High temperature corrosion problems during gasification of biomass and waste

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CHALMERS

CORTUS ENERGY

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Background - gasification

- Ideally: Use any carbon source for producing synthesis gas (CO/H_2)
- Use as raw material or use for heat/power production

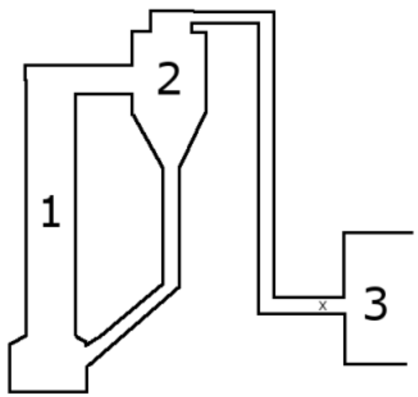
Field exposures, Värö

- Forest based feedstock
- CFB process
- Traditional bed material

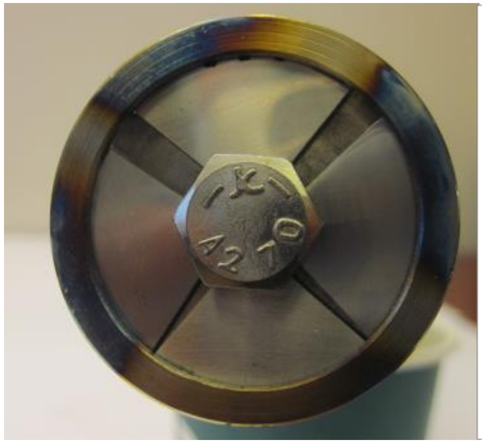
	H_2	CO_2	H_2O	CH_4	CO	Remarks
Värö	10-15	10-15	10-15	5	15-20	Air blown

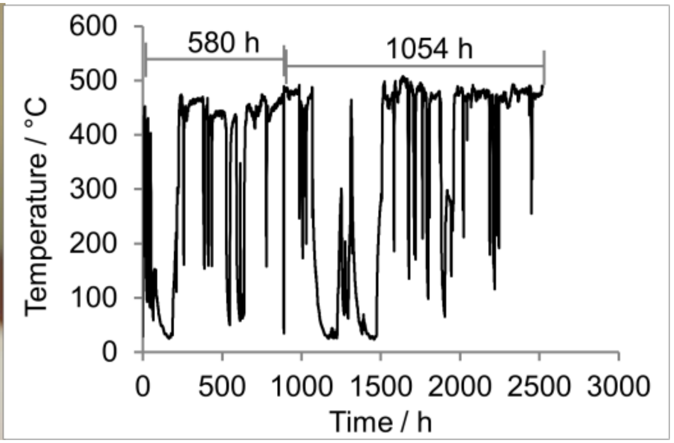
Exposures from Värö - experimental

- Three exposures were performed on different occasions in a non-cooled probe at the inlet of the lime kiln
  - One exposure 20 min (4 min above 350°C)
  - One intermediate exposure (580 h above 350°C)
  - One long-term exposure (1054 h above 350°C)



1:Gasifier, 2: Cyclone, 3: Lime kiln
X: Position of corrosion probe

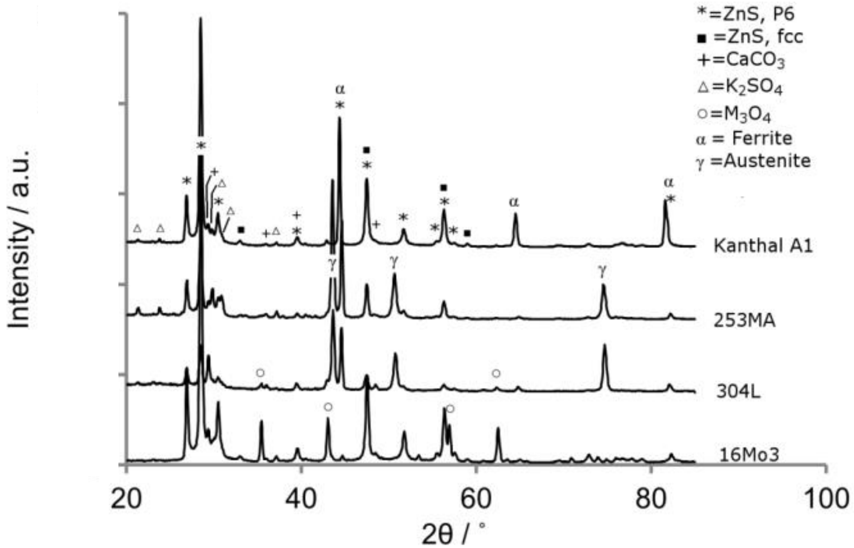


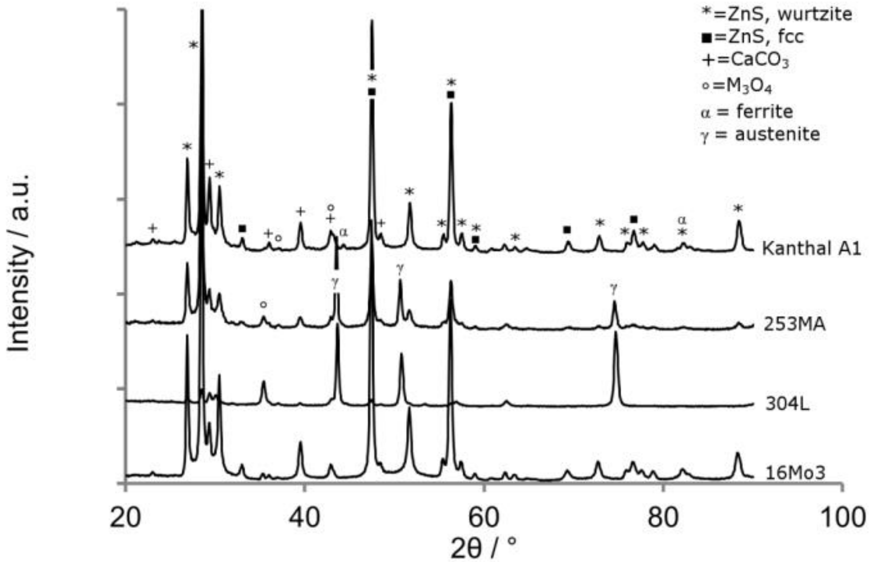


Exposed materials

Material	Fe	Cr	Ni	Si	Mn	Övrigt
16Mo3	Bal	-	-	-	0.4-0.9	Mo 0.25-0.35
253MA	Bal	20.75	11.11	1.61	1.44	Ce
304L	Bal	18.25	8.05	0.28	1.63	
Kanthal A1	Bal	21.2	-	0.18	0.08	Al 5.6

Results: XRD results



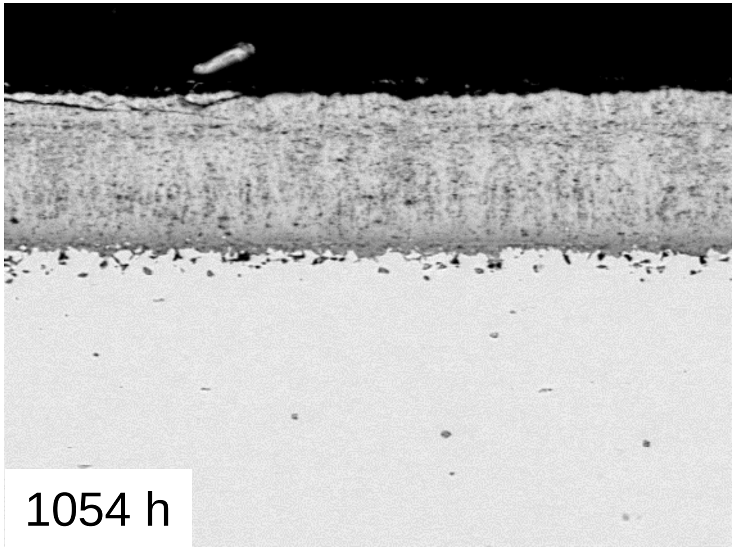


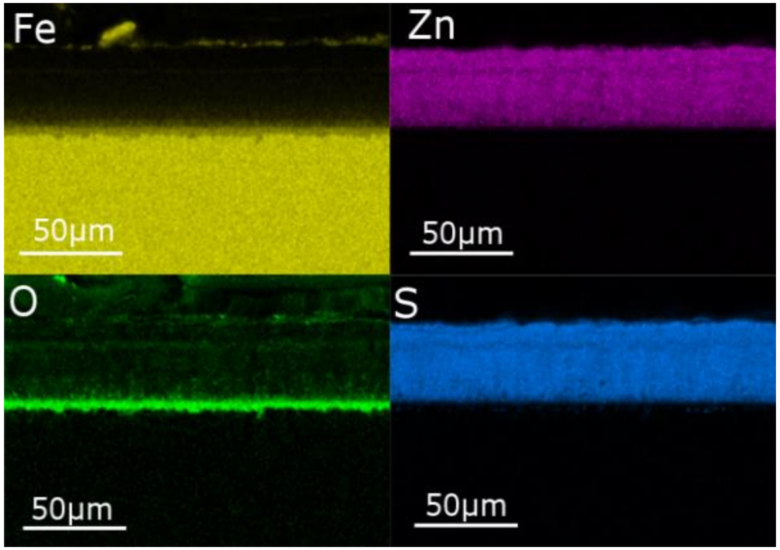
580 h

1084 h

- All exposures show presence of $CaCO_3$ and ZnS
- K_2SO_4 signal only after intermediate exposure
- Ferrite phase clearly distinguishable for intermediate exposure

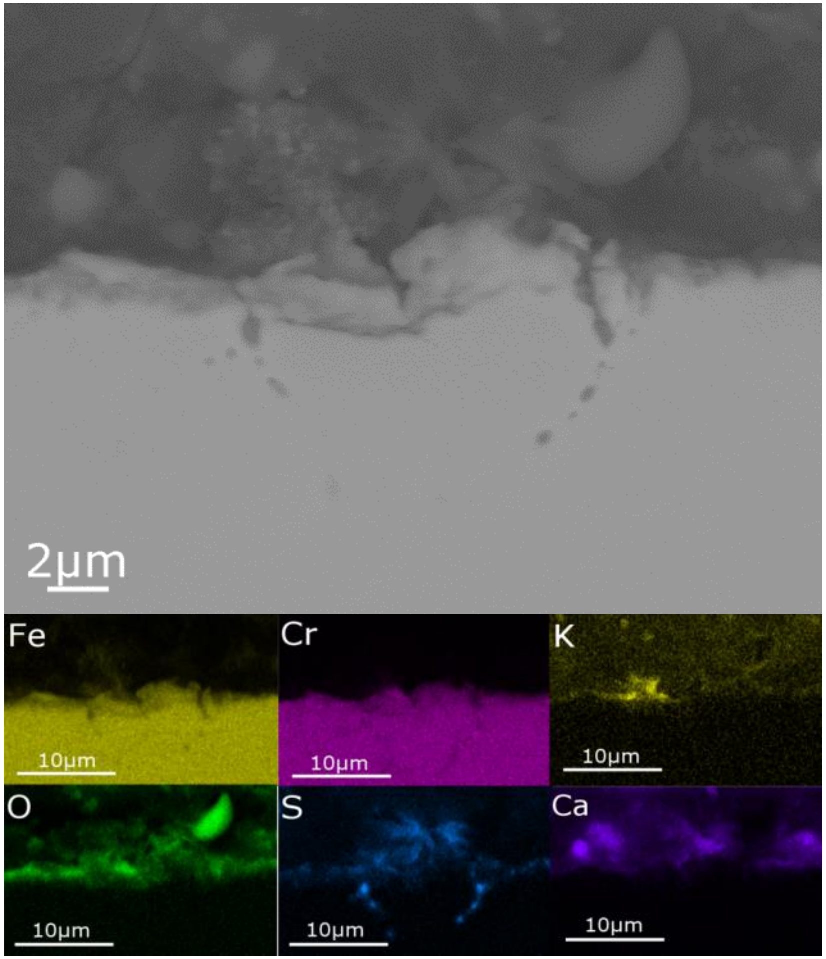
16Mo3 – long-term exposure

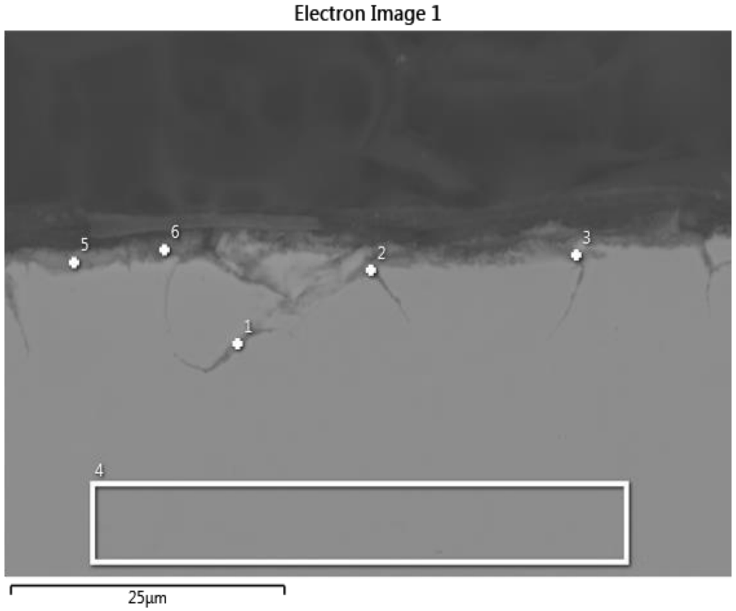




- Fe and O enriched at the metal/deposit interface.
- Zn and S abundant in outer deposit

304L – 1054 h



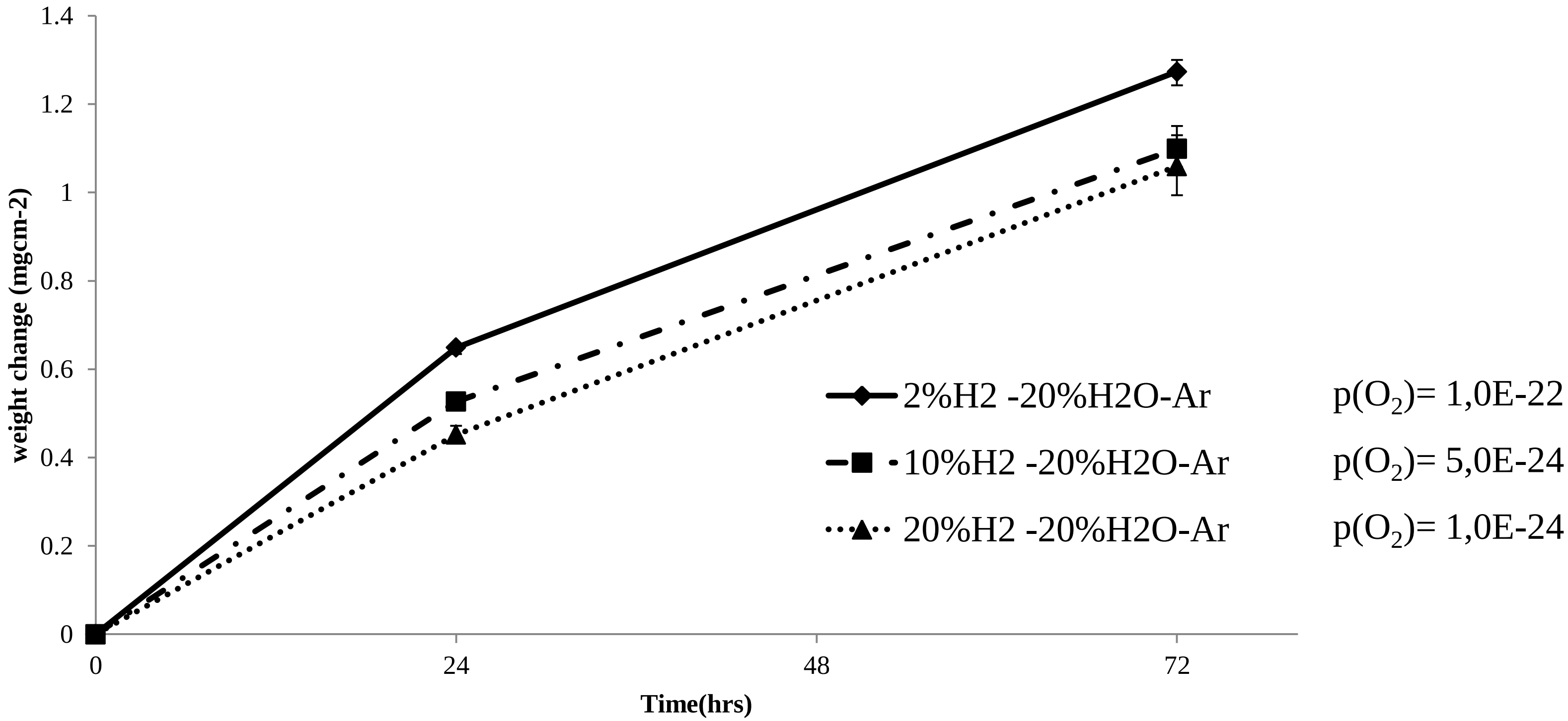


- Both inner oxidation and sulphidation
- Oxidation down to 10µm, sulphidation to 7 µm
- Samples show deposit on surface

Field exposures – final remarks

- Exposures were performed below 500°C and with temperature variations
- Cl levels of the fuel were present in levels comparable to literature. No Cl was detected on the samples
- Metal loss small for 16Mo3
  - Low alloyed steel shows potential at this temperature
- All materials show signal from deposit of ZnS and $CaCO_3$ (XRD)
- Zn was present in significant amounts on the surfaces. Zn is proposed to affect the materials´ behaviour
  - It is argued that zinc plays a key role in capturing sulphur in this environment, thus preventing iron from sulphidation.

Lab. Exposure
The Effect of H_2



- Samples : 304L
- Temperature= 600 °C

Composition [wt%]	Cr	Al	Mo	C	Mn	Si	Minor Add.	Fe	Ni
304L	18,18	-	0,53	0,022	1,53	0,31	Present	Bal.	8,10

Lab. Exposure
The Effect of H_2

24 hours | 72 hours

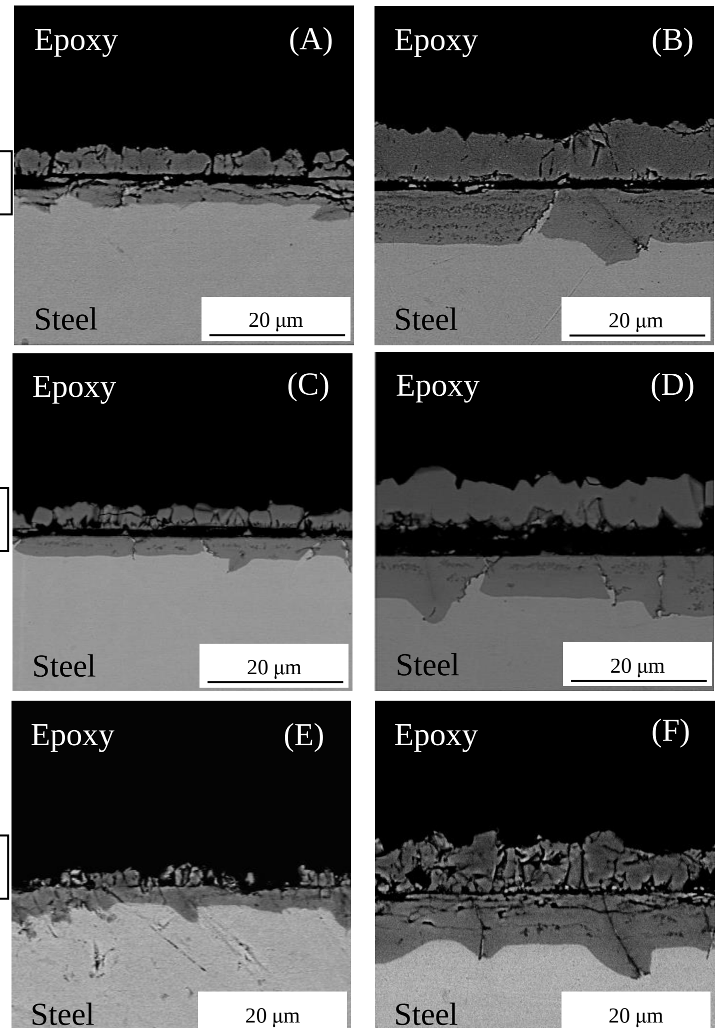
Increase in Time

Increase in H_2 content

$2\% \; H_2 - 20\% \; H_2O$

$10\% \; H_2 - 20\% \; H_2O$

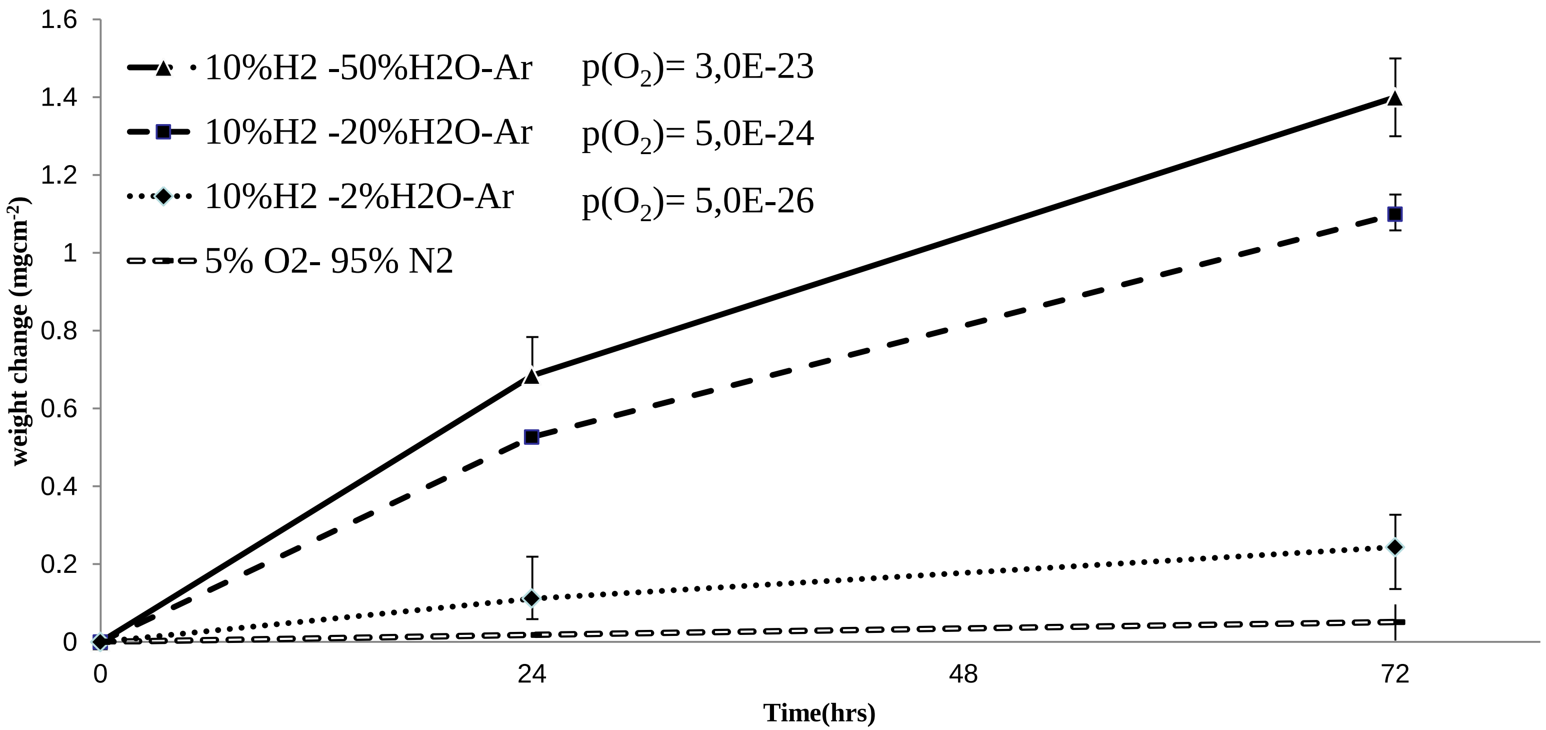
$20\% \; H_2 - 20\% \; H_2O$



Increase in oxide thickness

Lab. Exposure

The Effect of H_2O



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Lab. Exposure
The Effect of H_2O

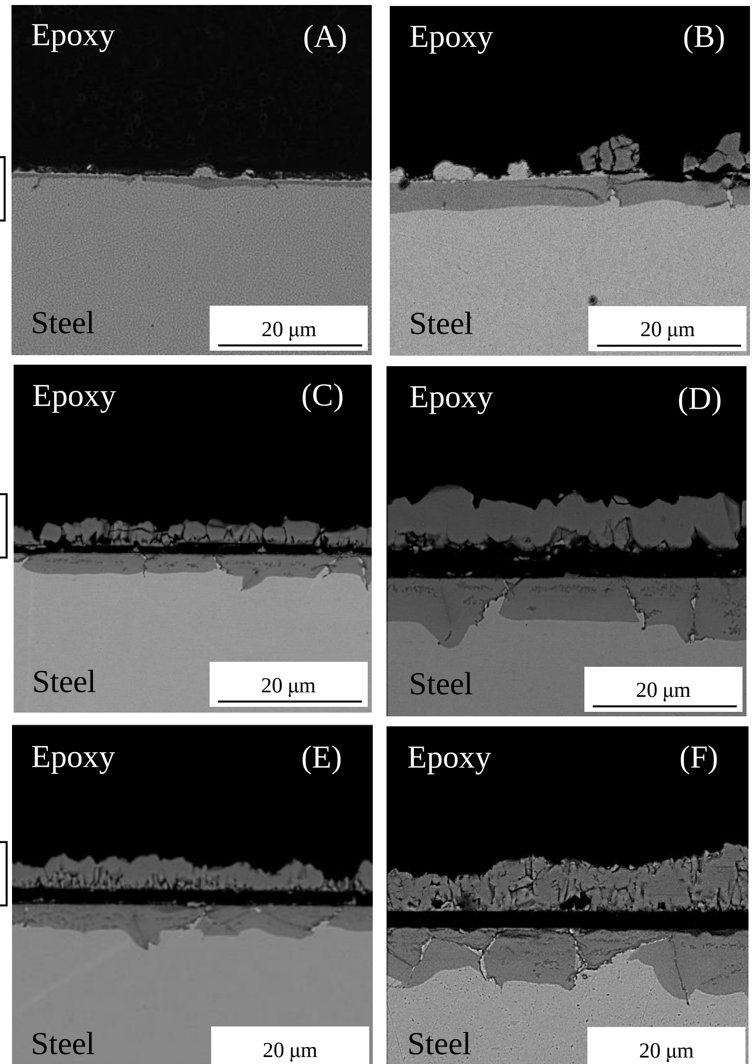
24 hours | 72 hours | Increase in Time

10% H_2 – 2% H_2O

10% H_2 – 20% H_2O

10% H_2 – 50% H_2O

Increase in H_2O content



Increase in oxide thickness

Increase in oxide thickness

The Effect of H_2 and H_2O

Final remarks

- Marginal chromia formers, e.g. 304L, can be subject towards accelerated corrosion in low oxygen activity environments.

- Breakaway may be triggered by a deep chromium depletion of the alloy substrate.

- The chromium depletion was deeper in H2-H2O environment than it is in, e.g. dry O2, because the pure chromia scale formed in H2-H2O environment grew faster than the Cr1-xFex)2O3 scale formed in air and dry O2.

Ongoing work

- Material exposures have been made in the Cortus’ gasifier in Köping
  - Very high temperature, ~1100 °C
- Samples were recently removed and are about to be investigated

310 S

Thank you for your attention!

- We would like to acknowledge:

Energimyndigheten

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Valmet

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