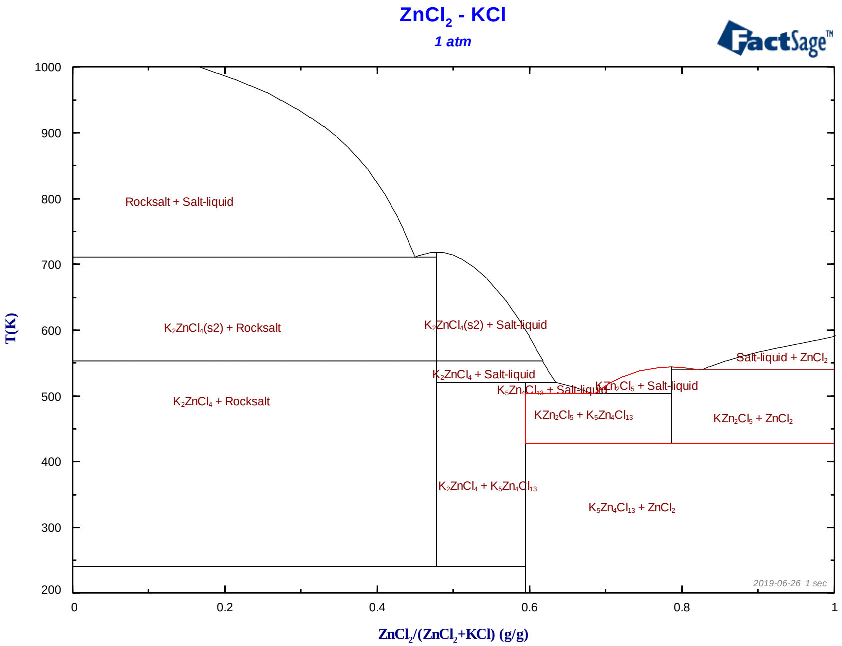
Sources of Zinc and Lead in combustion

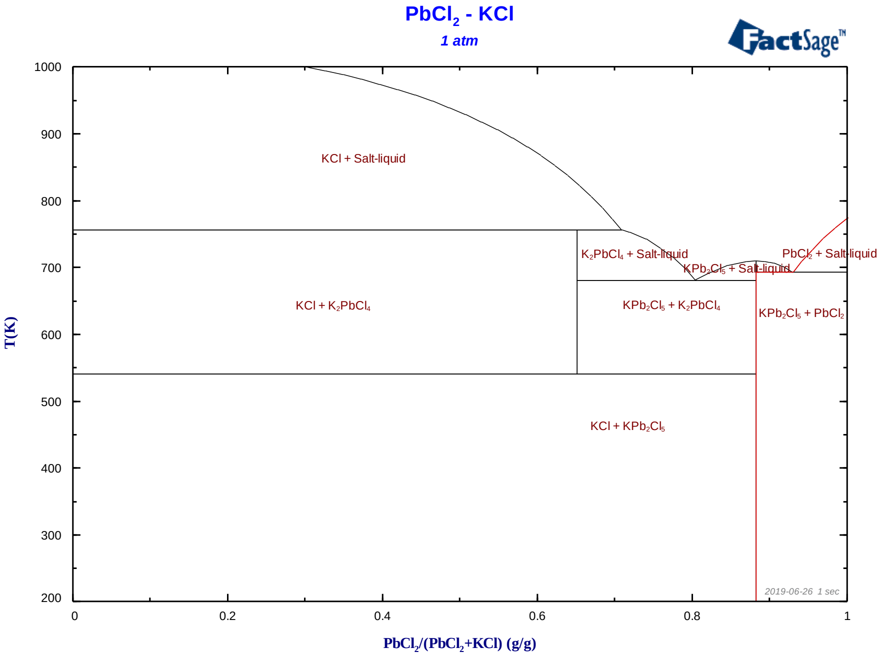
SLF

Recycled waste wood

Tires

Role of low-melt liquid in corrosion



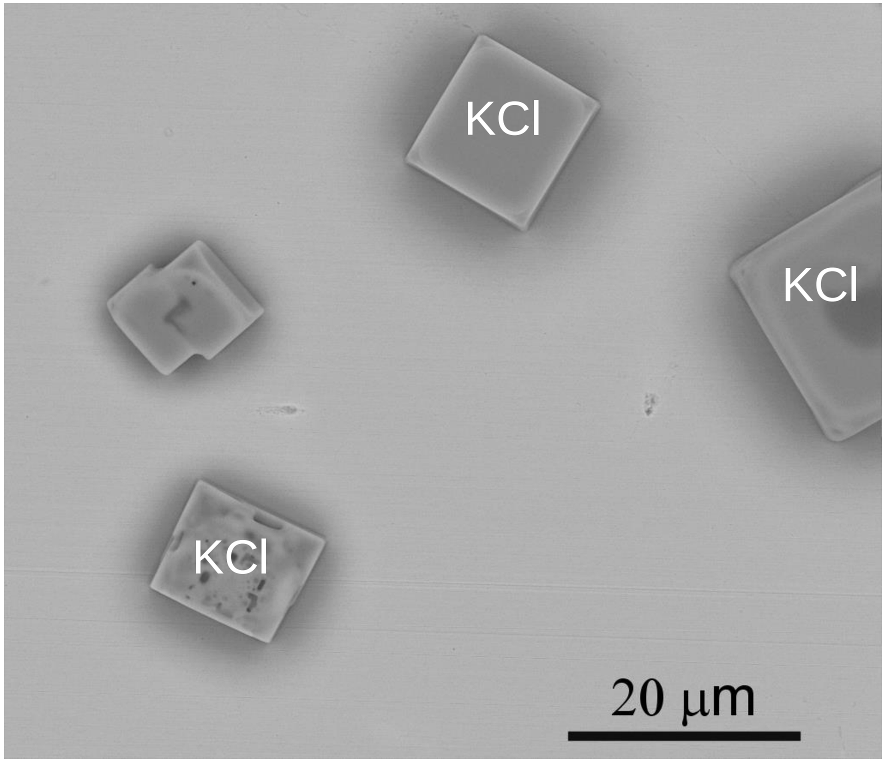


Composition [wt.%]	melting point [° C]
$ZnCl_2$	318
$PbCl_2$	489
KCl	770
50 $ZnCl_2$-50 KCl	~250

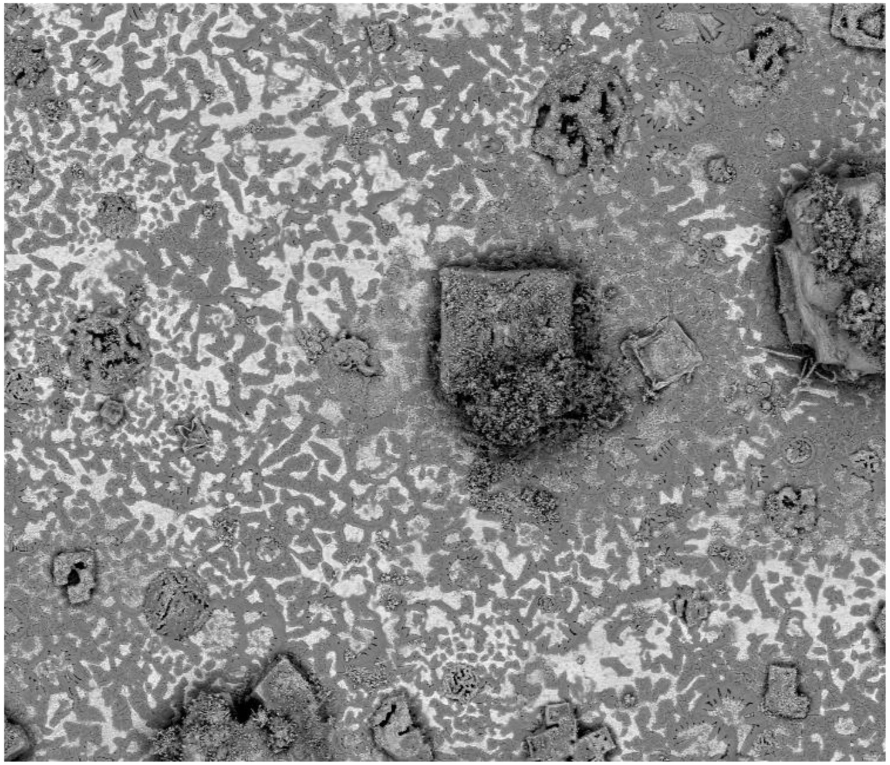
What are the mechanisms behind the fast initiation caused by KCl on high temperature corrosion of steels?

Initial corrosion process

Challenging to study but important to be able to understand the mechanisms

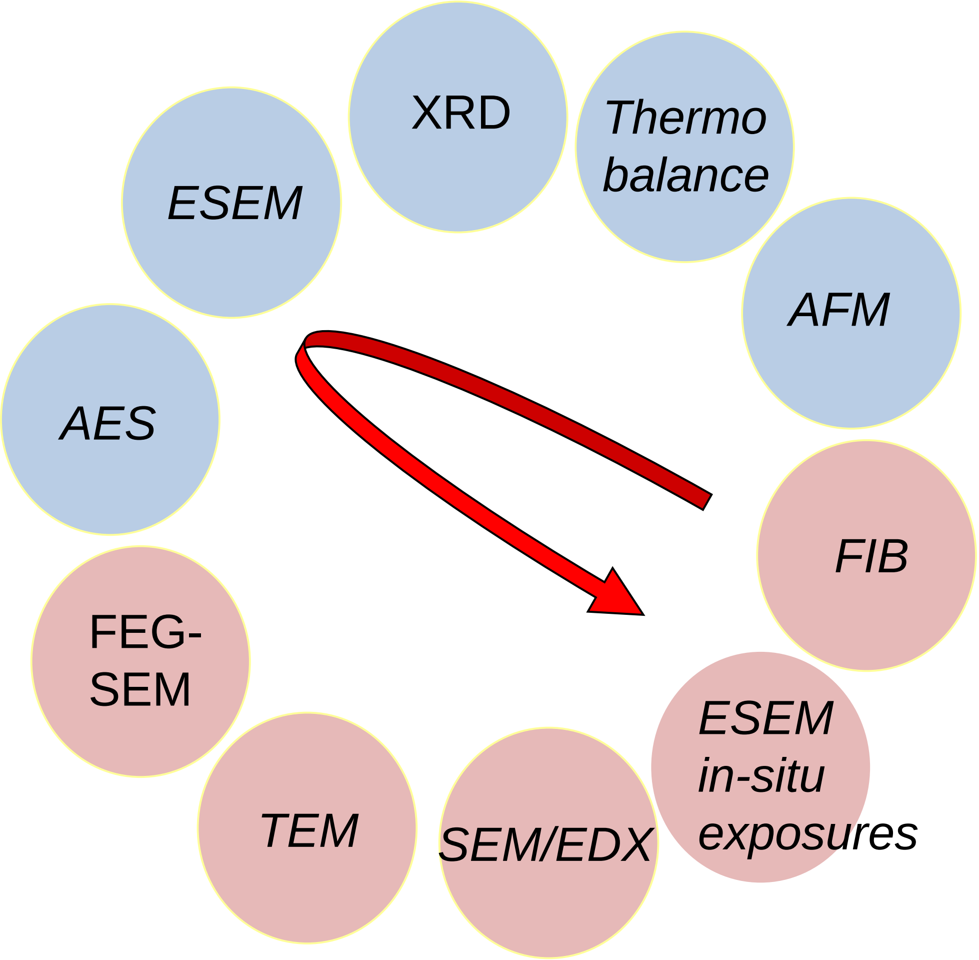


Before exposure



After 1 hour exposure

Example from lab studies



XRD

Thermo balance

ESEM

AFM

AES

FIB

FEG-SEM

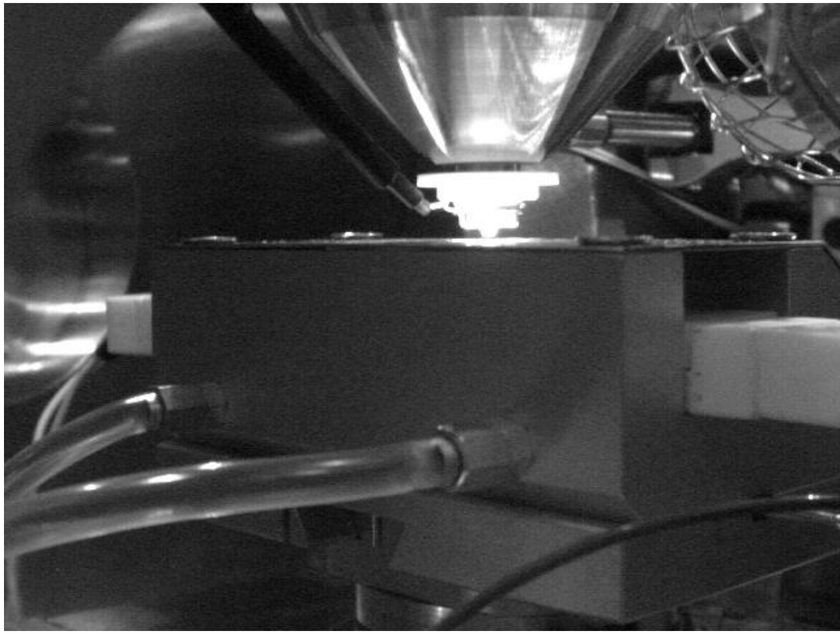
ESEM in-situ exposures

TEM

SEM/EDX

ESEM *in-situ* oxidation

A scanning electron microscope (SEM) is usually used to investigate the corrosion products after exposure.



A small furnace inside the SEM makes it possible to image the corrosion process at temperature.

ESEM *in-situ* oxidation

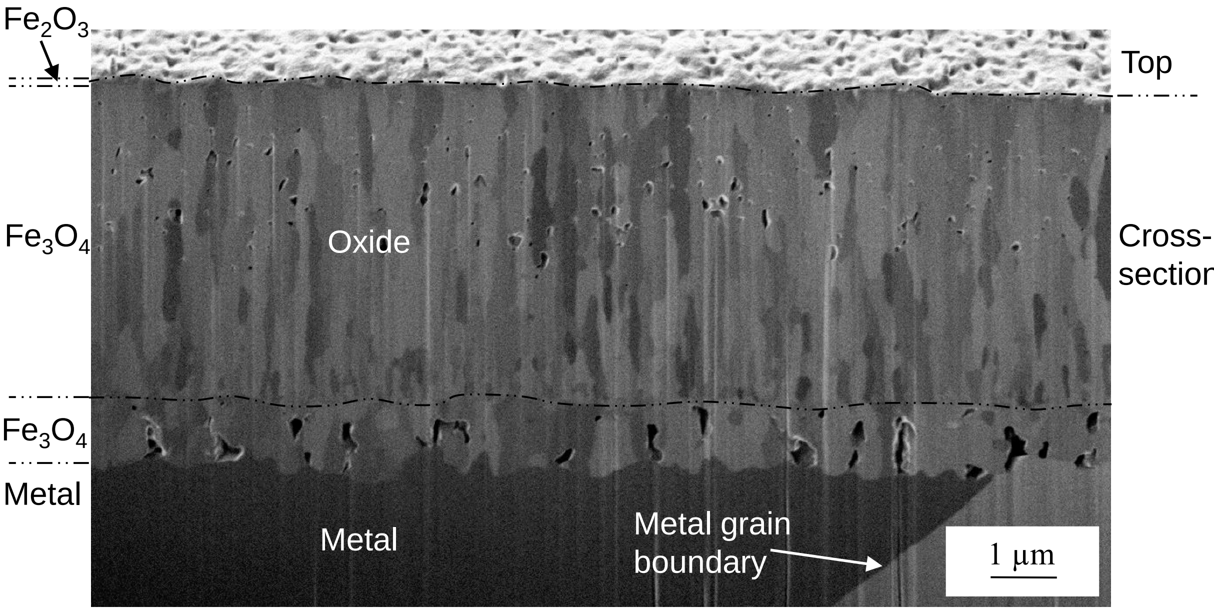
- Example 1: ESEM *in-situ* exposures of **Fe at 500ºC**.
  - Exposure time: **1 hour.**
  - Three atmospheres: Dry air, **wet air (~1% H_2O)** and H_2O.

- FIB - Cross-section milling and imaging to study the oxide microstructure.

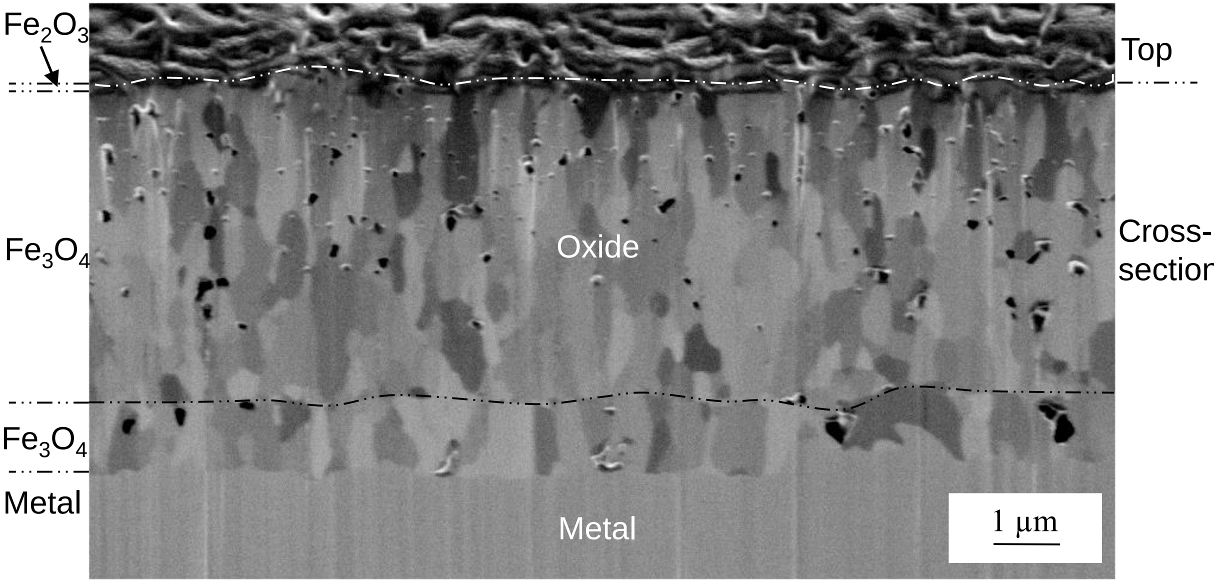
- **Furnace exposures as references.**

Jonsson, at al.. “Corrosion Science”, 2009. 51: p. 1914-1924.

ESEM *in-situ*
1h, dry air
500° C, 2.5 Torr
Ramp time: 50° C/min



Furnace (TG)
1h, O_2
525° C, 1 atm
Ramp time: 100° C/min



ESEM *in-situ* Oxidation

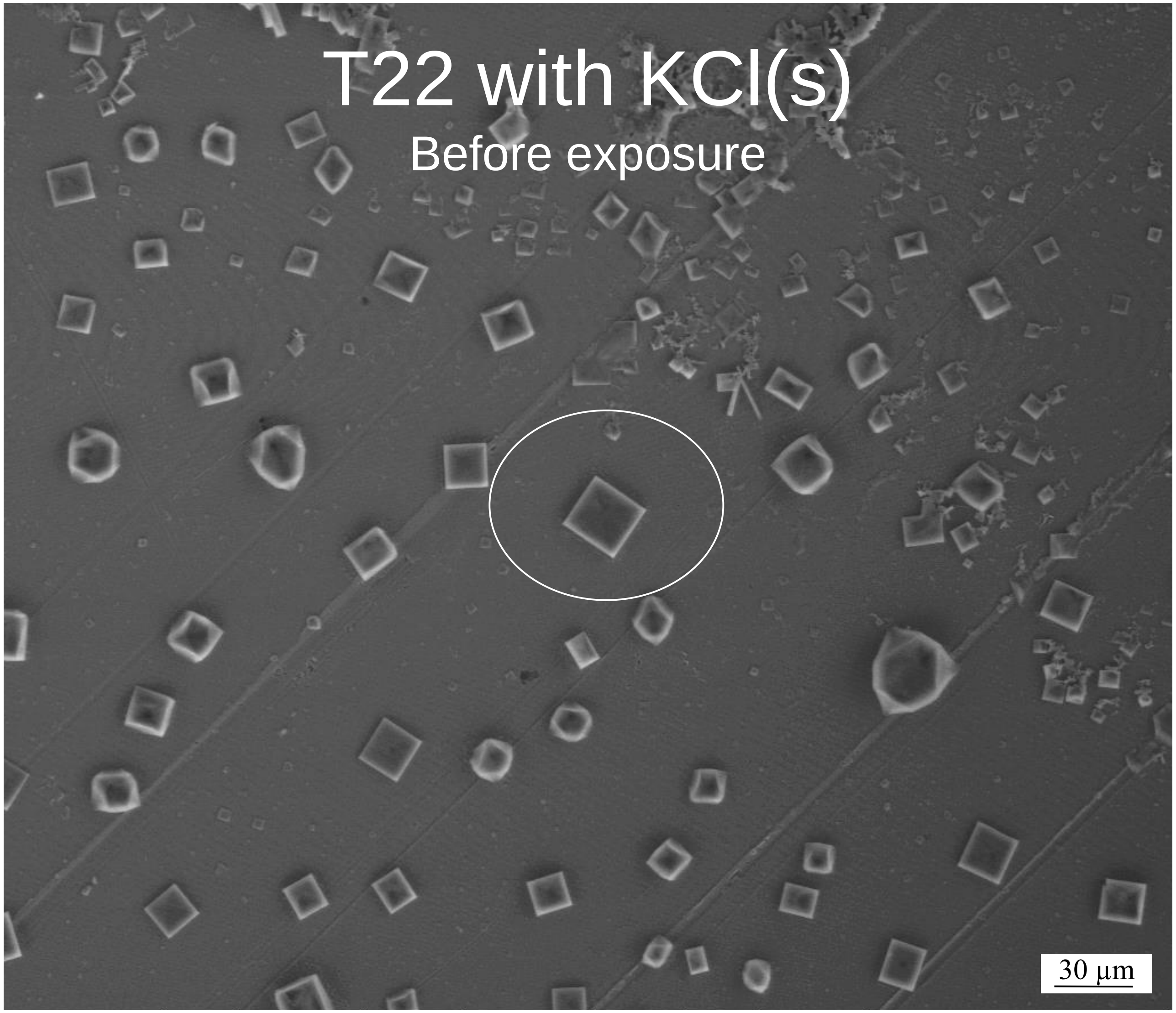
- Example 2: **T22 (2,25Cr-Fe) at 400ºC with KCl(s)**.
  - Exposure time: **≤1 hour.**

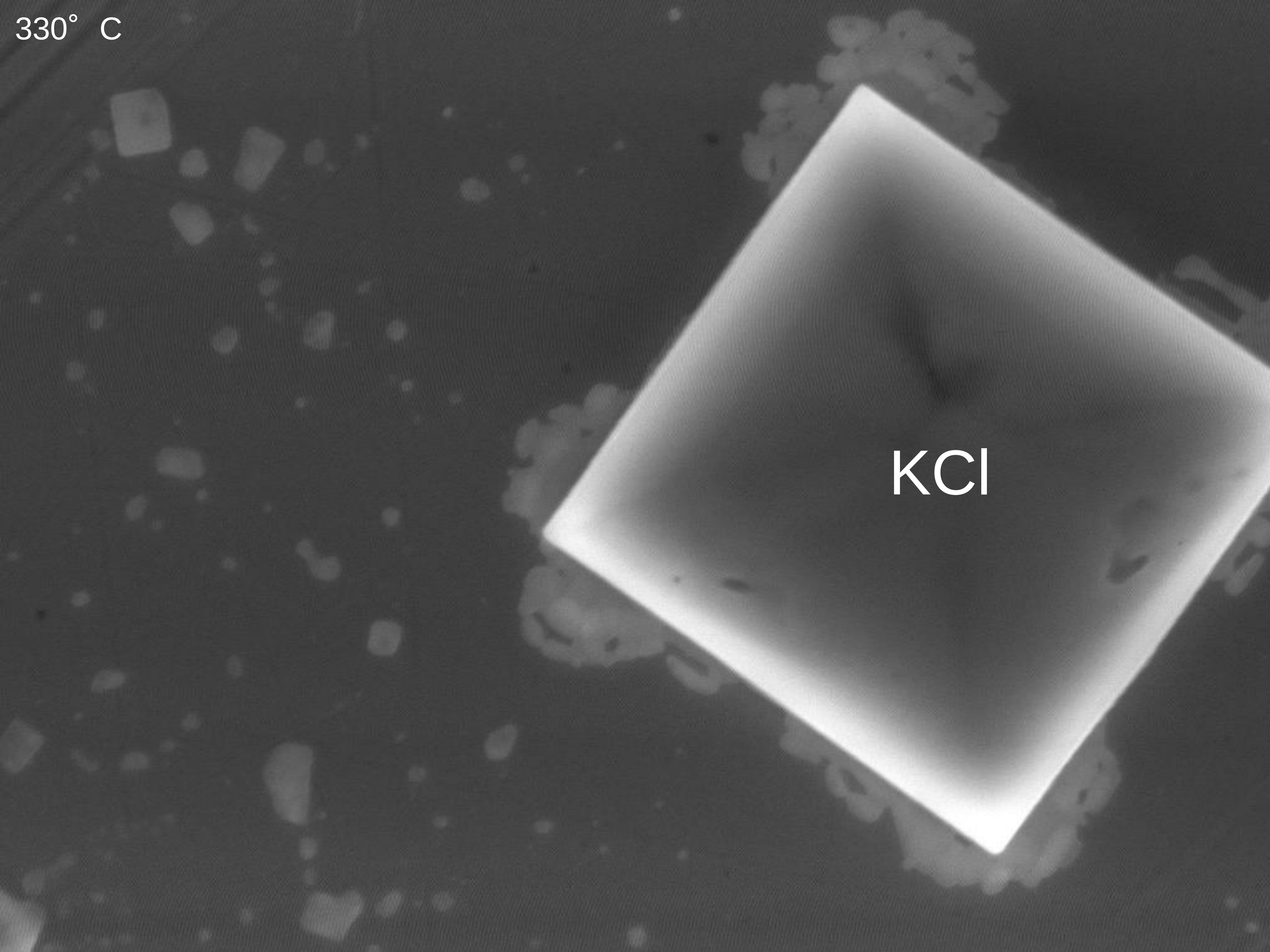
- A KCl particle is observed during the exposure at 400ºC. The corrosion products formed at the position of the initial KCl particle is the studied in detail after the exposure.

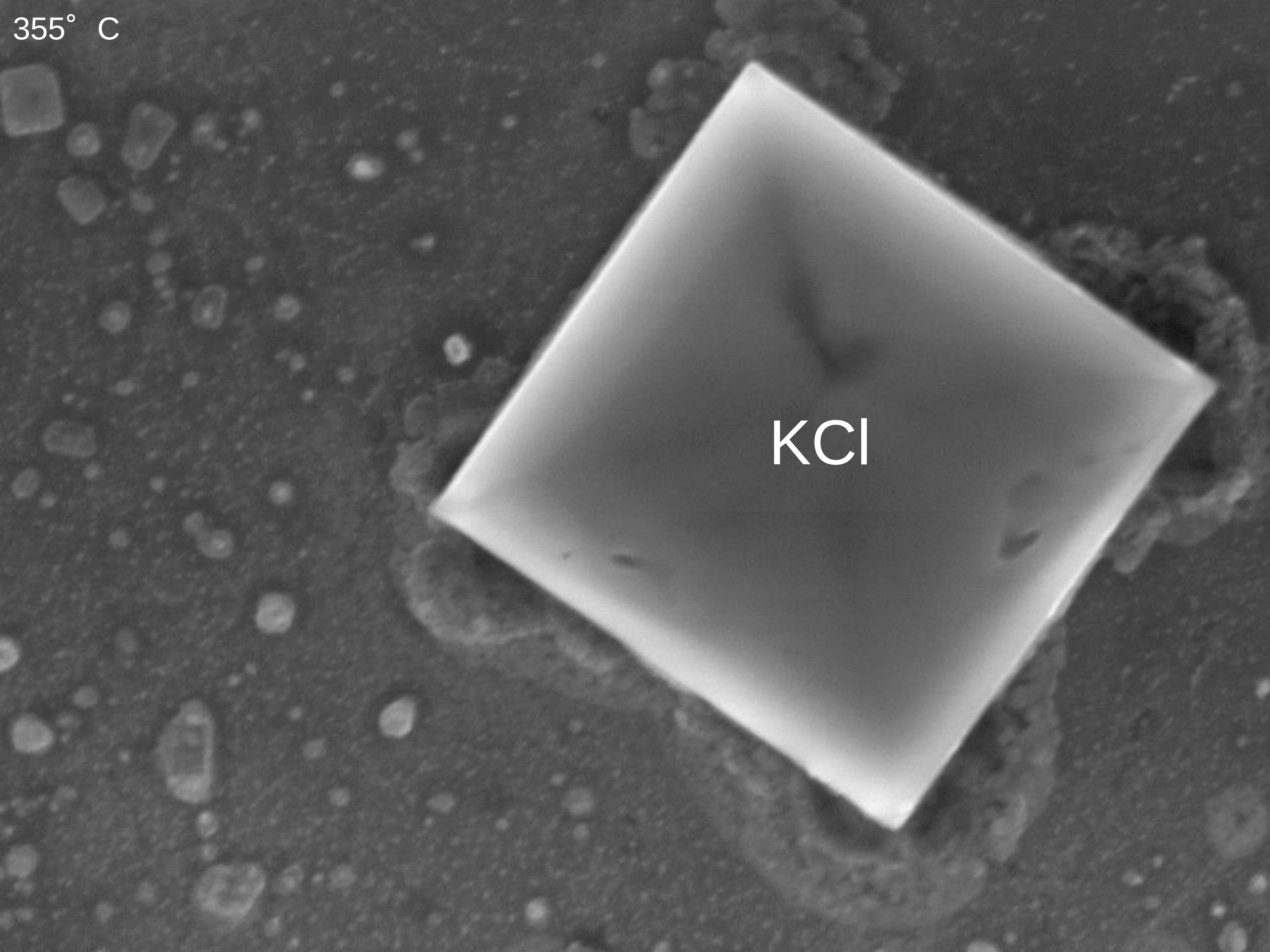
Jonsson, et al., ” Corrosion Science”, 2011, Vol. 53, pp. 2233.

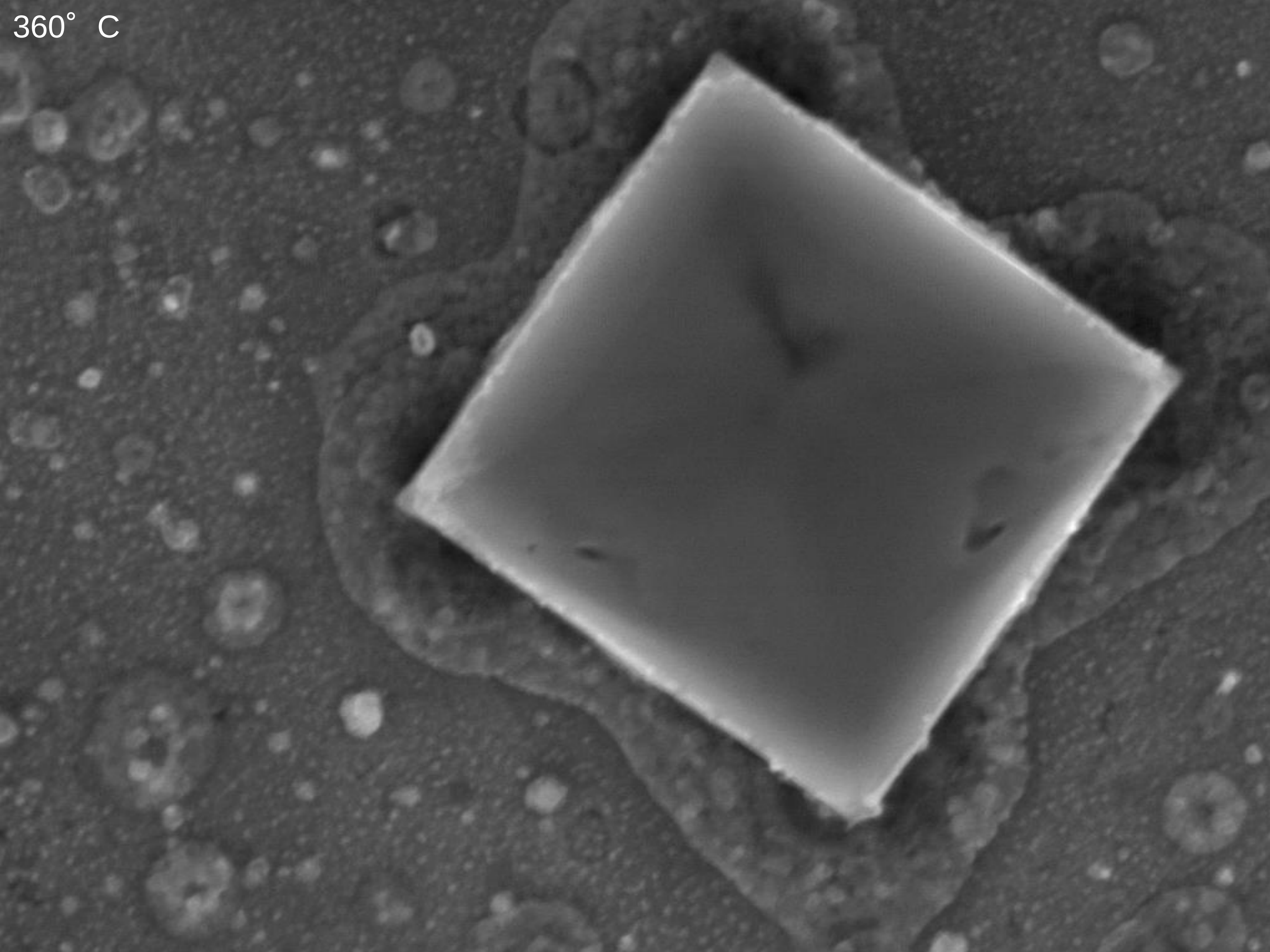
T22 with KCl(s)

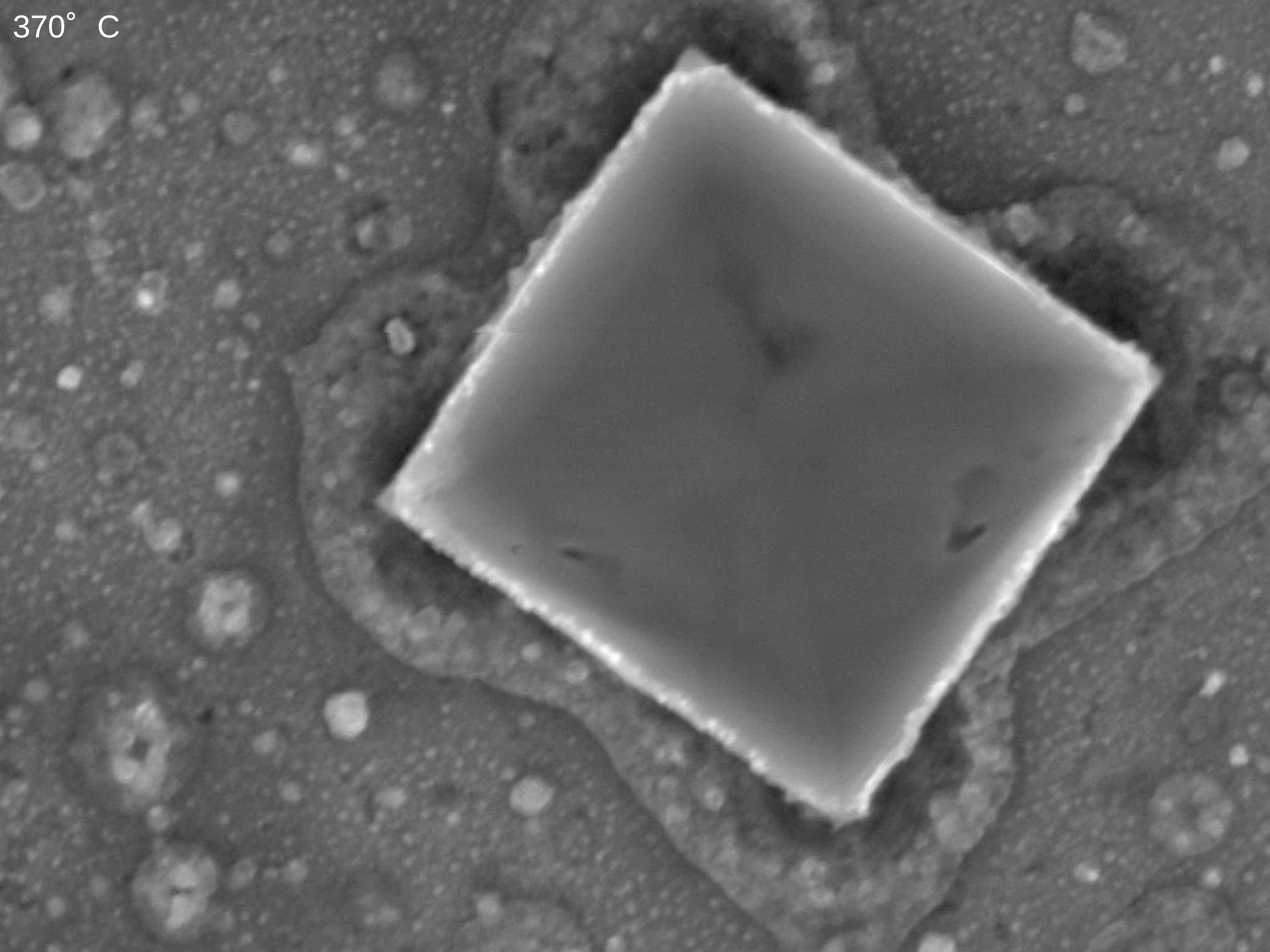
Before exposure

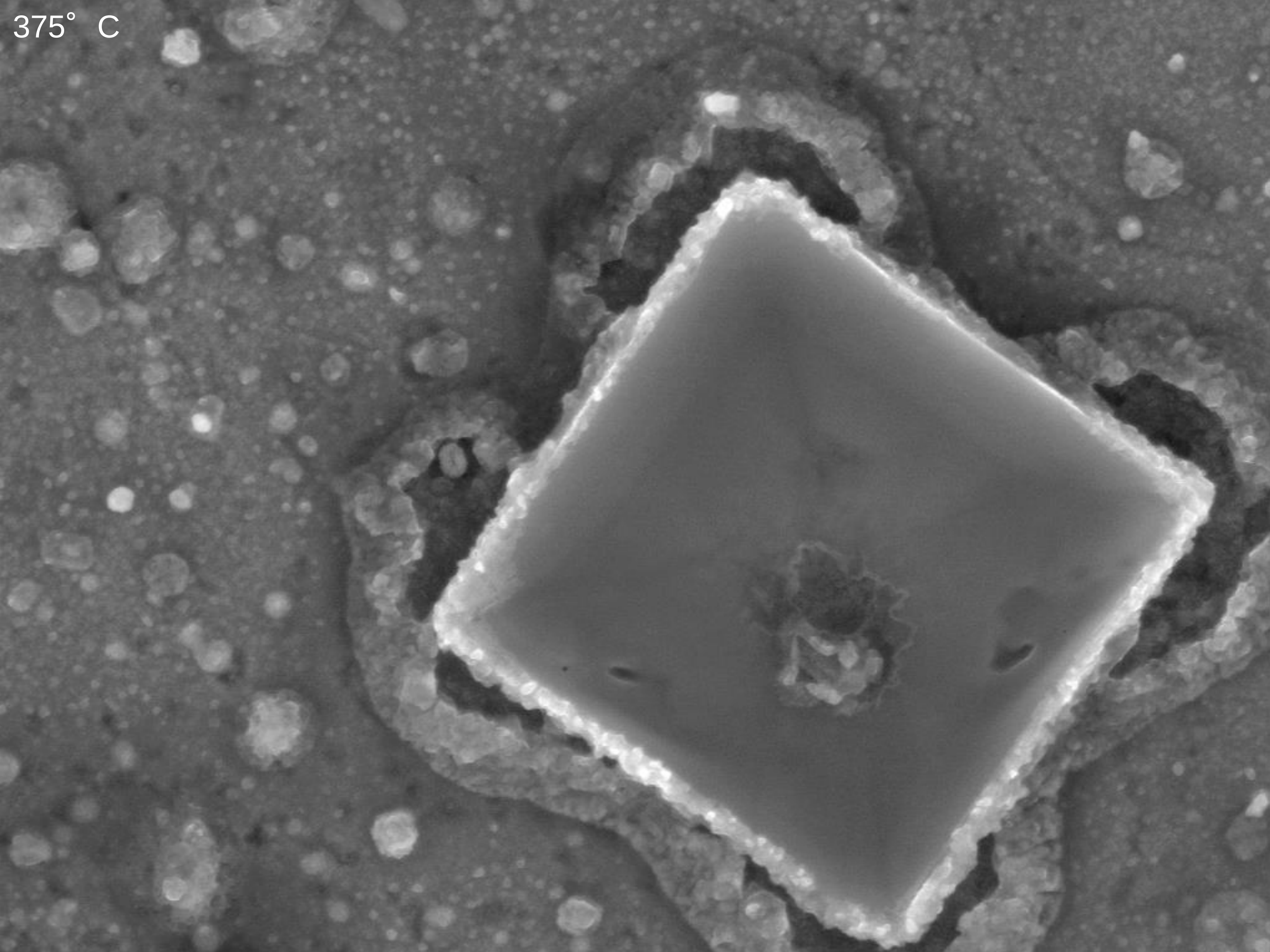


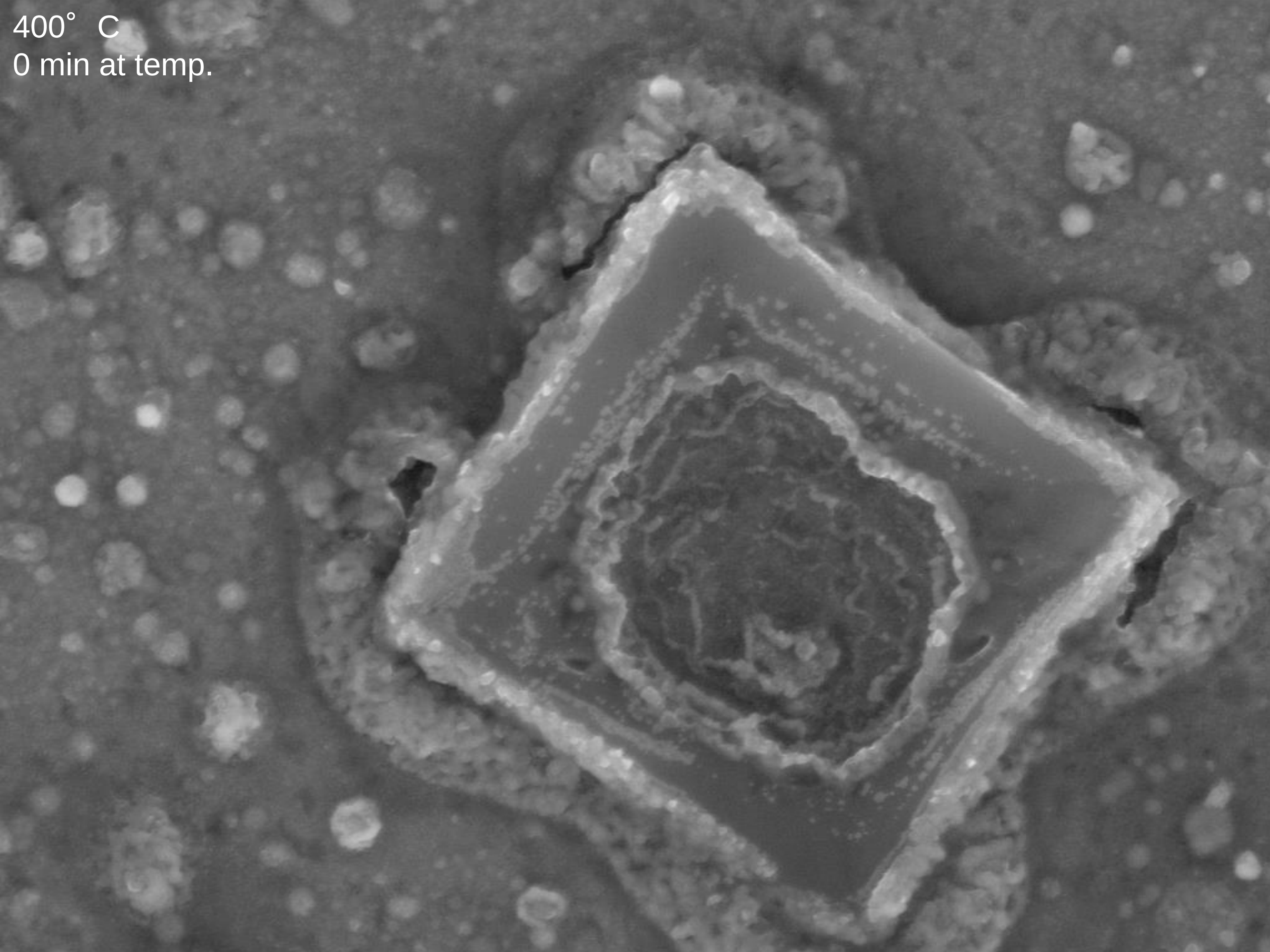

330° C
KCl


355° C
KCl

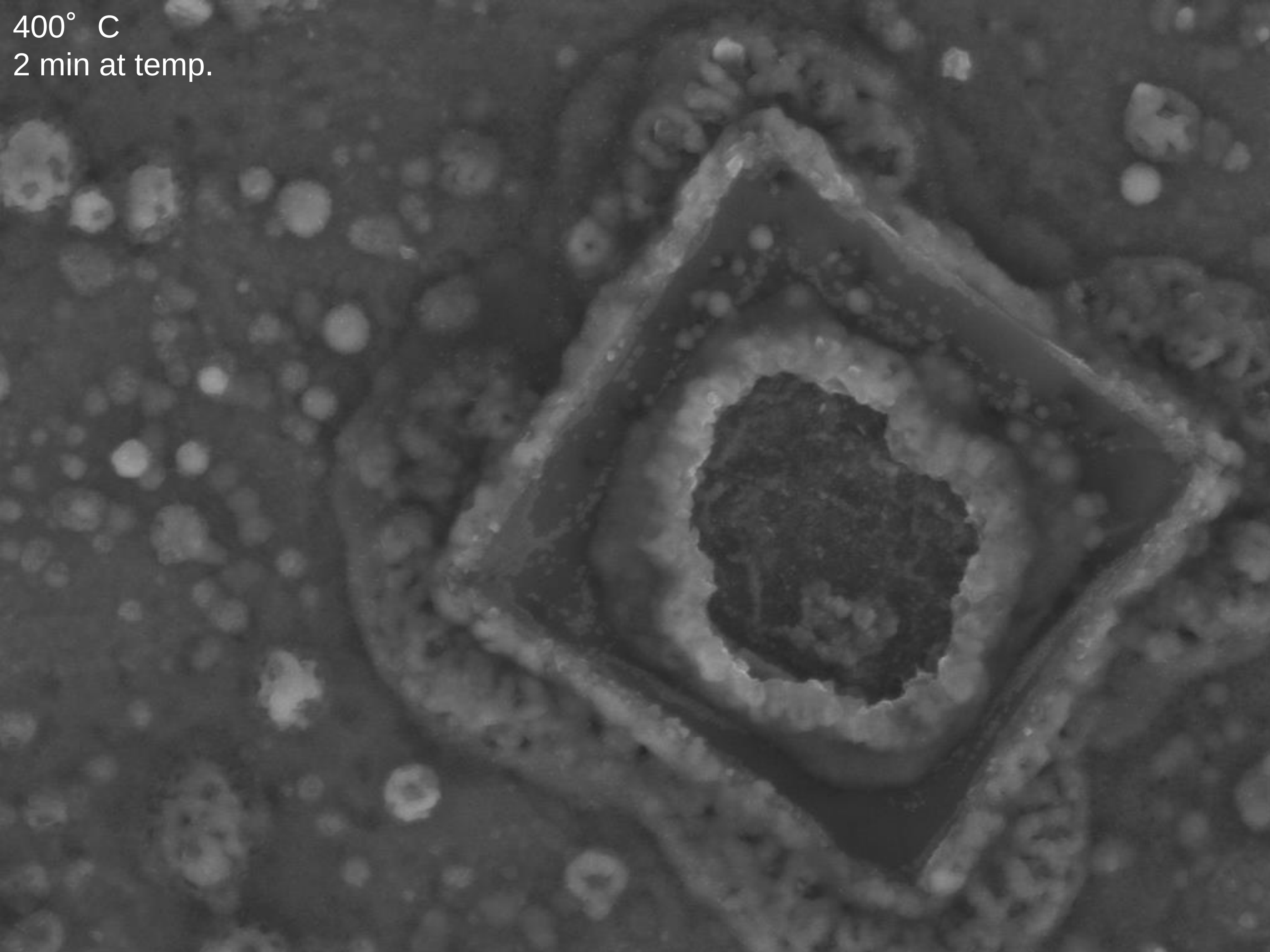

360° C


370° C

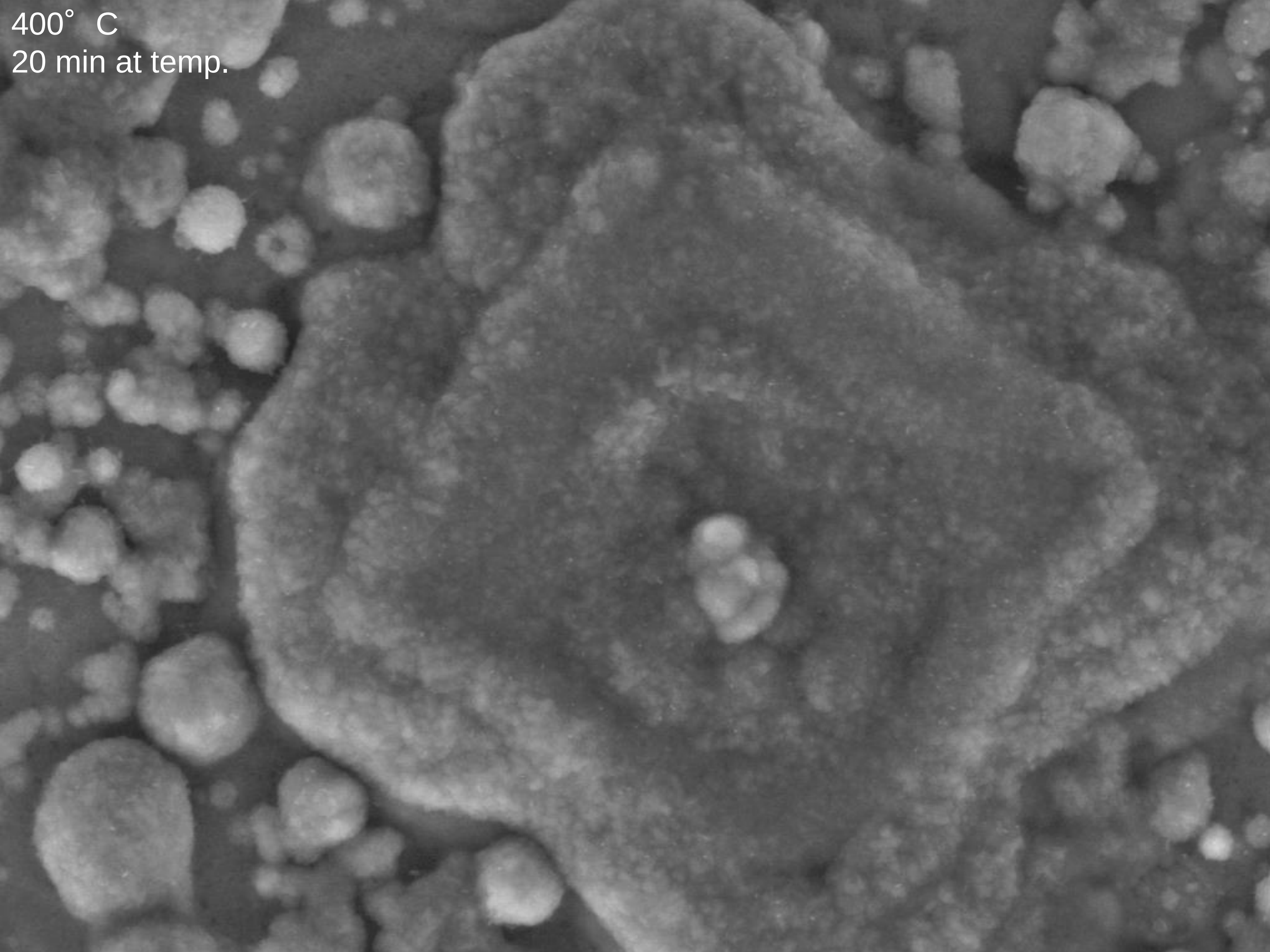

375° C



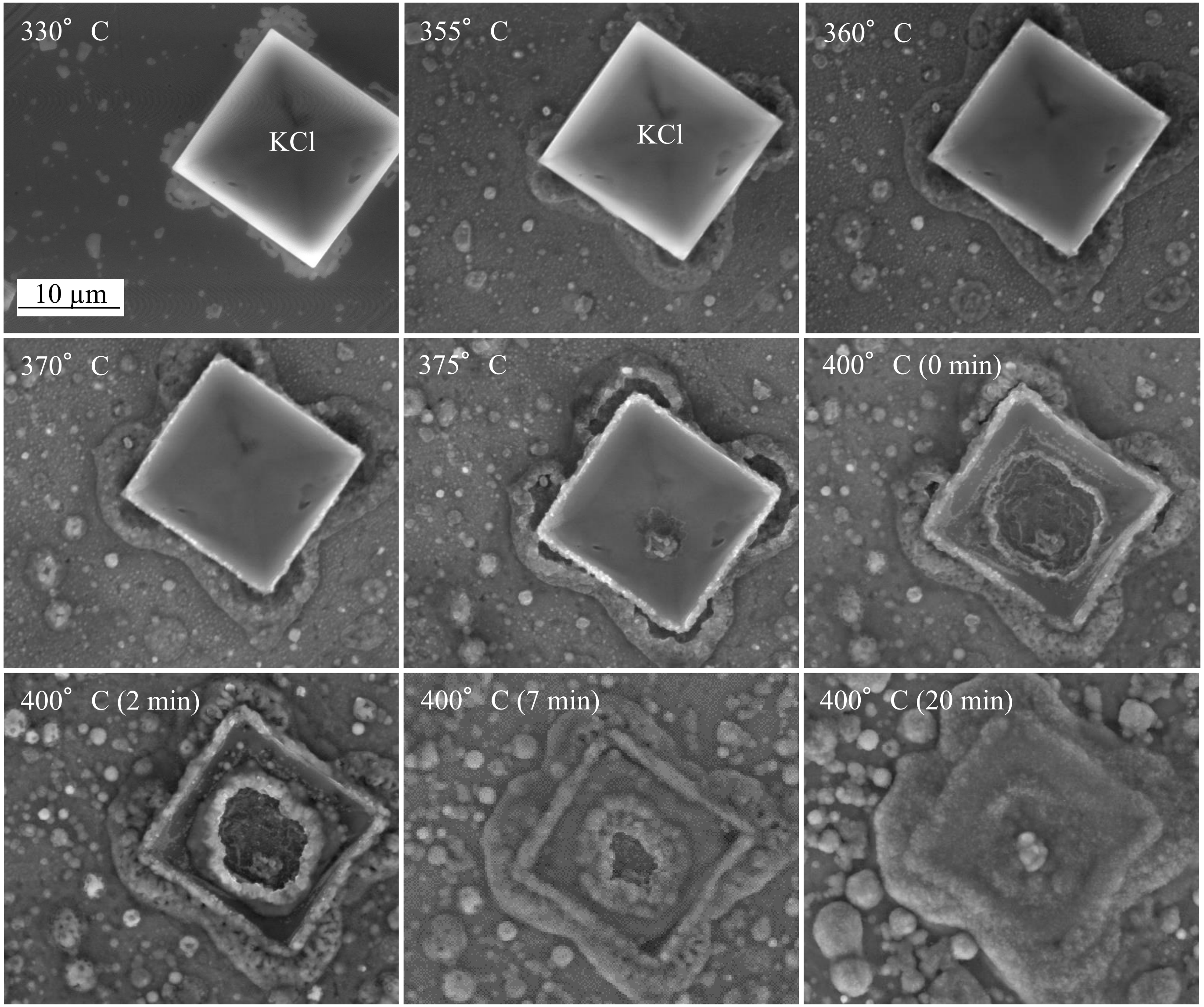
400° C
0 min at temp.



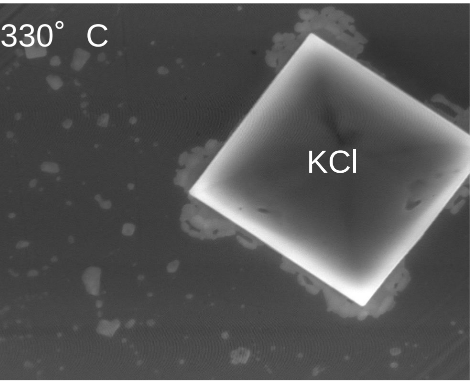
400° C
2 min at temp.

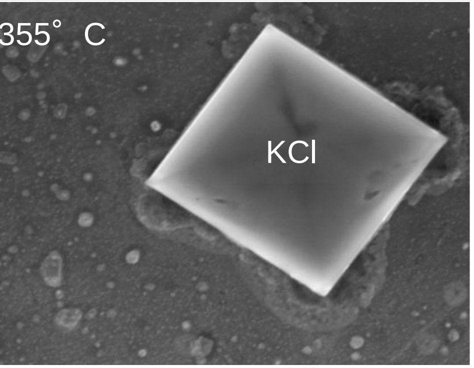


400° C
20 min at temp.

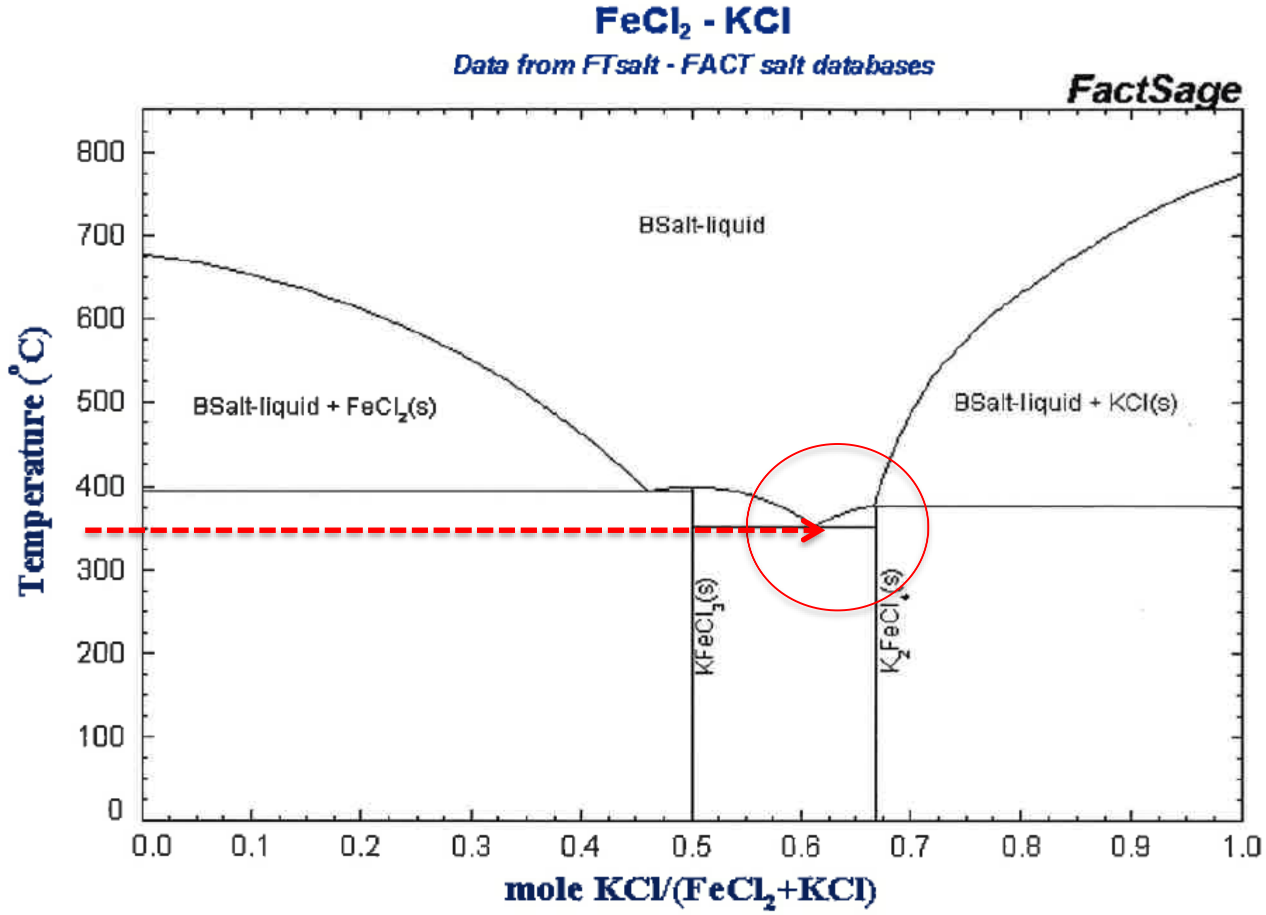

330° C
KCl
10 µm
355° C
KCl
360° C
370° C
375° C
400° C (0 min)
400° C (2 min)
400° C (7 min)
400° C (20 min)

Role of low-melt liquid in corrosion



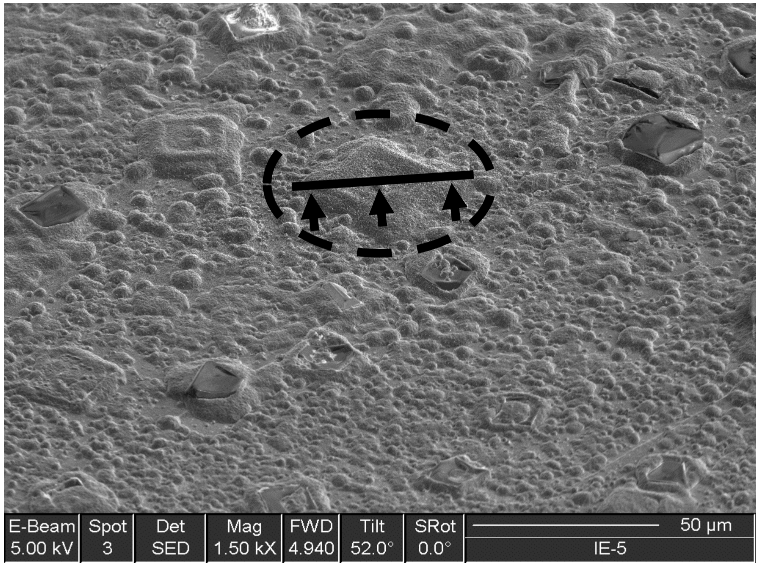


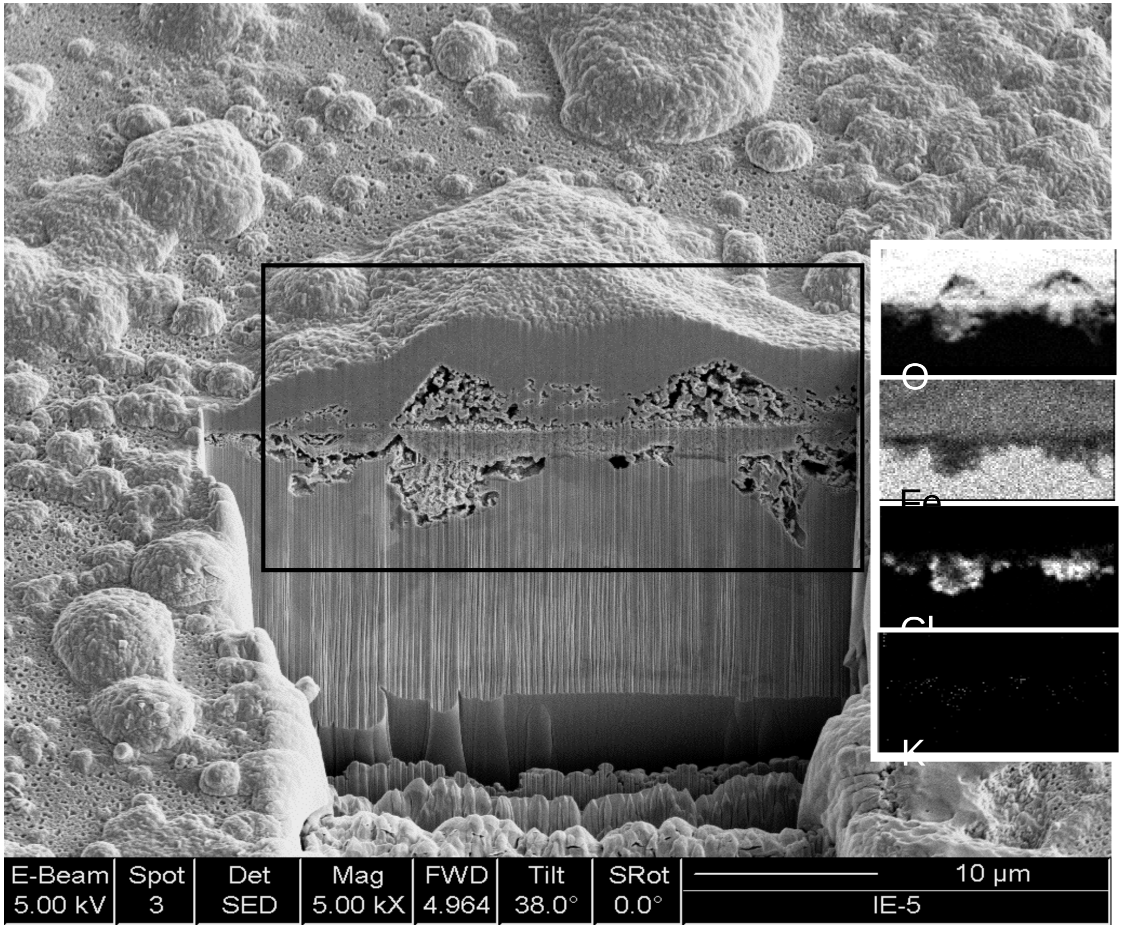
The minimum melting point in the $FeCl_2$/KCl system is about 350° C



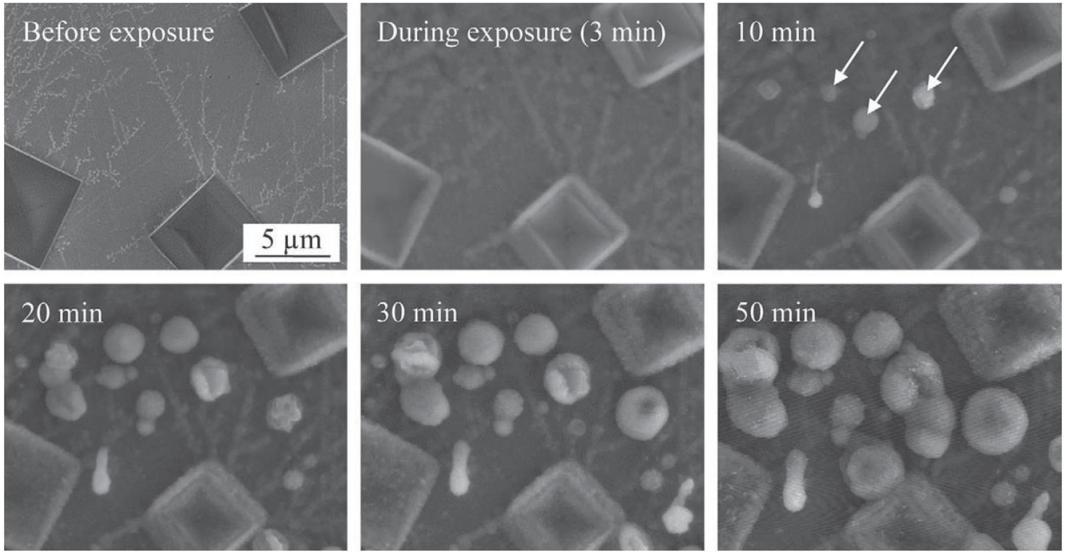
The sudden onset of rapid hematite growth at 355° C is suggested to be caused by the formation of a $FeCl_2$/KCl eutectic melt on the surface

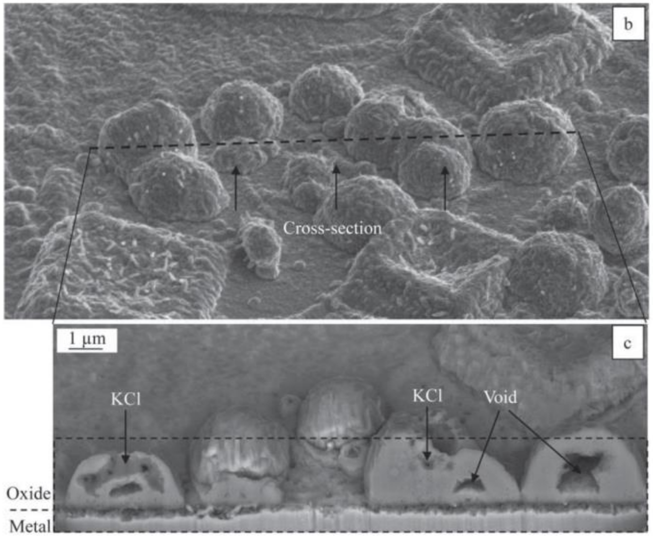
Chemical analysis of the corrosion products

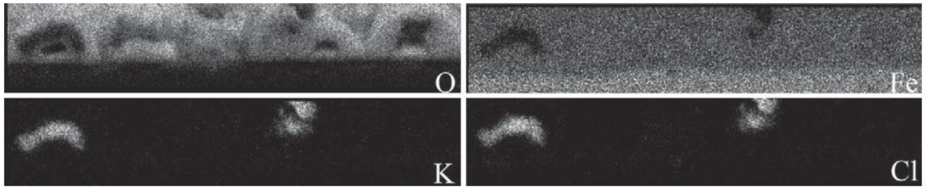




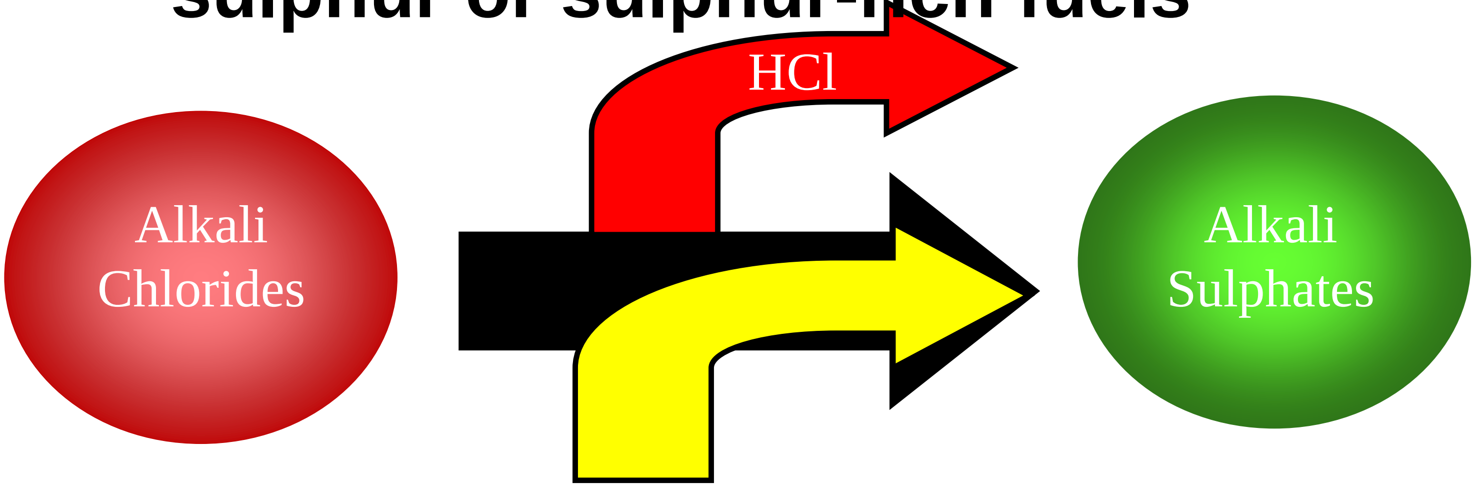
Chemical analysis of the corrosion products







Change the fireside environment by adding sulphur or sulphur-rich fuels

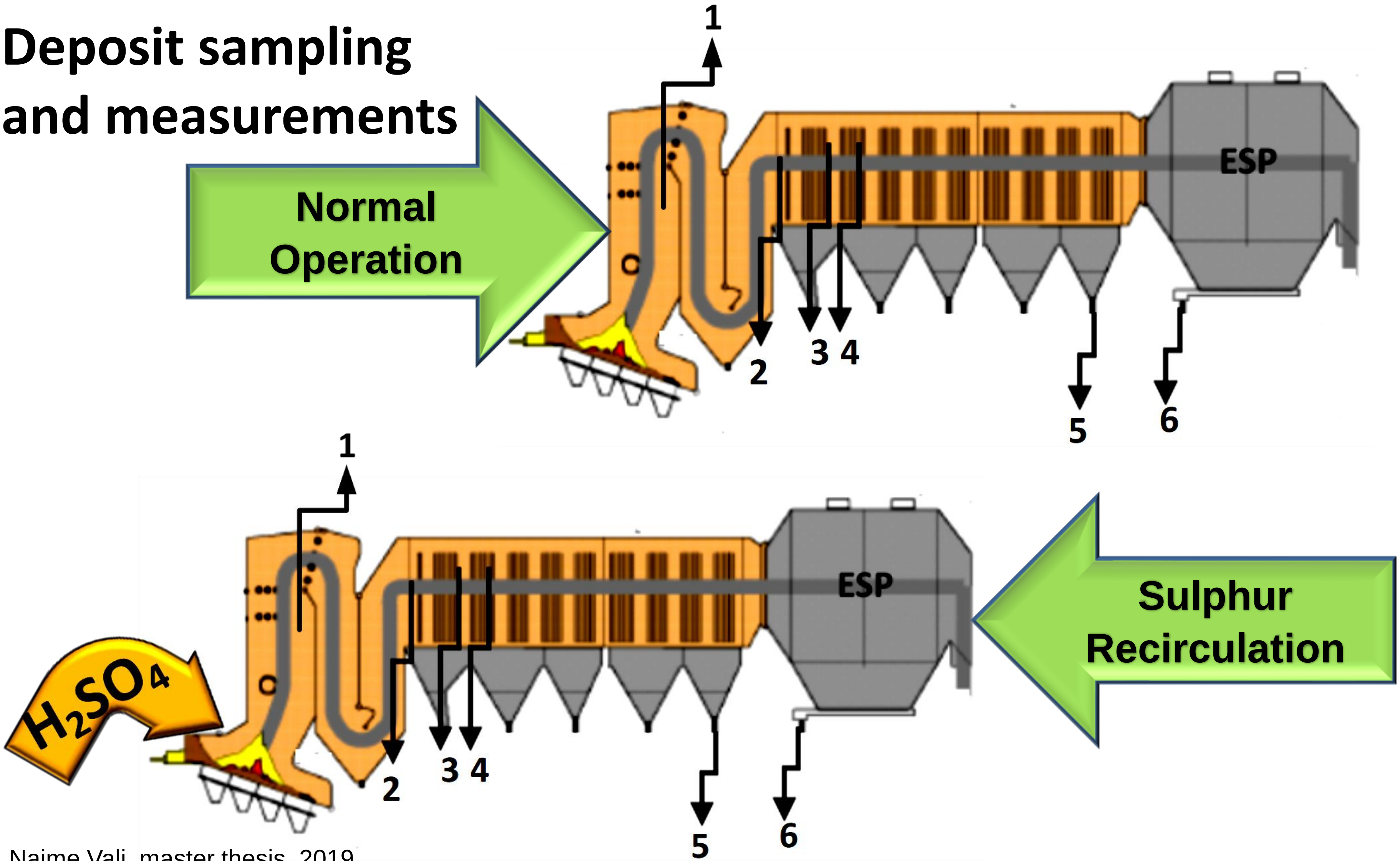


Adding sulphur or sulphur-rich fuels

- Elemental sulphur
- Ammonium sulphate
- Sulphur recirculation
- Municipal sewage sludge

Andersson, et al., ”Waste Management”, 2014, Vol. 34, pp. 67.

Deposit sampling and measurements



Naime Vali, master thesis, 2019.

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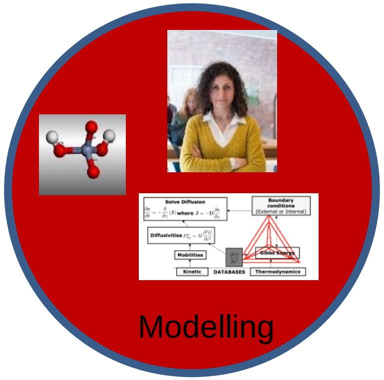
We created a strong computational platform for thermodynamic/kinetic modelling of high temperature oxidation.

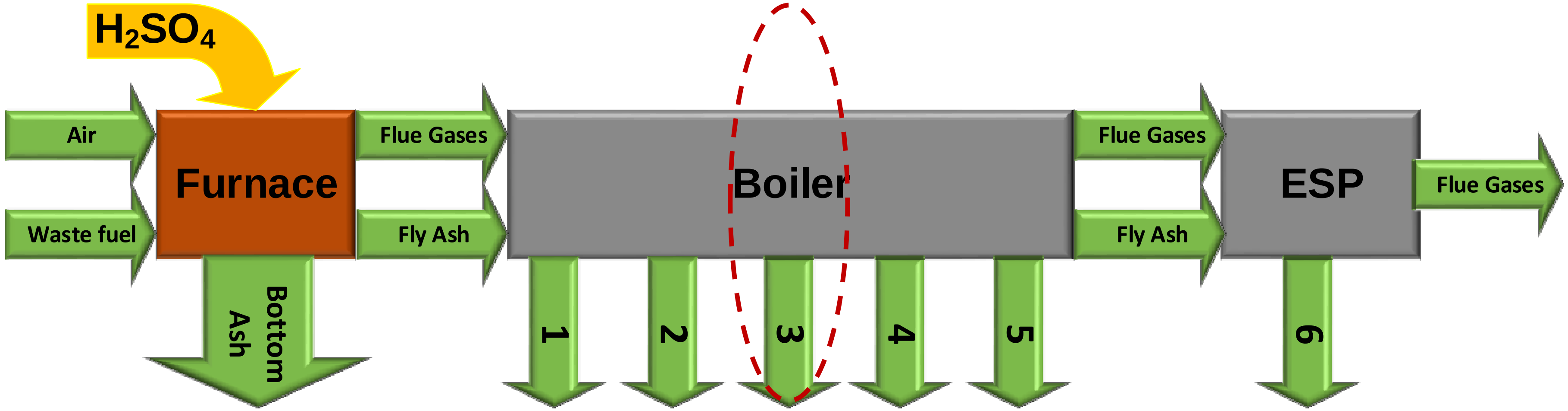


Our current tools can be used in different ways:

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

Equilibrium calculations to predict possible phases and explain the process,

Boiler applications: Equilibrium calculations using FactSage: master thesis from Borås university,



- ✓ **Assumptions:**
- ✓ **No kinetics, Thermodynamically stable compounds are considered**
- ✓ **Reference: 1 Nm^3 of dry flue gas**
- ✓ **Mass loss is negligible**
- ✓ **Flue Gas: Unchanged**

Naime Vali, master thesis, 2019.

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!

Acknowledgments

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Naime Vali and Annita Petersson: Borås university

Thanks for your attention!