HTC Project 3b

High Temperature Corrosion in systems for heat storage (corrosion in melts for concentrated thermal solar power)

Presented by LG. Johansson, E . Hamdi and
P. Dömstedt

Project Organization

- *Project leader:* LG Johansson, Chalmers
- *Companies:* SANDVIK, KANTHAL® Part of Sandvik Group, Azelio
- *Researchers in HTC :* LG Johansson, JE Svensson, C Geers, P Szakalos
- *PhD students:* E. Hamdi, P. Dömstedt

Project plan

- **Project Goals:**
- Investigate corrosion processes relevant to Concentating Solar Power (CSP) plants in order to generate new ideas and strategies for solving the serious materials challenges facing this industry. The project deals with the interaction between melts used for heat transport (HTF) and heat storage and focuses on the mechanisms of corrosion attack

Project plan

The project consists of two parts:

- Corrosion in carbonate and chloride melts

AND

- Corrosion in an Al-Si eutectic melt

Background

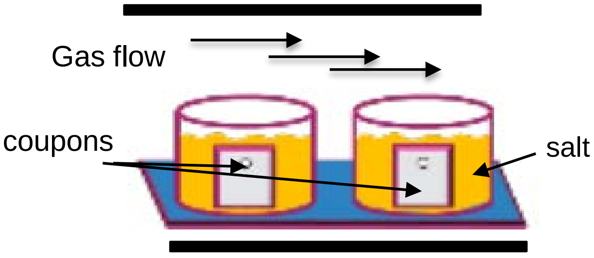
- State-of-the-art CSP plants that generate power in a steam turbine presently use a eutectic mixture of sodium nitrate and potassium nitrate (= “solar salt”). Because that mixture decomposes spontaneously > 600ºC, the drive towards higher power efficiencies and higher temperatures (>700ºC) has meant that more thermally stable HTF´s, based on alkali carbonates, chlorides, fluorides or liquid metals are now being considered. However, today’s plants are constructed of materials that are unable to withstand corrosion at the higher working temperature in the presence of the “new” HTF´s.

High Temperature Corrosion of alloys in Molten Salts for Heat Storage

Part I: Molten Salts

EXPERIMENTAL SET UP

Old system



- Partial immersion of coupons
- Refilling is needed for long exposures
- ***After Exposure "for carbonates salt":***
  coupons are washed out in warm water (60 ºC) with ultrasonic treatment
- Gravimetric investigations, not possible!



“DREAM” SET UP!

- Fully immersion of coupons
- Carbonate blend freezes ~ 450 ºC
  - If the salt freezes while the coupon is still immersed
  - Salt needs to be washed out, 60 ºC with ultrasonic
  - Hard to evaluate highly biased surface (leached)
  - Weigh the coupons after the exposures!

7x longer

Longer cylinders,
Longer crucibles?

Temperature 750-1000 ºC
Protect the cylinders!

Two cylinders,
More crucibles
6*2= 12 coupons at one exposure,
same conditions

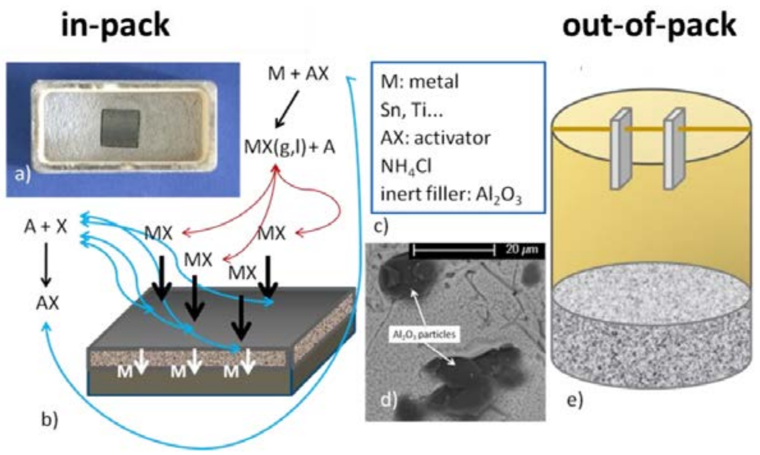
NEW SET UP,

CHALLENGES & SOLUTIONS

1.Cylinder, 253 MA

At high temperature exposures, may not survive?!

<u>Aluminum diffusion coated furnace cylinders</u>



C. Geers, "Inhibition of coking and metal dusting on conventional alloys by using a nickel-tin intermetallic coating," 2013.

NEW SET UP,

CHALLENGES & SOLUTIONS

- ✓ Longer crucibles, longer exposures without refilling.
- ✓ Coupons are totally immersed in the salt.
- ✓ Easier removal of salt.

EXPERIMENTAL SET UP

New set up

Aluminum diffusion coated vessels

Longer crucibles 100 mm

- ✓ Longer crucibles, longer exposures without refilling.
- ✓ Coupons are totally immersed in the salt.
- ✓ Easier removal of salt.

EXPERIMENTAL SET UP (CONT.)

Molten Salt	**Nitrates (60 wt% $NaNO_3$- 40 wt% KNO_3)**	**Carbonates (33 wt% Li_2CO_3 -32 wt% Na_2CO_3- 34 wt% K_2CO_3)**	**Chlorides (65 wt% KCl- 32% $MgCl_2$)**
Gas	Air	CO_2	Argon
Temperature Range ºC	550-680	750-900	800-1000

- ✓ Ar, CO_2 connected
- ✓ Temperature Range ***~ 1000 ºC***
- ✓ Long exposures without refilling
  10-13 g of salt instead of ~1,7 g
- ✓ Role of oxygen and water as crucial impurities
- ✓ Sample dimensions

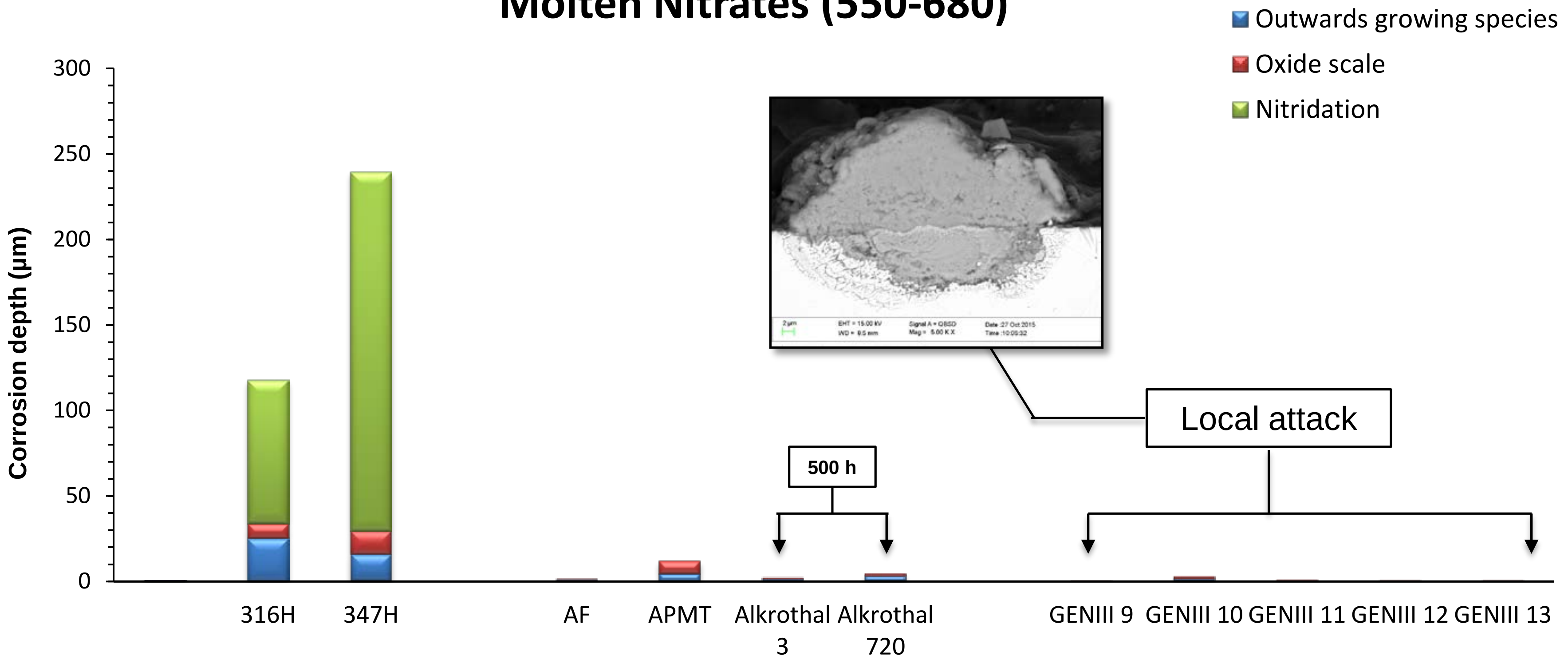
NEXT SET UP!!

Planning to extend our work

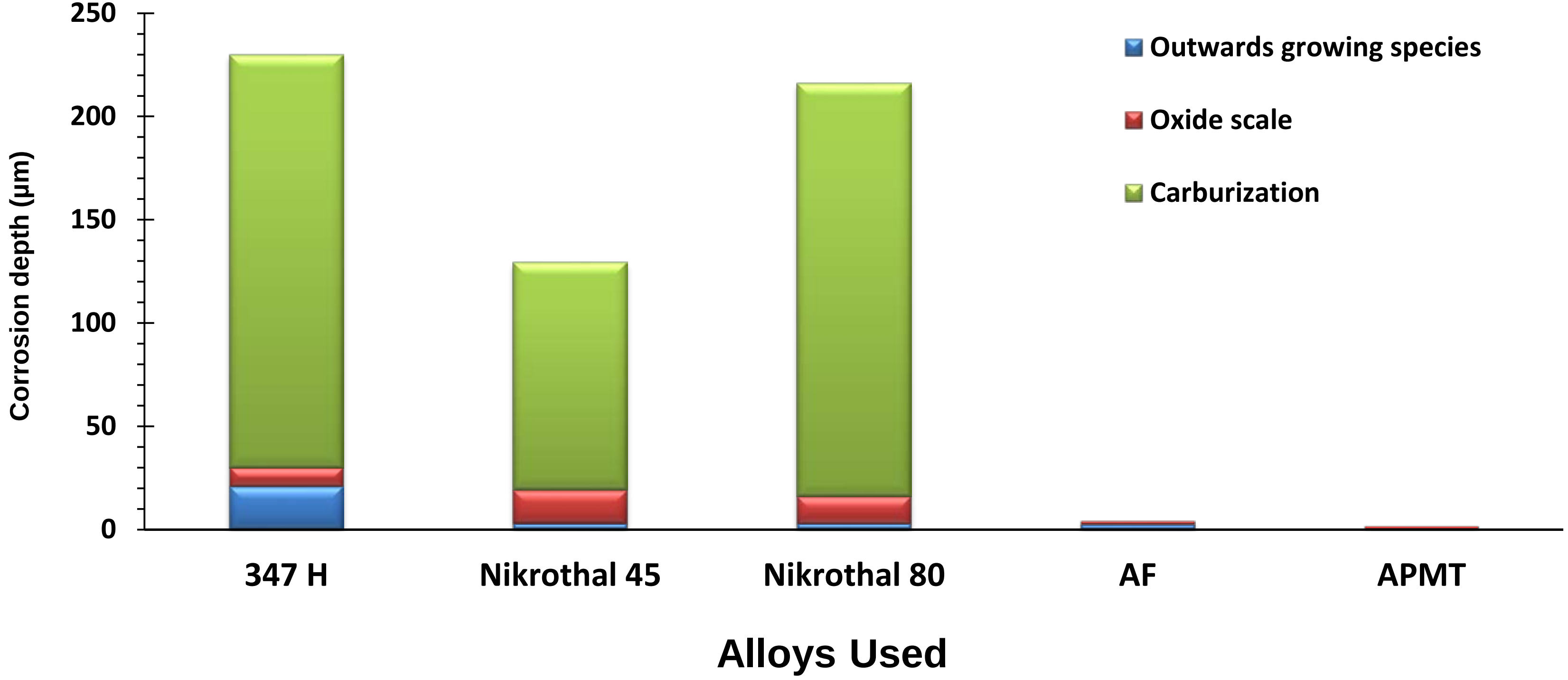
Building new set up!

Suggestions?!!

Corrosion of Chromia vs. Alumina Forming Alloys
Molten Nitrates (550-680)



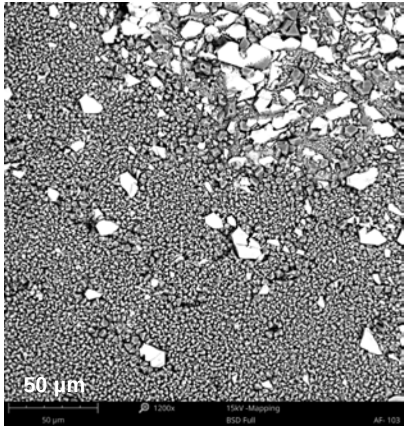
Corrosion of Chromia vs. Alumina Former Alloys
Molten Carbonates



NEW EXPOSURES AT 900 ºC

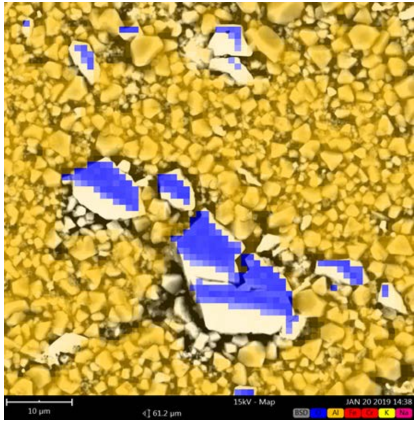
Kanthal AF

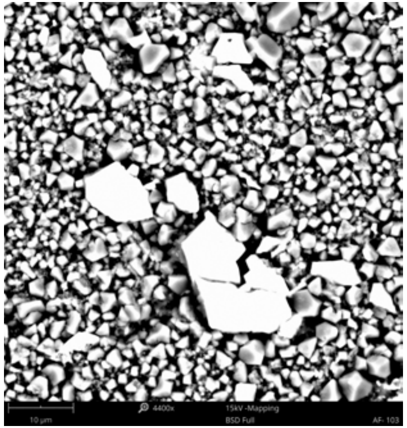
- Macroscopic analysis
- Optical imaging
- SEM/EDX on BIB prepared cross sections
- Structural characterization



In progress

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	66.09	50.91
13	Al	Aluminium	29.84	38.77
26	Fe	Iron	2.82	7.59
24	Cr	Chromium	0.83	2.07
19	K	Potassium	0.25	0.47
11	Na	Sodium	0.18	0.19





10 µm

ACKNOWLEDGMENT

“Esa Väänänen”

Research Engineer

Chemistry and Chemical Engineering

Chalmers University of Technology


THANK YOU ☺

Energimyndigheten

The High Temperature Corrosion Centre, Chalmers

HTC 3b - Corrosion resistant materials in molten Al-Si alloy

Peter Dömstedt, Mats Lundberg and Peter Szakálos

KTH Royal institute of Technology, Division of Surface & Corrosion Science, Stockholm

peterdom@kth.se,

KTH VETENSKAP OCH KONST

AZELIO SOLAR POWER WHEN YOU NEED IT

SANDVIK

KANTHAL® Part of Sandvik Group

Image Source: *https://investorintel.com/market-analysis/making-graphene-2d-materials-liquid-metal/*

Azelio Technology

- **Stirling** based **CSP** with **TES**
  - **Al-Si alloy** as **PCM**
  - **Na** as **HTF**

- **253 MA** steel with corrosion protective **coating** against **Al-Si** alloy

Al-Si Alloy Corrosion test

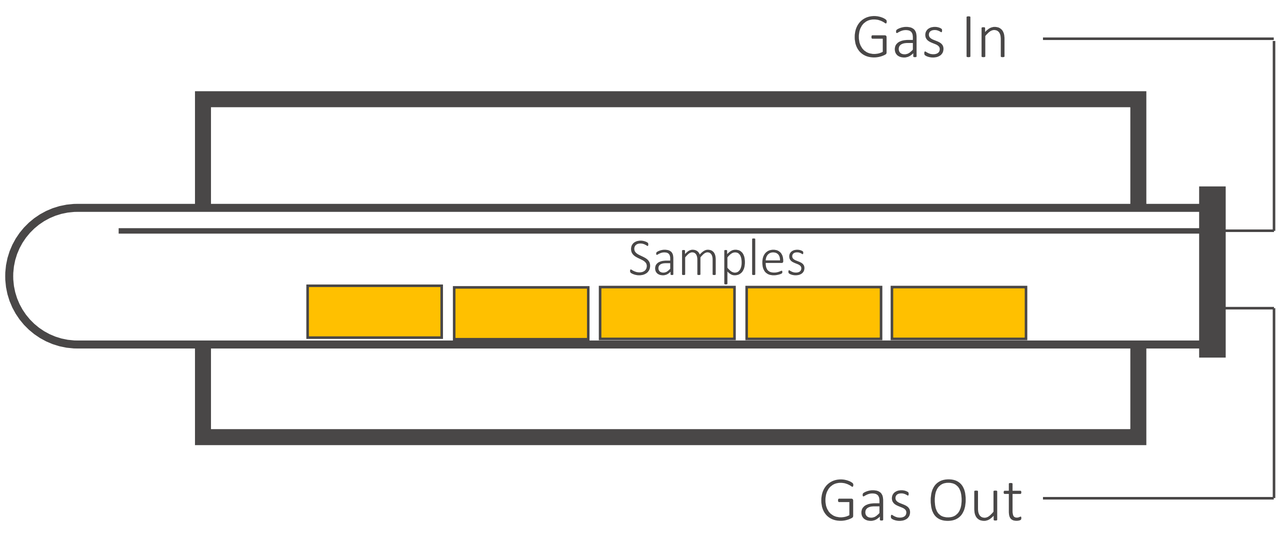
- **Cyclic** exposure from **540-600°C**
  - T_{melt}(Al-Si) – **577°C**

- **COSTA** tube furnace **(KIT)**

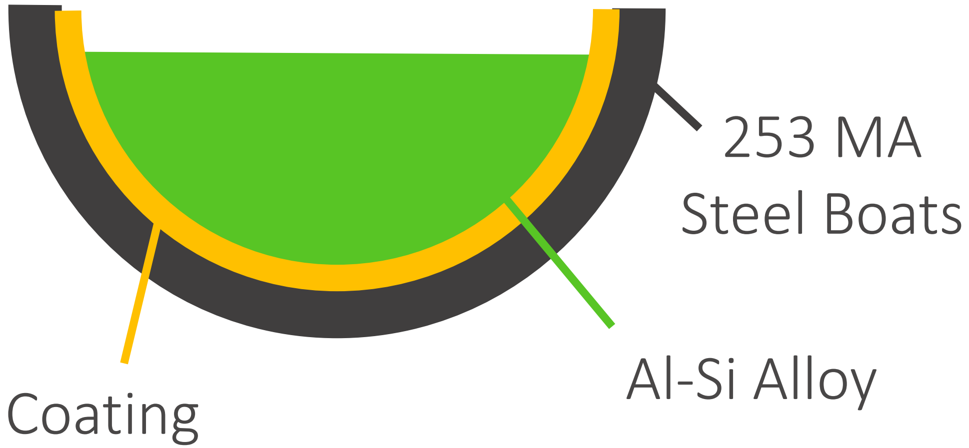
- **253 MA** containers
  - **Coated** on the inside
  - Filled with **AL-Si alloy**

Al-Si Alloy Exposures

Tube Furnace



Samples



Aluminium titanate Al_2TiO_5

- Good **corrosion protection** against **molten Al**
- Low **wettability** with **molten metals**
- Properties of **Al_2TiO_5 coatings:**
  - Good **shock resistance**
  - Stable up to over **1000°C**
  - High **chemical** and **thermal** stability
  - Low **thermal expansion**
  - Low **thermal conductivity**

Collaboration with **Nanoker** (Spain)

- **Dopants** altering coating **properties** (thermal expansion)

Other coatings

- Titanium Diboride **(TiB_2)**
  - high **hardness** and **wear resistance**
  - high **thermal expansion** and **conductivity**
- Boronising **(FeB, Fe_2B)**
  - high **hardness** and **wear resistance**
  - high **thermal expansion** and **conductivity**
- Yttria Stabilised Zr **(YSZ)**
  - High **chemical** and **thermal** stability
  - Intermediate **thermal expansion**

Steel/Coating Properties

Material/Coating	Therm. Expan. Coef. (10^{-6} 1/K)	Thermal Conductivity (W/mK)
FeB (Boronising)	~ 20	~ 12
Austenitic Steels	~ 15	~ 16-22
Fe_2B (Boronising)	~ 10	~ 20
Ferritic/Martensitic Steels	~ 10	~ 25-30
TiB_2	~ 7	~ 25
YSZ	~ 5	~ 1
Al_2TiO_5	~ 1	~ 1.5

References

1. https://www.azelio.com/
2. https://keranova.se
3. https://nanoker.com
4. https://www.worldscientific.com/doi/abs/10.1142/S0218625X06008670
5. H. Hayashi, et al., Thermal expansion coefficient of yttria stabilized zirconia for various yttria contents, *Solid State Ionics*, **176**(5-6): p. 613-619, 2005
6. H. Zhao, et al., Morphology and thermal conductivity of yttria-stabilized zirconia coatings, *Acta Materialia*, **54**: p. 5195–5207, 2006.
7. https://www.azom.com/properties.aspx?ArticleID=52
8. http://avionmfg.com/pdfs/Boronizing-AVION.pdf
9. https://www.azom.com/article.aspx?ArticleID=4388
10. https://www.azom.com/properties.aspx?ArticleID=492
11. https://www.ceramtec.com/ceramic-materials/aluminum-titanate/
12. http://folk.ntnu.no/zhiliang/Zhiliangs-Papers-in-PDF-format/ZZ-J043-2008-JECS-Micol%20Grande%20and%20Mari-Ann.pdf
13. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4872694/