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CORROSION AND OXIDATION OF FeCr ALLOYS FOR SOLID OXIDE FUEL CELLS (SOFC) AND SOLID OXIDE ELECTROLYSIS CELLS (SOEC)

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Energy and materials
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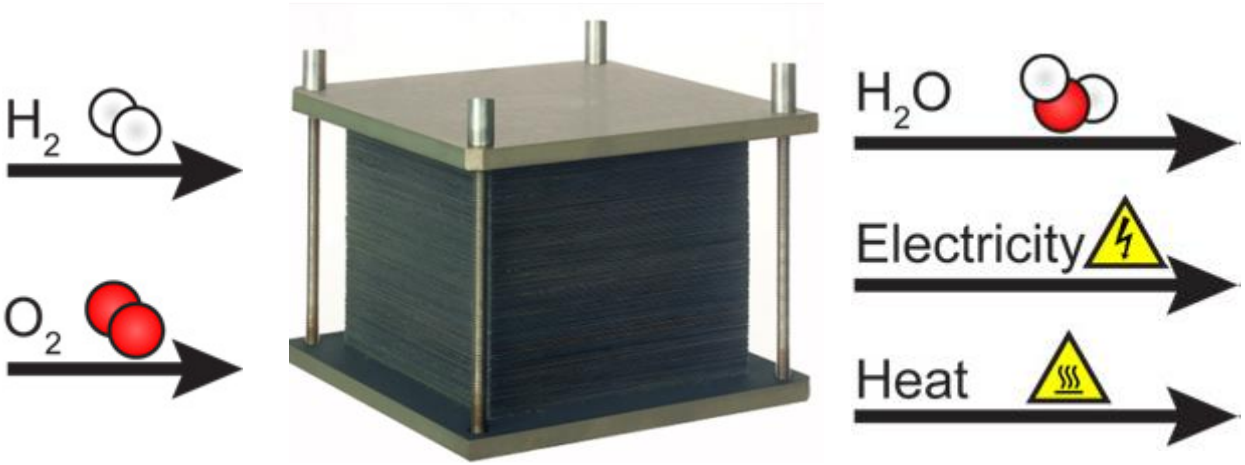
What is a Fuel Cell?



Chemical Energy → Electrical Energy

Different Fuel Cell types

PEM Fuel Cell

80°C

H_2 fuel

Solid Oxide Fuel Cell (SOFC)

600-800°C

H_2, CH_4, Diesel

Advantages and Usage of Solid Oxide Fuel Cell

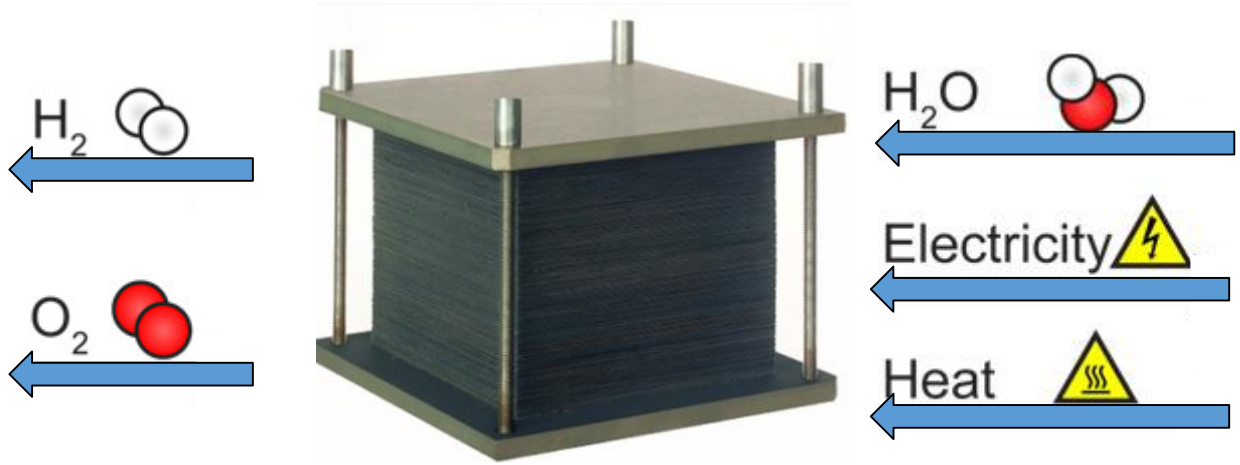
- Efficient power generation (60 el%)
- Fuel flexible
- Low emissions
- Scalable

Truck or RV Auxilliary Power Units (APUs)

Combined Heat & Power (CHP)

Off-grid power generation/ Backup Power

What is a Electrolysis Cell?

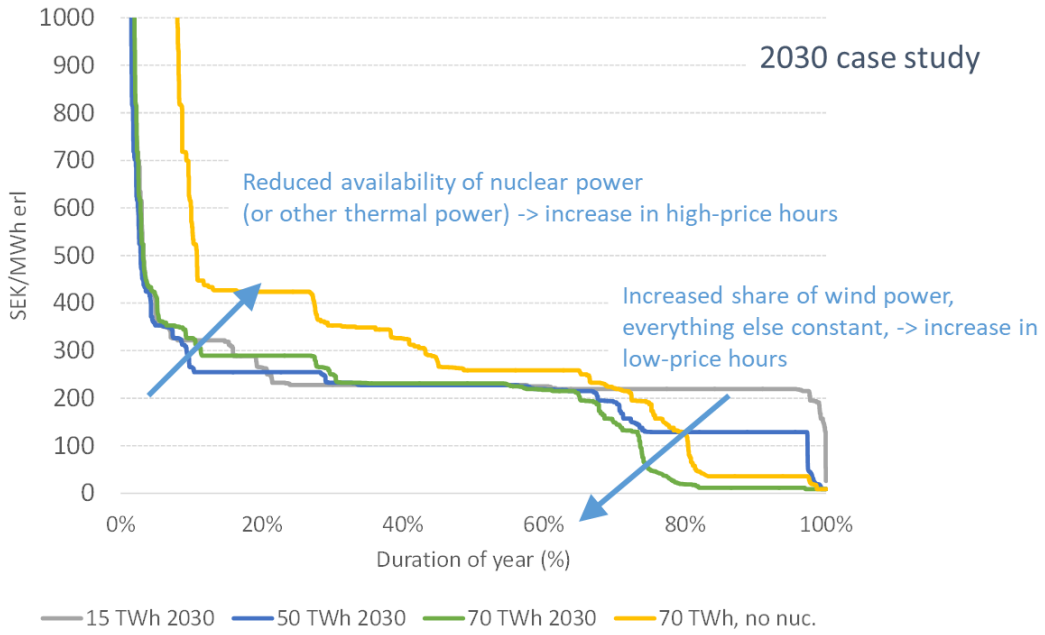


Chemical Energy ← Electrical Energy

CO, CH_4 ← CO_2

SOEC as a complement to renewables

More wind and less nuclear – the impact on the electricity-price duration curve



- More wind and less nuclear generate a steeper profile of the price duration curve over the year.
- Hydro and increased interconnector capacity dampen impacts!

FJÄRRSYN

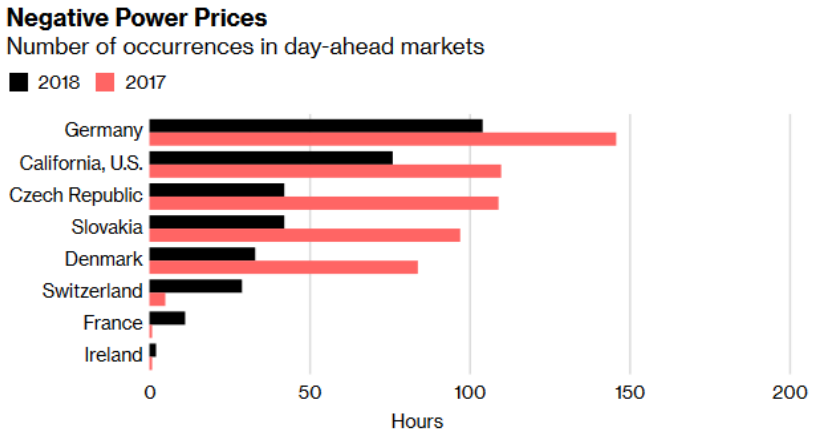
Slide:
Håkan Sköldberg (Profu)

SOEC as a complement to renewables

The New York Times

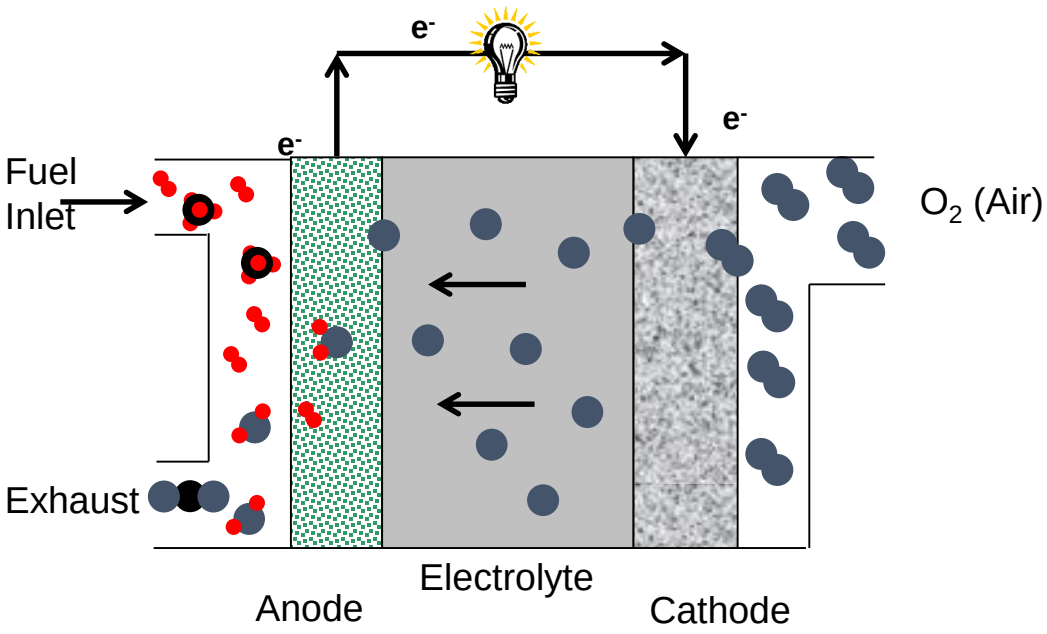
Power Prices Go Negative in Germany, a Positive for Energy Users

Power from wind and solar waxes and wanes with the breeze and sunshine, not in response to when it is most needed. Gordon Welters for The New York Times



www.bloomberg.com

Solid Oxide Fuel Cell



Cathode: $O_2 + 4\ e^- \rightarrow 2\ O^{2-}$

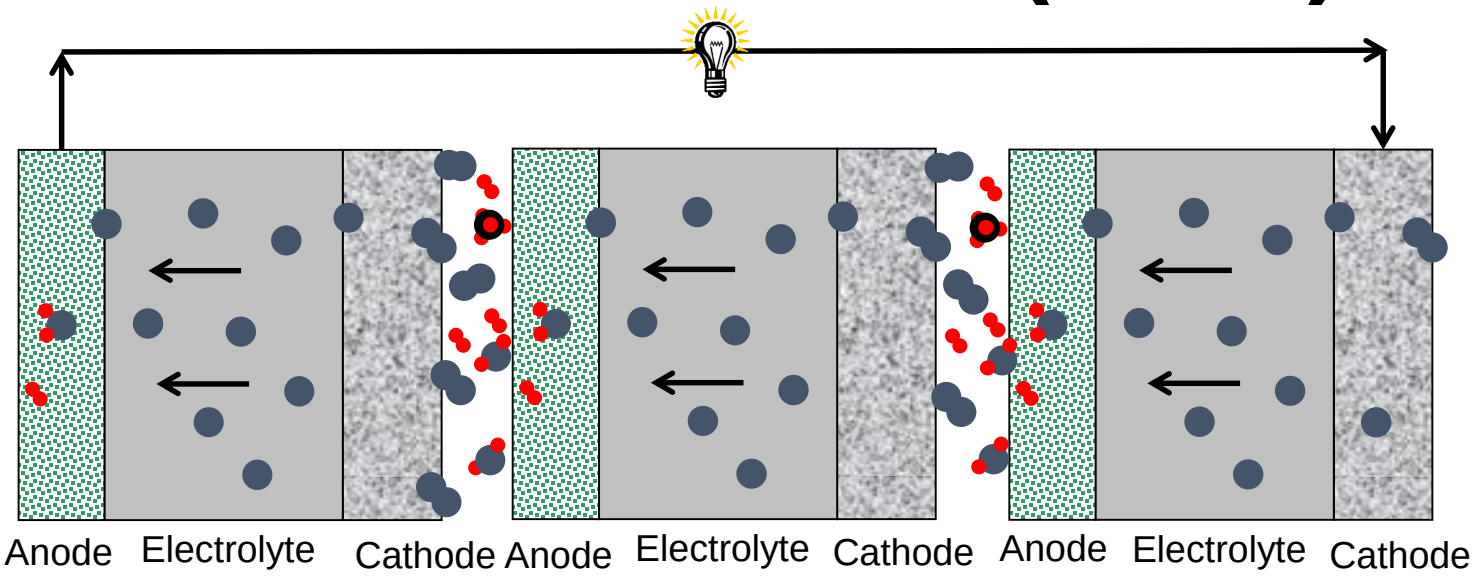
Anode: $2\ O^{2-} + 2\ H_2 \rightarrow 2\ H_2O + 4\ e^-$

Total reaction: $O_2 + 2\ H_2 \rightarrow 2\ H_2O$

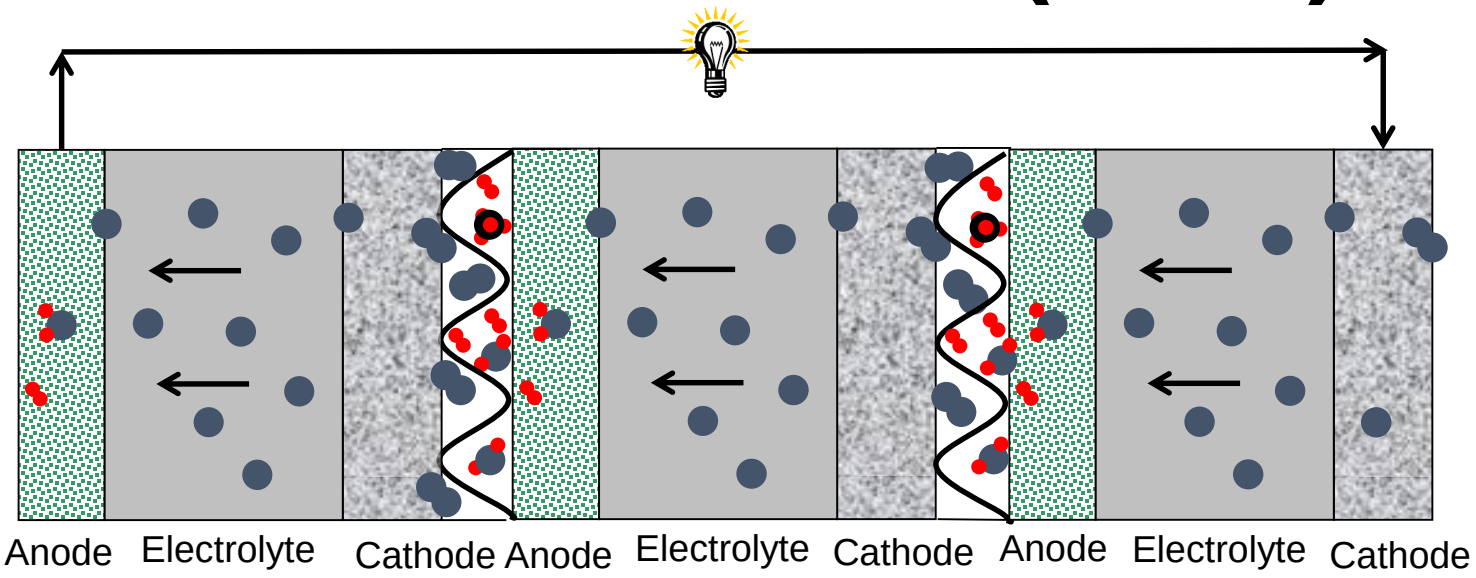
~1V

Temperatur: 600-900°C

Solid Oxide Fuel Cell (SOFC)



Solid Oxide Fuel Cell (SOFC)

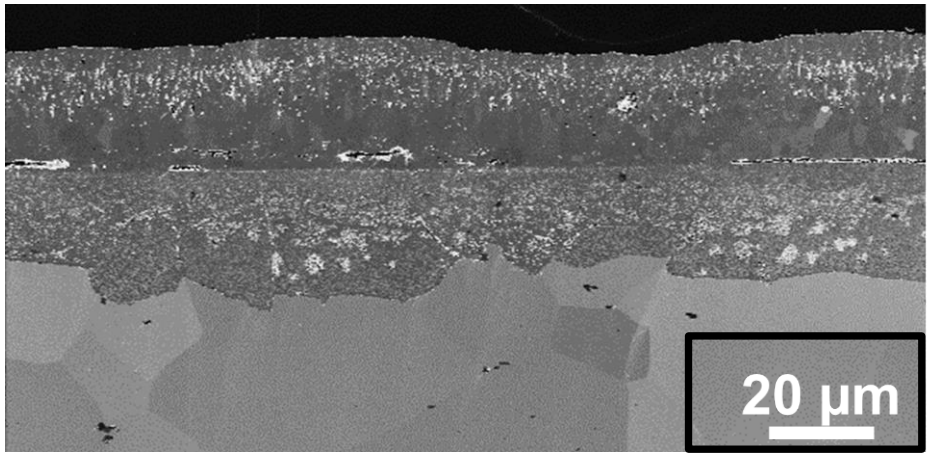


Requirements for Interconnect:

- Similar thermal expansion as the ceramics used in SOFC
- Good electrical conductivity
- Designed to form conductive oxide scales
- Formability
- Cheap to produce

Stainless steel (ferritic)

Not so stainless...



Coatings to:

- Minimize Cr-evaporation
- Increase the corrosion resistance
- Decrease the scale resistance

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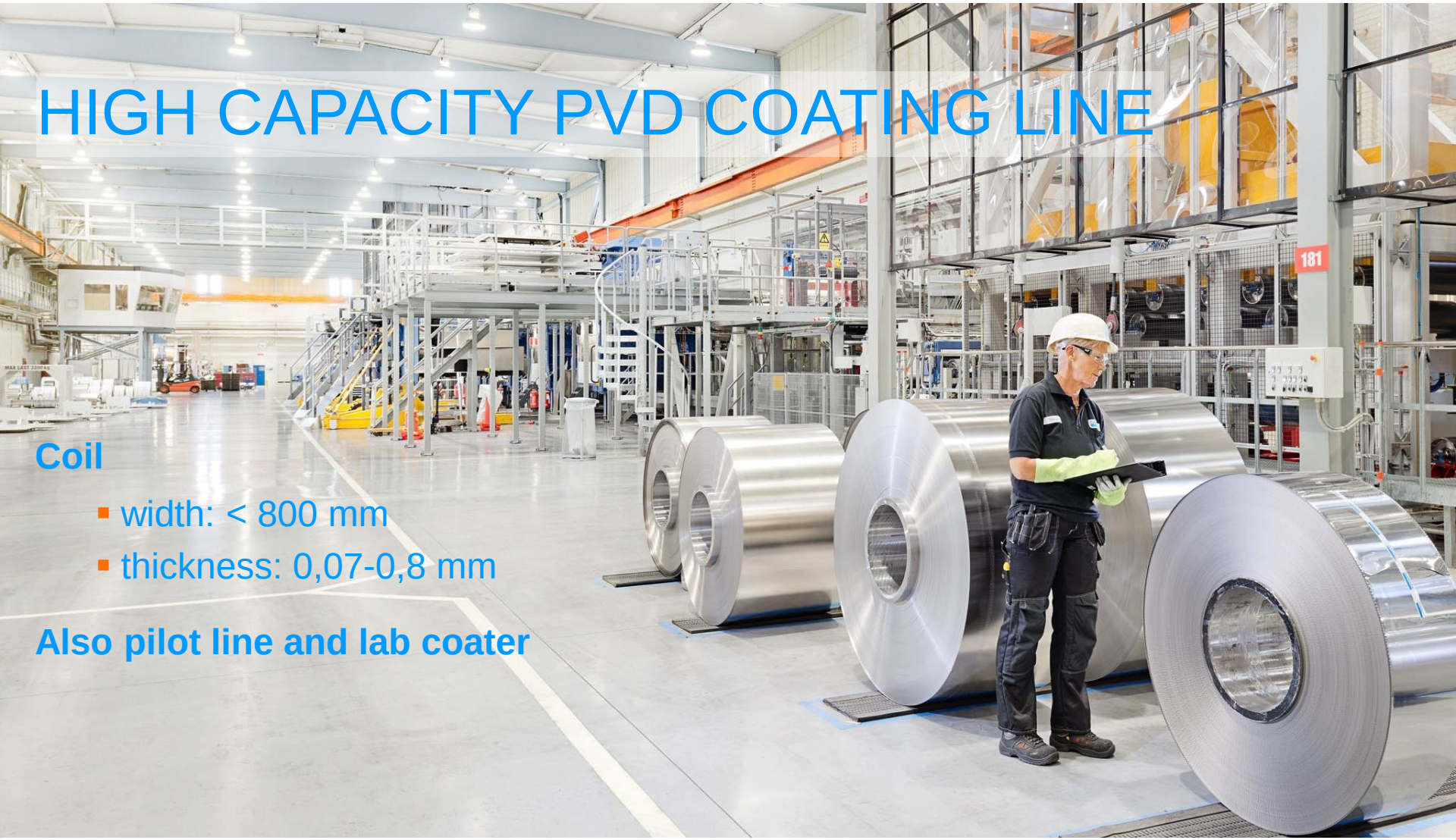
HIGH CAPACITY PVD COATING LINE

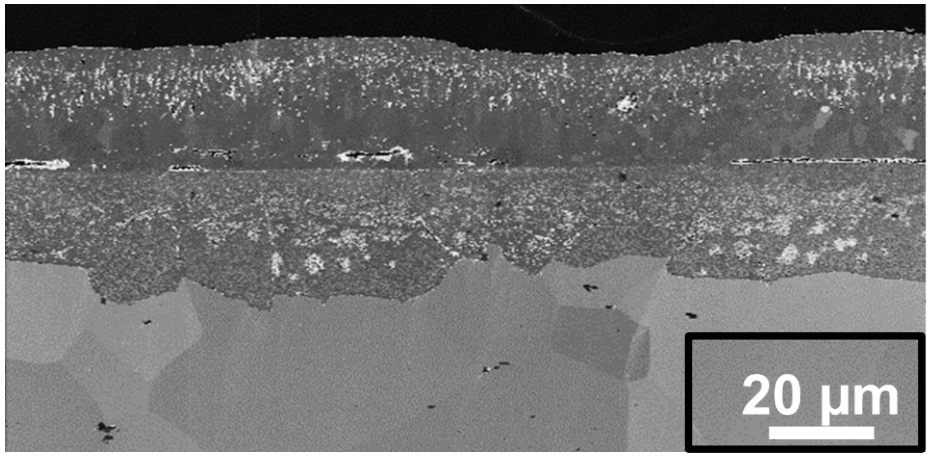


Coil

- width: < 800 mm
- thickness: 0,07-0,8 mm

Also pilot line and lab coater

Not so stainless...



Coatings to:

- **Minimize Cr-evaporation**
- Increase the corrosion resistance
- Decrease the scale resistance

Problems at Interconnect level

Cr Evaporation

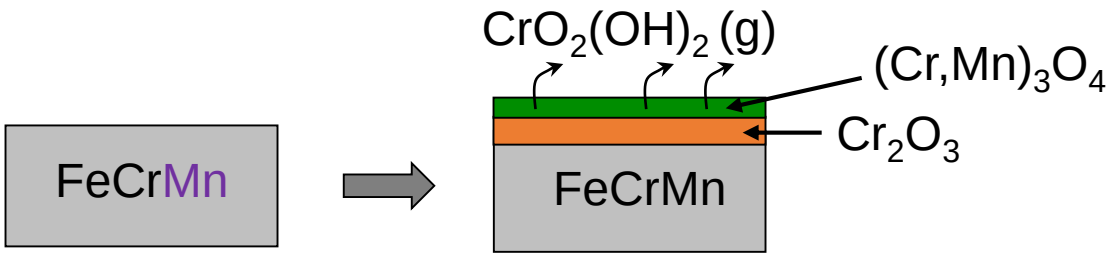
- Chromium evaporation:

$$Cr_2O_3(s) + 2\,H_2O(g) + 1.5\,O_2(g) \longrightarrow 2\,CrO_2(OH)_2(g)$$

poisoning the cathode!

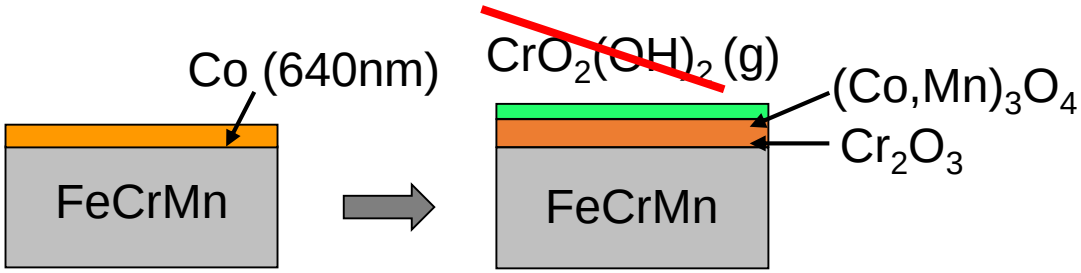
Possible ways to overcome Cr-evaporation

Change substrate composition:



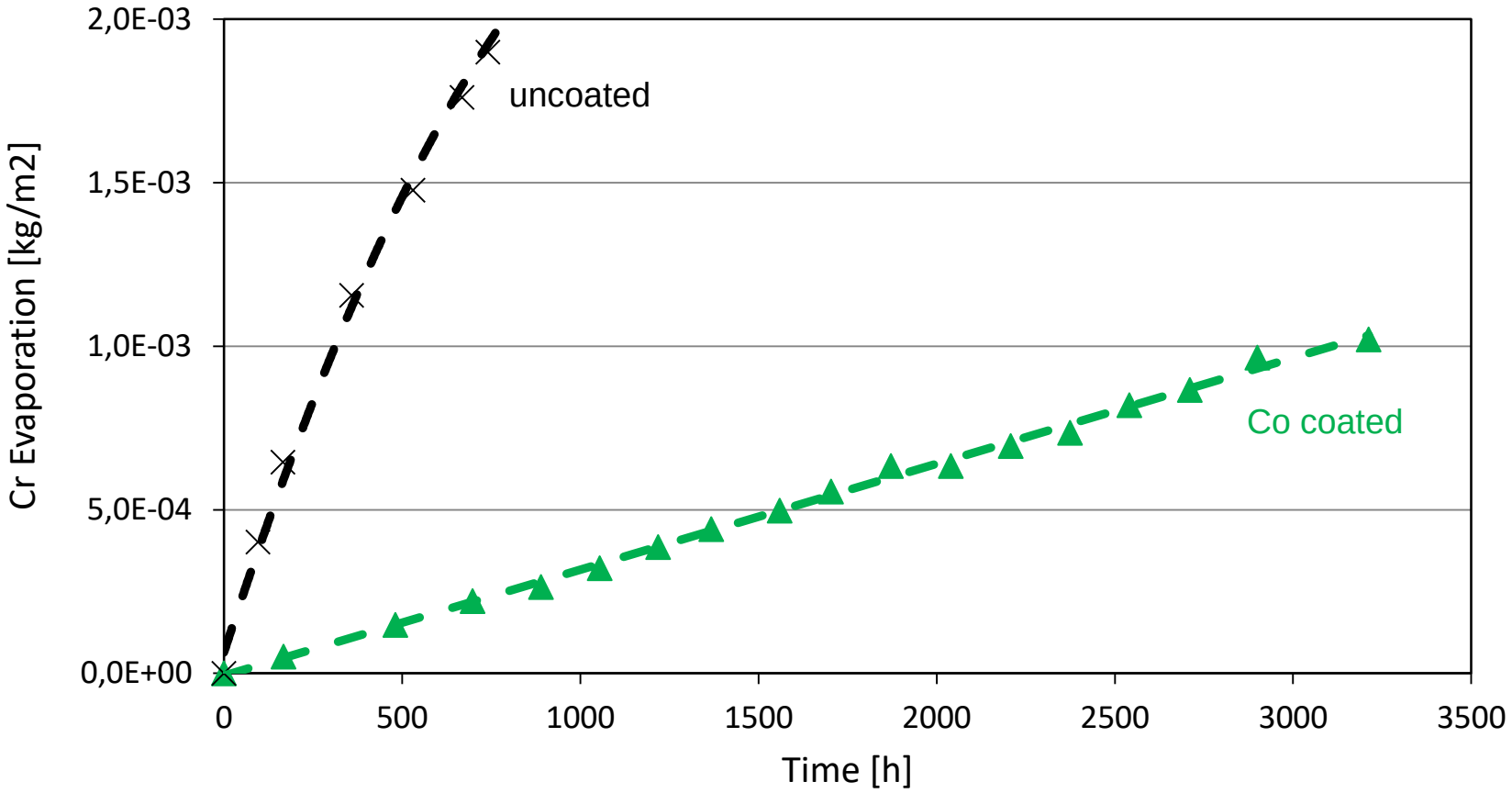
Decreases Cr-evaporation, however, still too high!

Apply Co coatings:



Minimize Cr evaporation by presence of $(Co,Mn)_3O_4$

Chromium Evaporation-3000 hours exposure

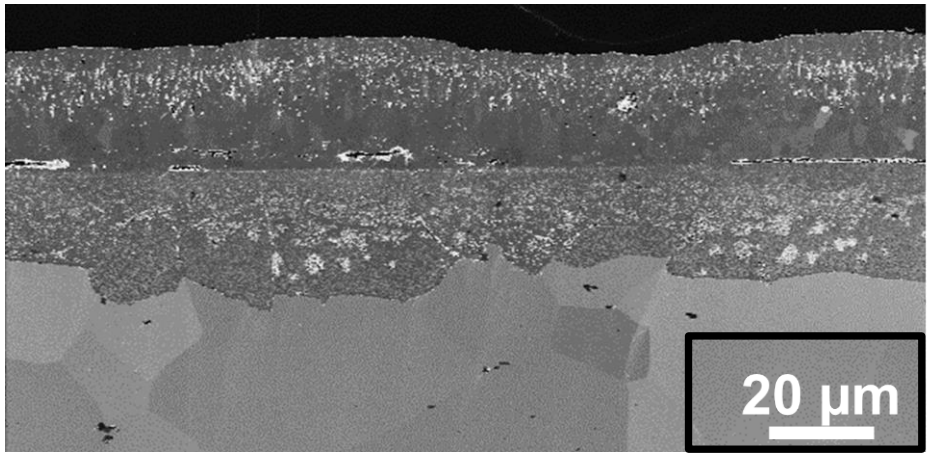


Cobalt coating reduces chromium evaporation by a factor of 10!

Sanergy HT, 850°C, 6000ml/min

J. Froitzheim, et al. J. of Power Sources, Vol.220, p.217, 2012

Not so stainless...

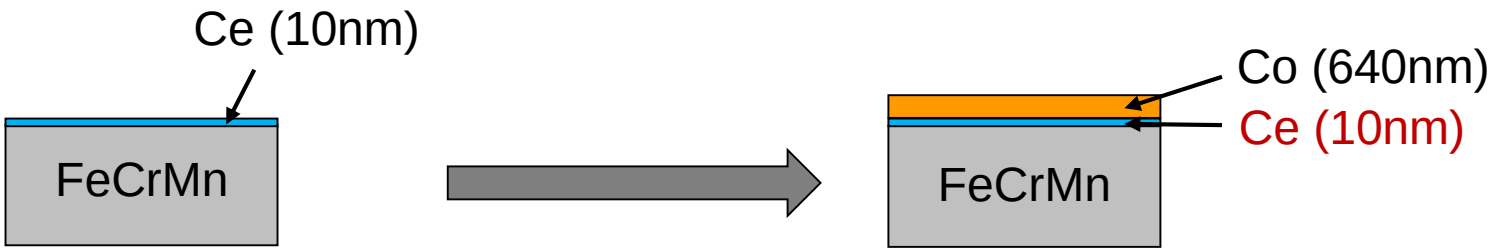


Coatings to:

- Minimize Cr-evaporation
- **Increase the corrosion resistance**
- Decrease the scale resistance

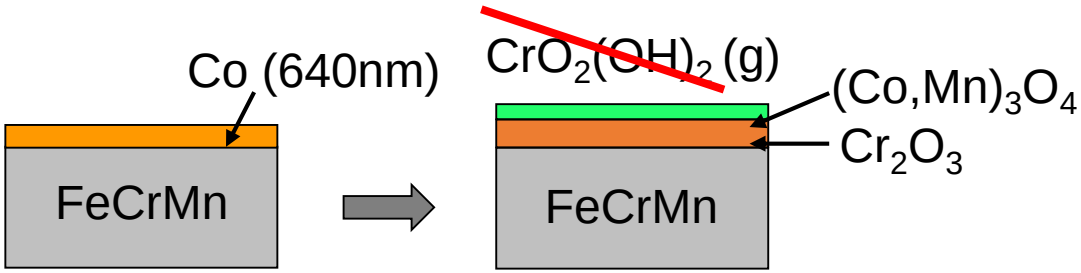
Possible ways to decrease oxide scale growth rate

Apply Ce coating:



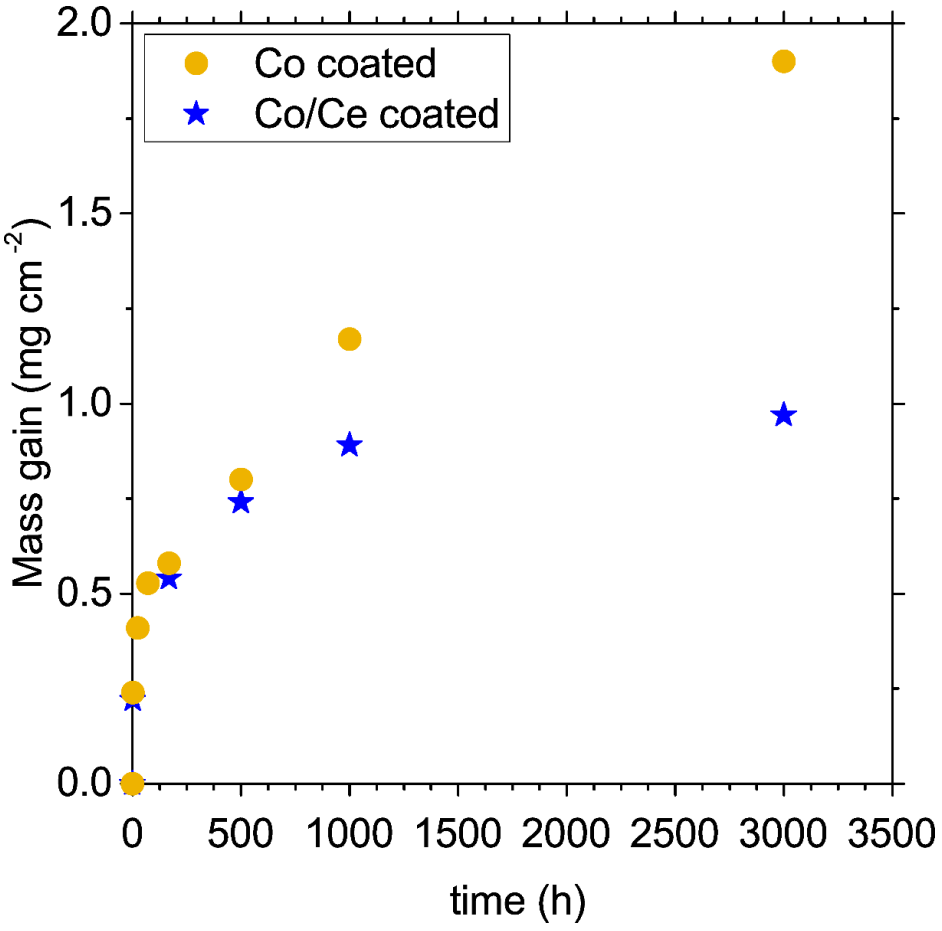
Decrease in oxide scale growth

Apply Co coatings:



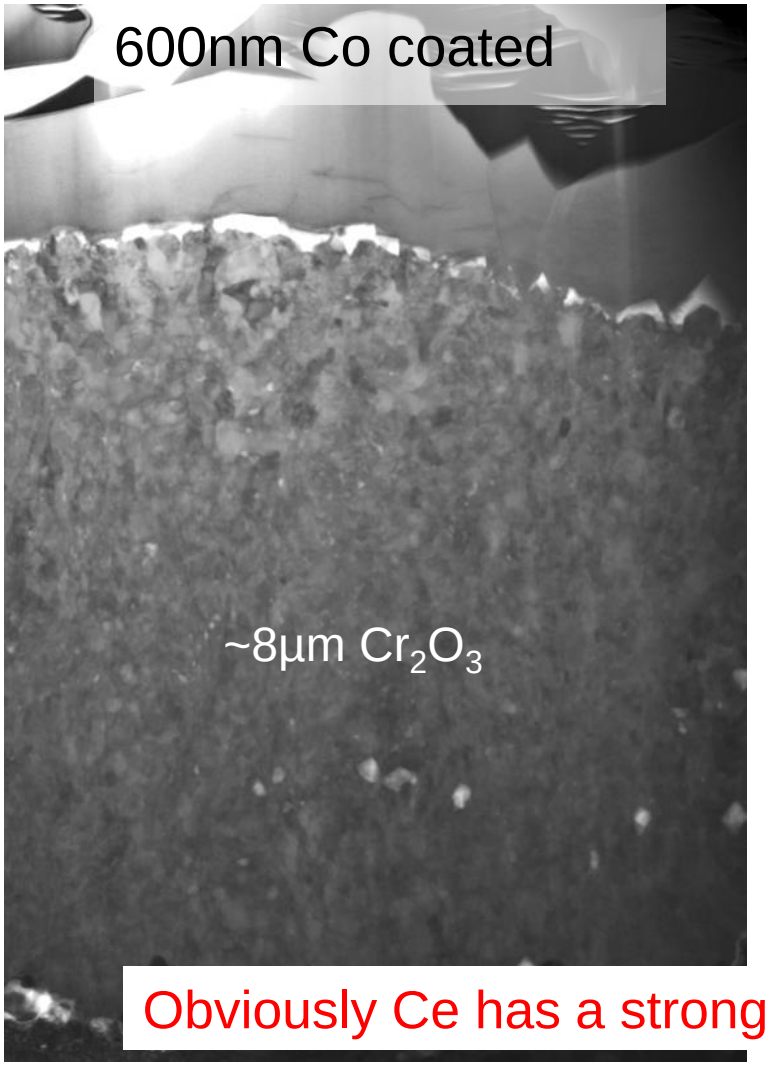
Minimize Cr evaporation by presence of $(Co,Mn)_3O_4$

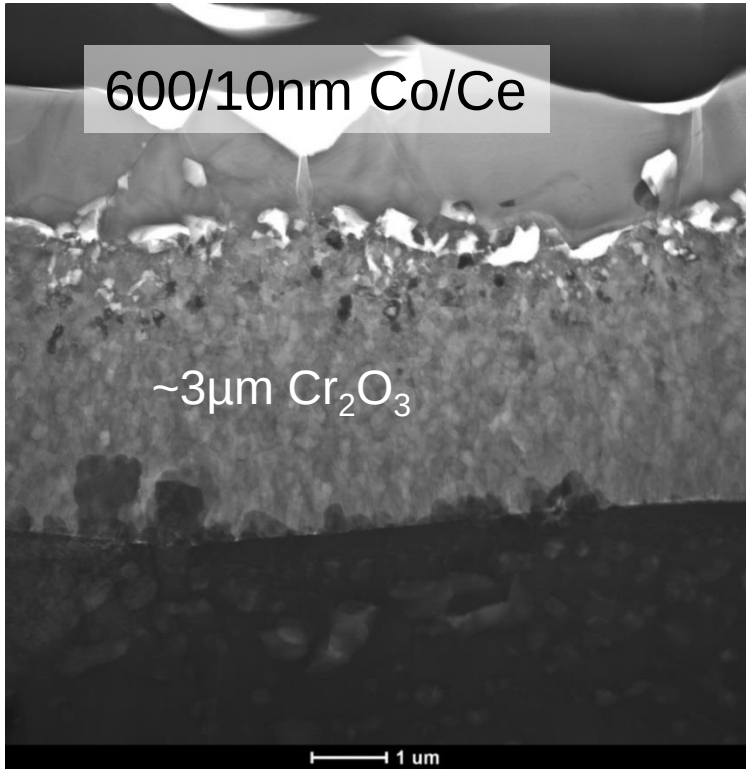
Mass gain



Co+Ce has lower mass gain than Co

Sanergy HT 3000h, 850°C, air 3% H_2O

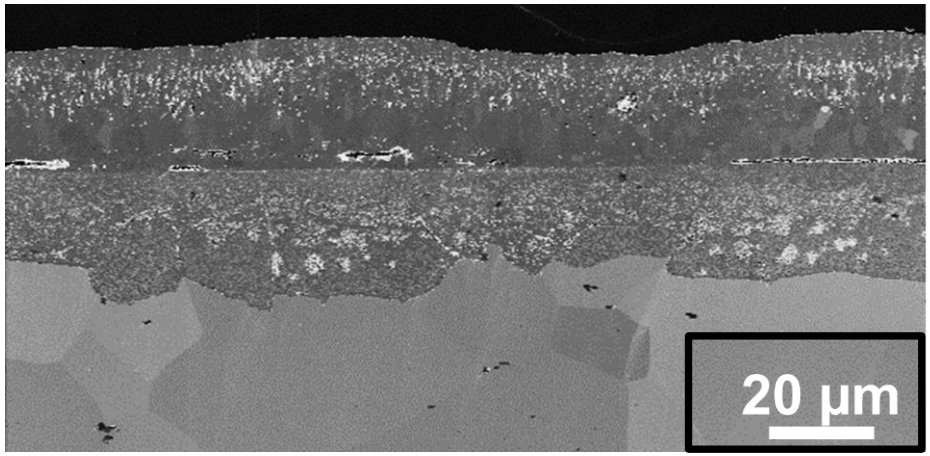




Obviously Ce has a strong effect on oxide scale growth

Sanergy HT 3000h, 850°C, air 3% H_2O

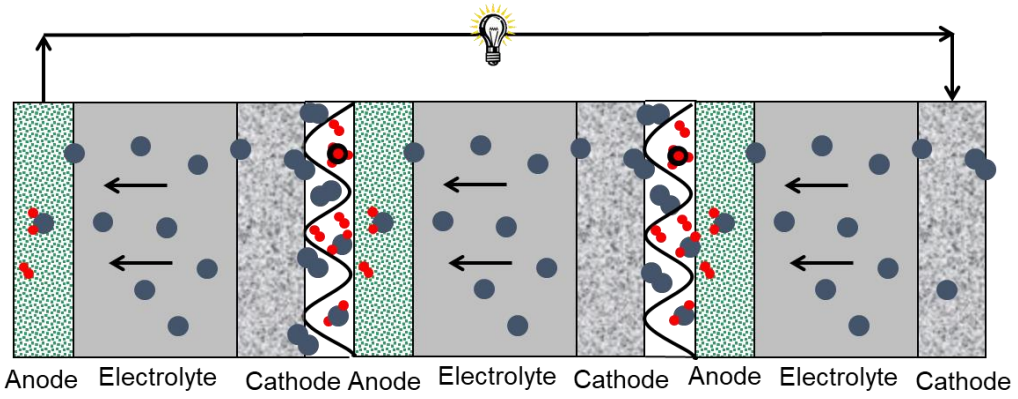
Not so stainless...

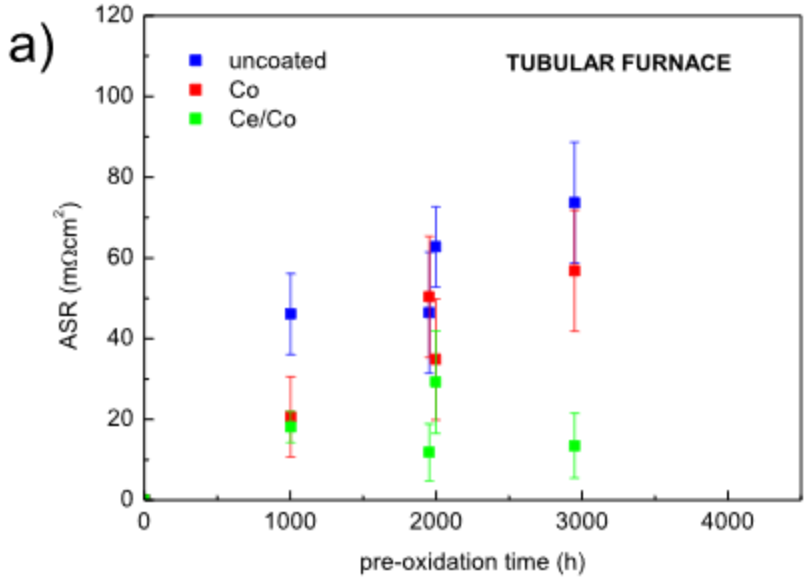


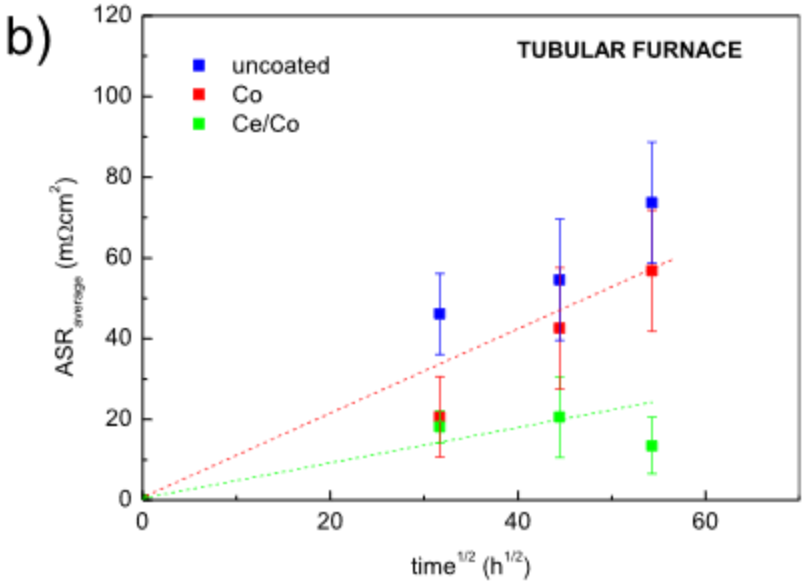
Coatings to:

- Minimize Cr-evaporation
- Increase the corrosion resistance
- **Decrease the scale resistance**

Scale resistance







Sanergy HT 3000h, 850°C, air 3% H_2O

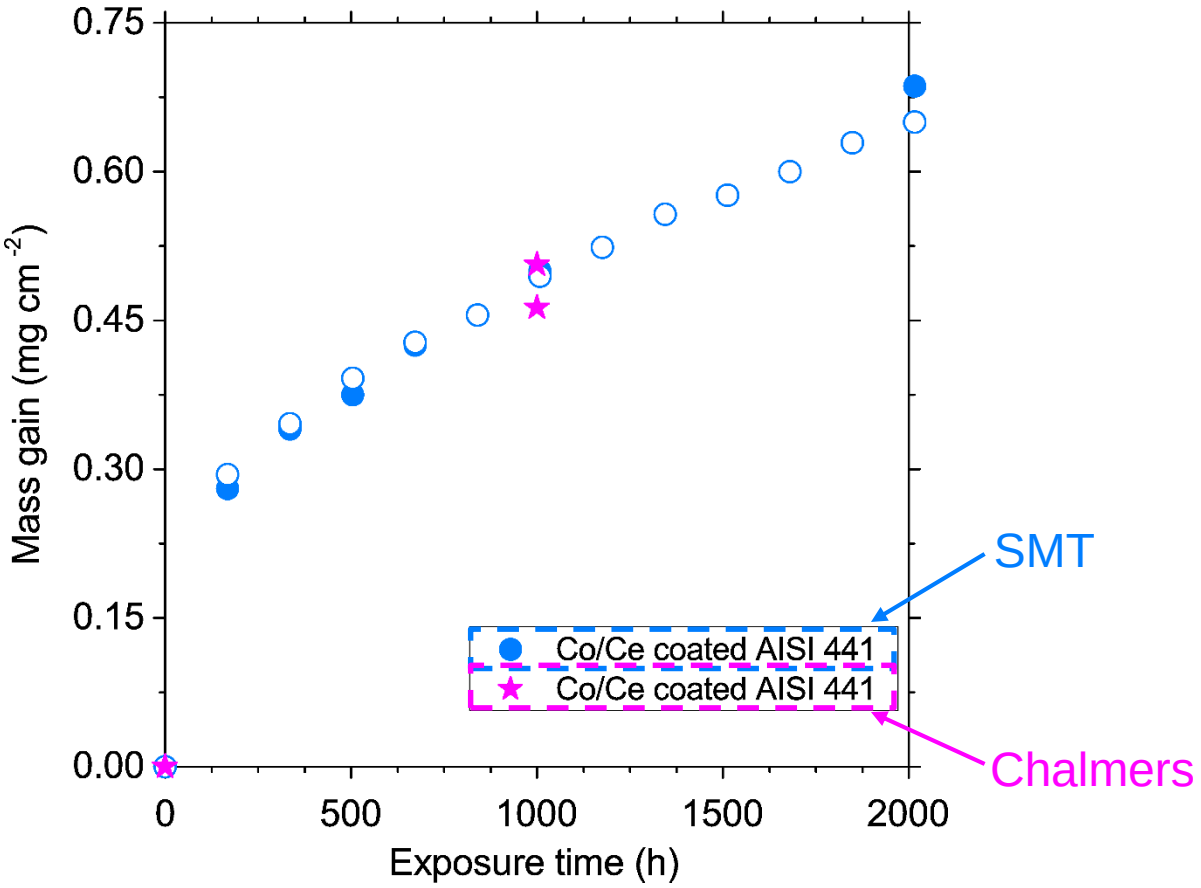
Magraso et al. IJHE, **40**, 27 p.8579

The long-term stability of Co/Ce coatings

37 000 h

Mass gains

Exposure



Initial increase of 0.21 mg/cm^2 can be attributed to the oxidation of Co

AISI 441, 800°C

Mass gains
Exposure

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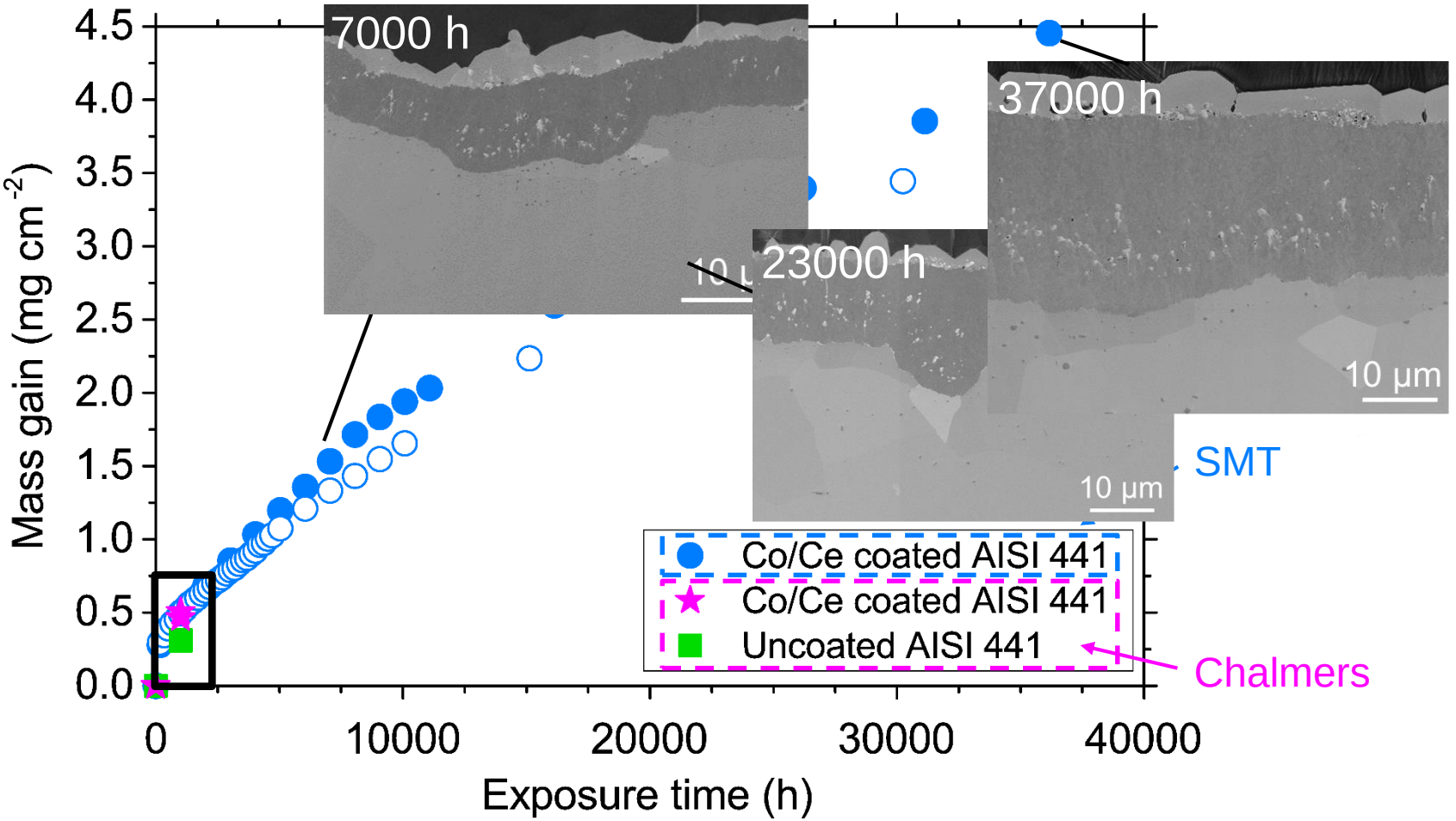
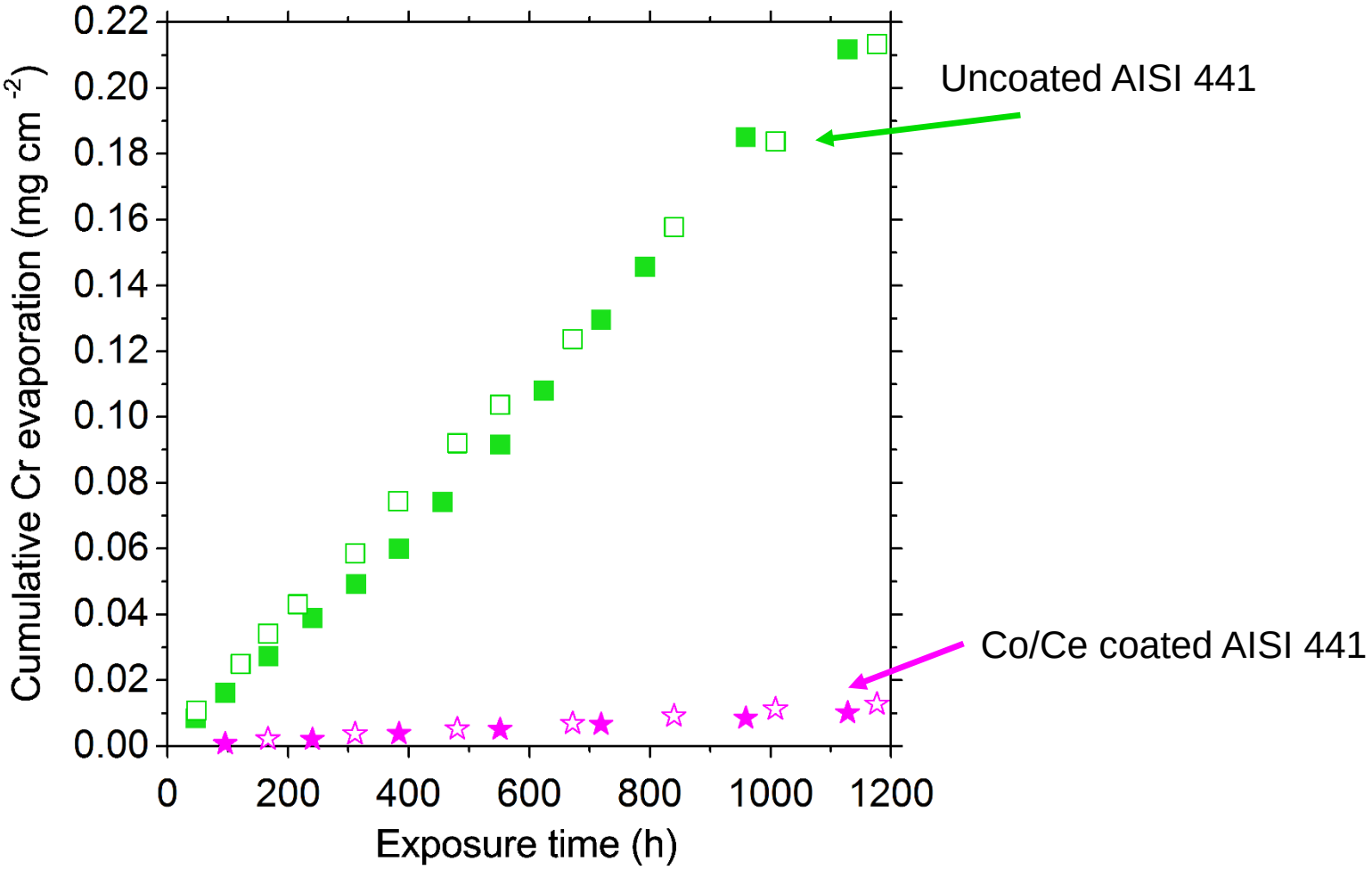


near parabolic growth

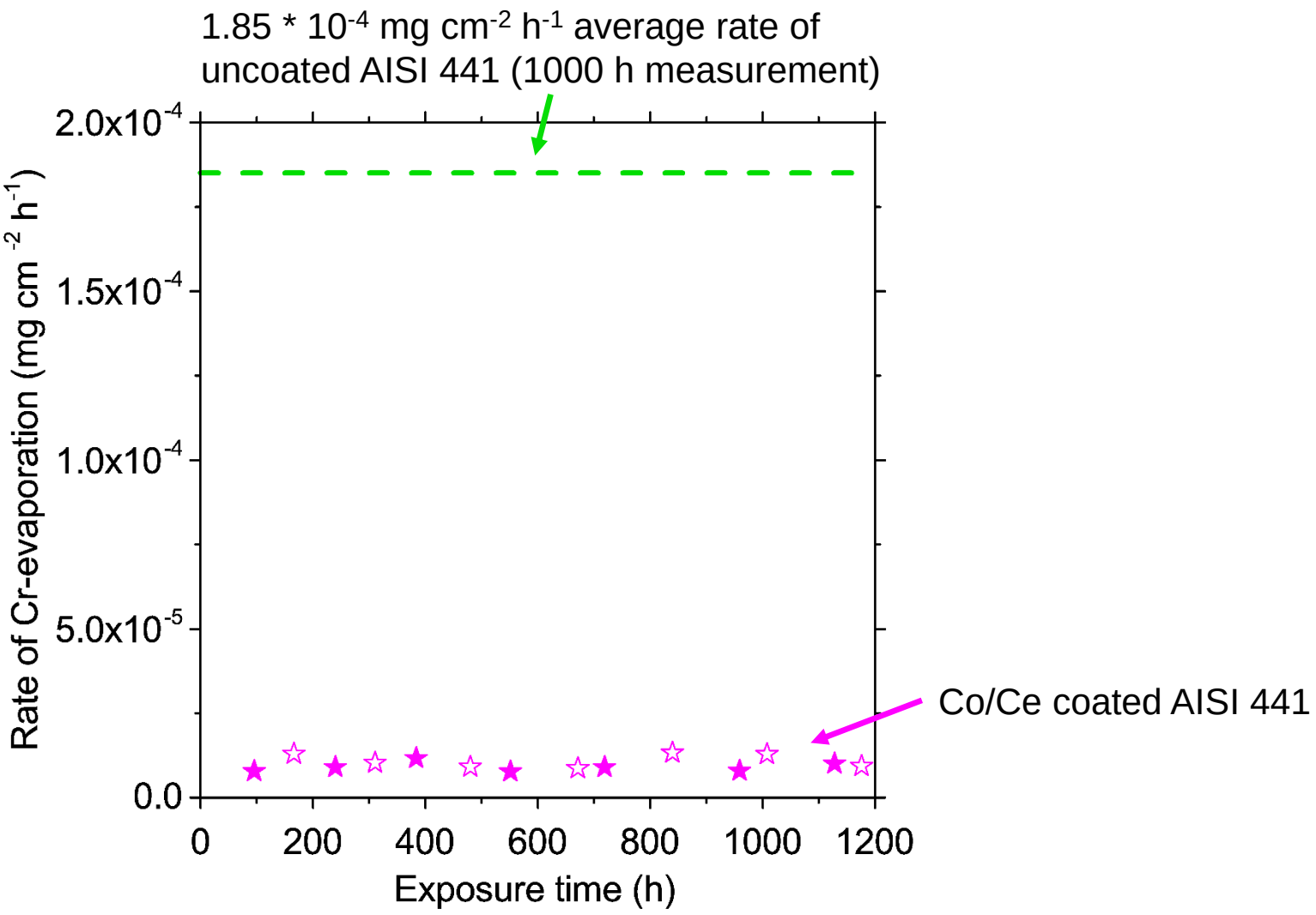
AISI 441, 800°C

Cumulative Cr-evaporation



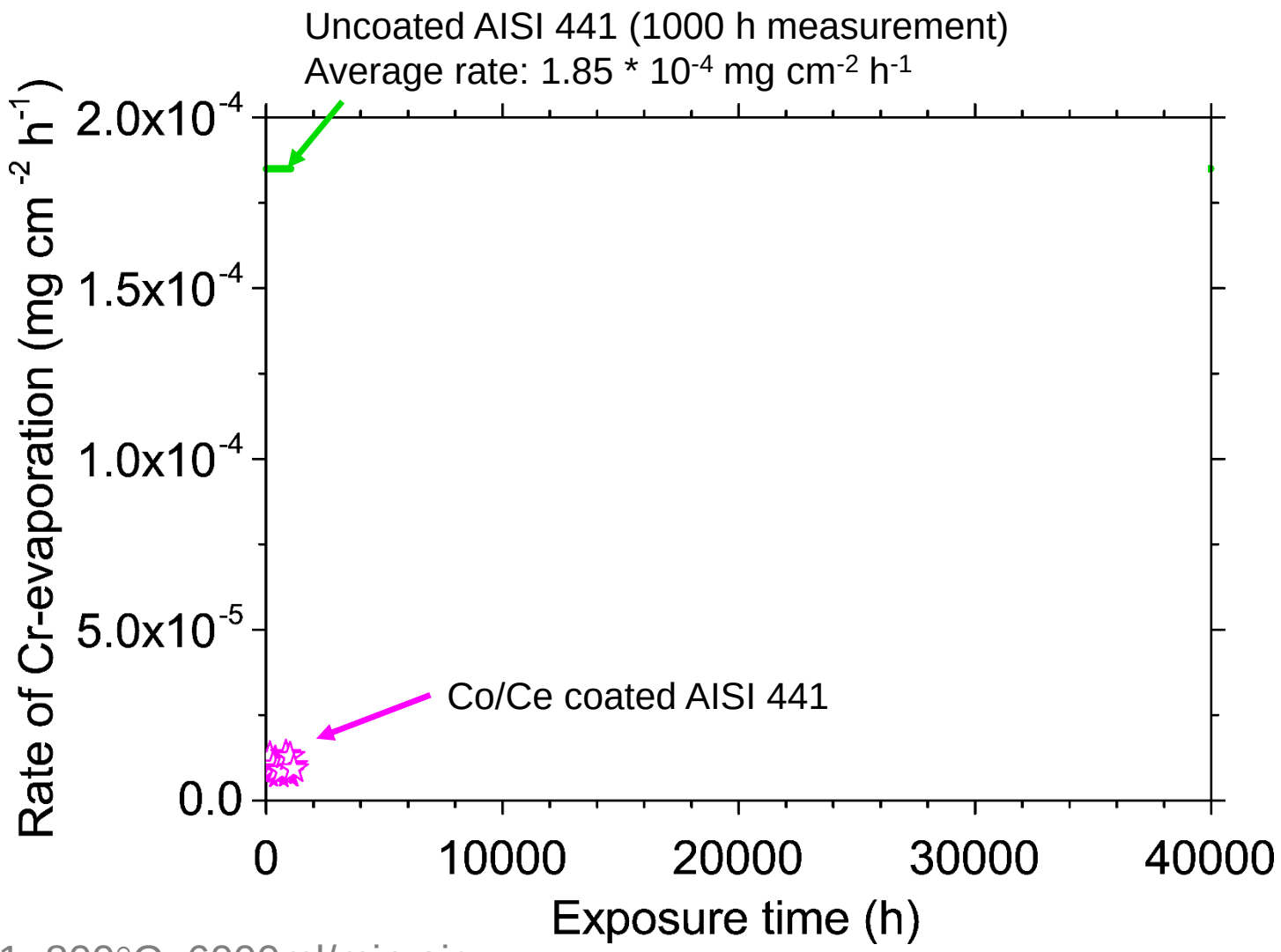
AISI 441, 800°C, 6000ml/min air

Cr-evaporation rate



AISI 441, 800°C, 6000ml/min air

Cr-evaporation rate



AISI 441, 800°C, 6000ml/min air

Conclusions

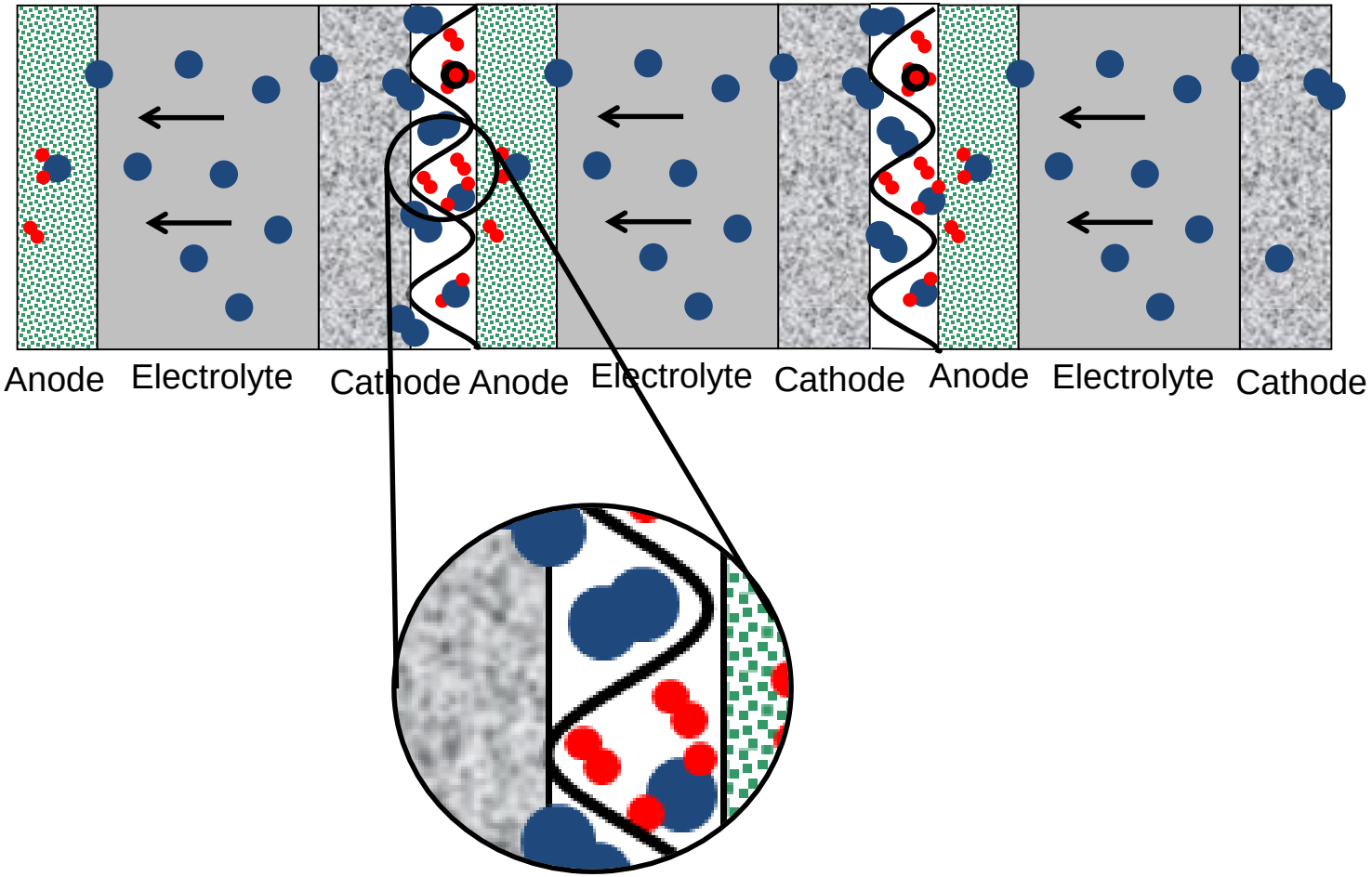
Conclusions - Co/Ce coatings

- Co/Ce coatings are highly effective against Cr-evaporation and oxide scale growth

- After 37 000 h Co/Ce coated AISI 441 exhibits:
  - Cr-evaporation rates comparable to initial rates
  - ASR values well below 50 mΩ cm^2
  - Approximately 17 – 20 µm thick Cr_2O_3 layer

Co/Ce coated AISI 441 shows excellent long-term stability in air at 800 °C

Dual Atmosphere Effect



Exposure conditions

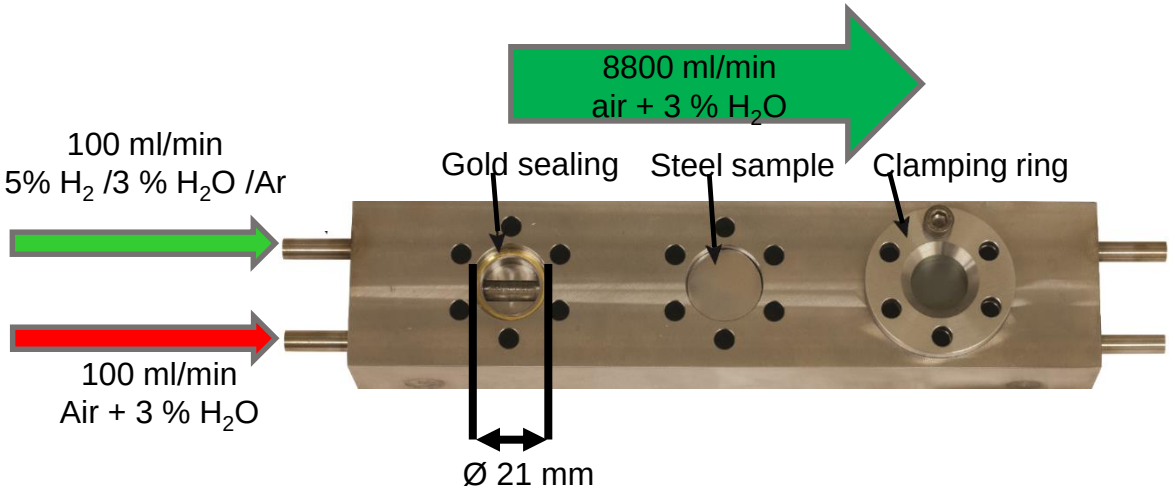
wt%	Fe	Cr	Si	Nb	Mn	Ni	Ti	P	C	S	RE
AISI 441	Bal.	17.74	0.55	0.37	0.3	0.19	0.15	0.027	0.015	0.002	no

Pre-oxidation:

3 h (or as indicated) at 800 ° C

Exposure:

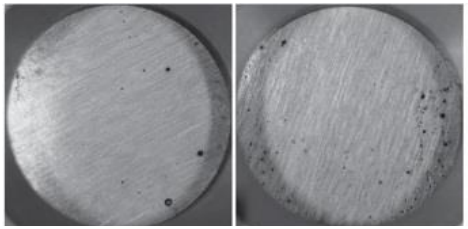
600 ° C



Visual inspection – air side

Single atmosphere

600 °C

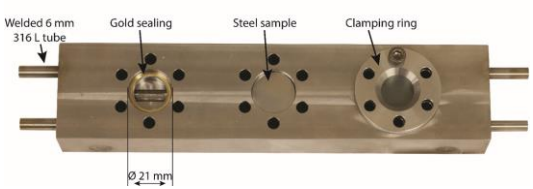


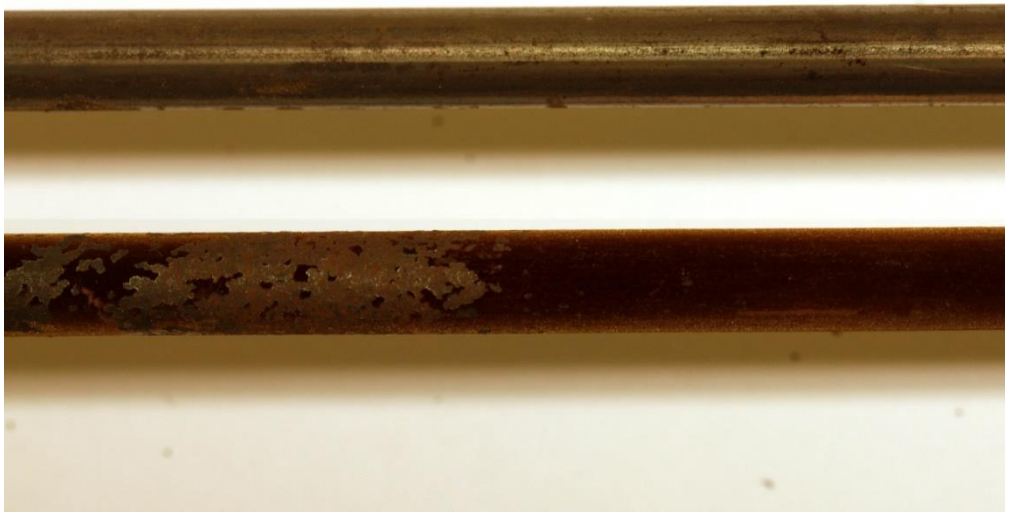
No obvious effect

No obvious effect

All 441, 1000h

316L piping to sampleholder

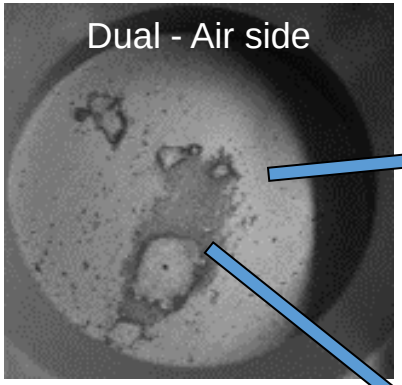




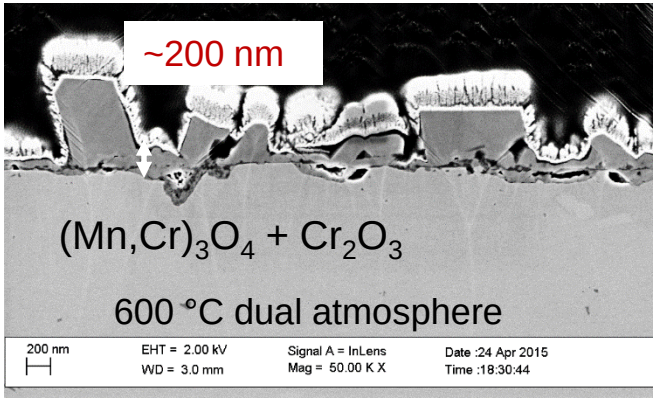
Air-3%H_2O tube

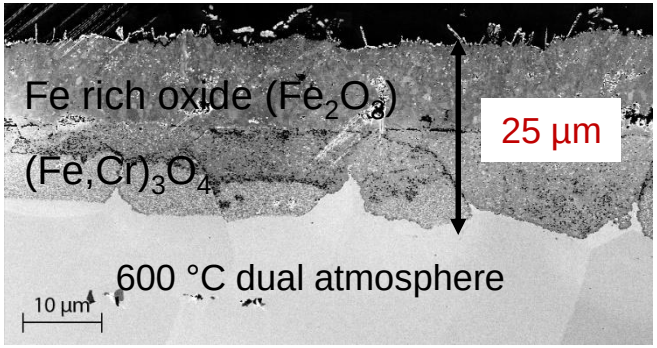
Ar-H_2+H_2O tube

Air side scale morphology



441, 1000h, 600°C





Summary (1)

- Dual atmosphere effect is real.
- Especially pronounced at low temperature.
- At 600°C hydrogen impedes the formation of a protective oxide on the air side.

  → Formation of fast growing Fe oxide (breakaway corrosion).

Pre-oxidation - a strategy to protect the steel?

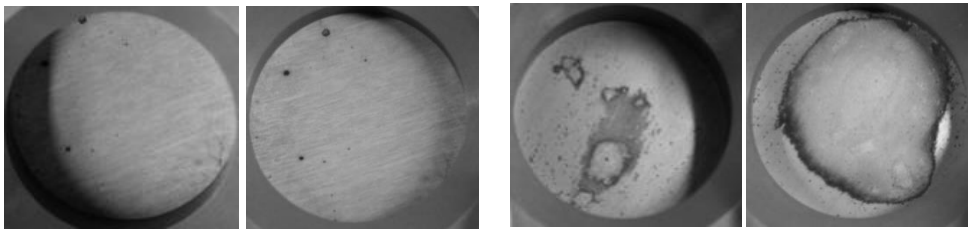
Importance of pre-oxidation

Preoxidation 800°C 3h, air

Single atmosphere

Dual atmosphere

600 °C



1000 h 3000 h 1000 h 3000 h

Strong dual atm effect

No Preoxidation

600 °C

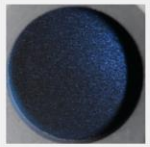
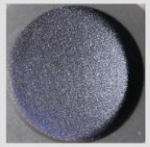
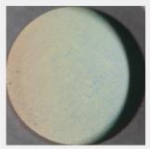
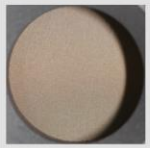
2000 h 2000 h

Stronger dual atm effect

Pre-oxidation – Does it work in the long run?

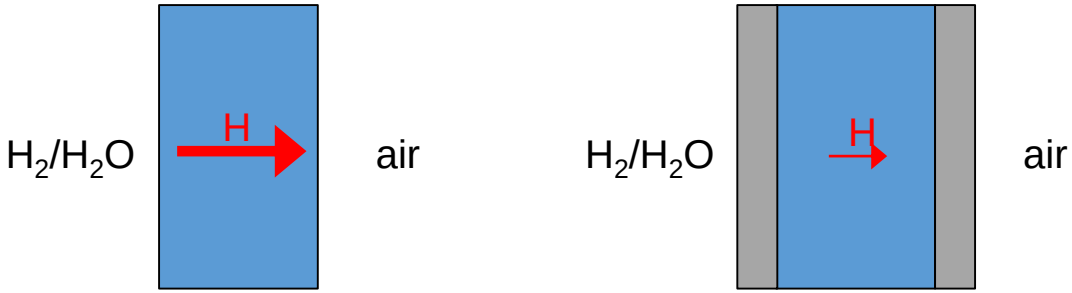
- Material: 5 x AISI 441
- Pre-oxidation: 800 ° C, low flow (~250 sml/min), air + 3 % H_2O
- Different pre-oxidation times chosen:
  - 0 min
  - 11 min
  - 45 min
  - 180 min
  - 280 min

Visual inspection (air side)

$t_{exposure}$ / $t_{pre\text{-}oxidation}$	0 h	40 000 h	80 000 h
0 min			
11 min			
45 min			
180 min			
280 min			

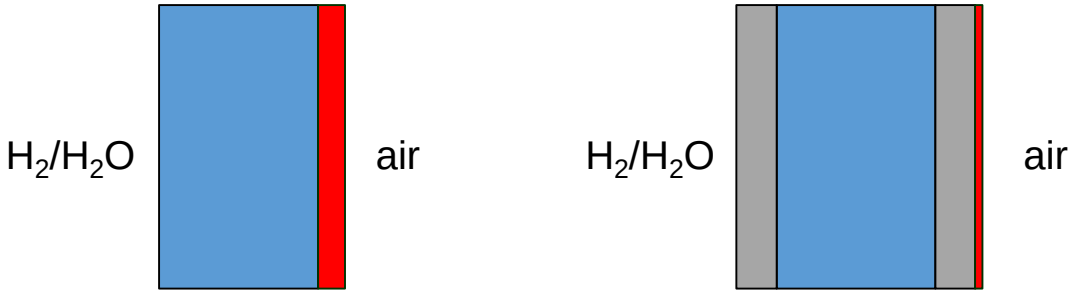
Pre-oxidation helps because…

…of reduced hydrogen ingress due to the oxide scale on the fuel side?

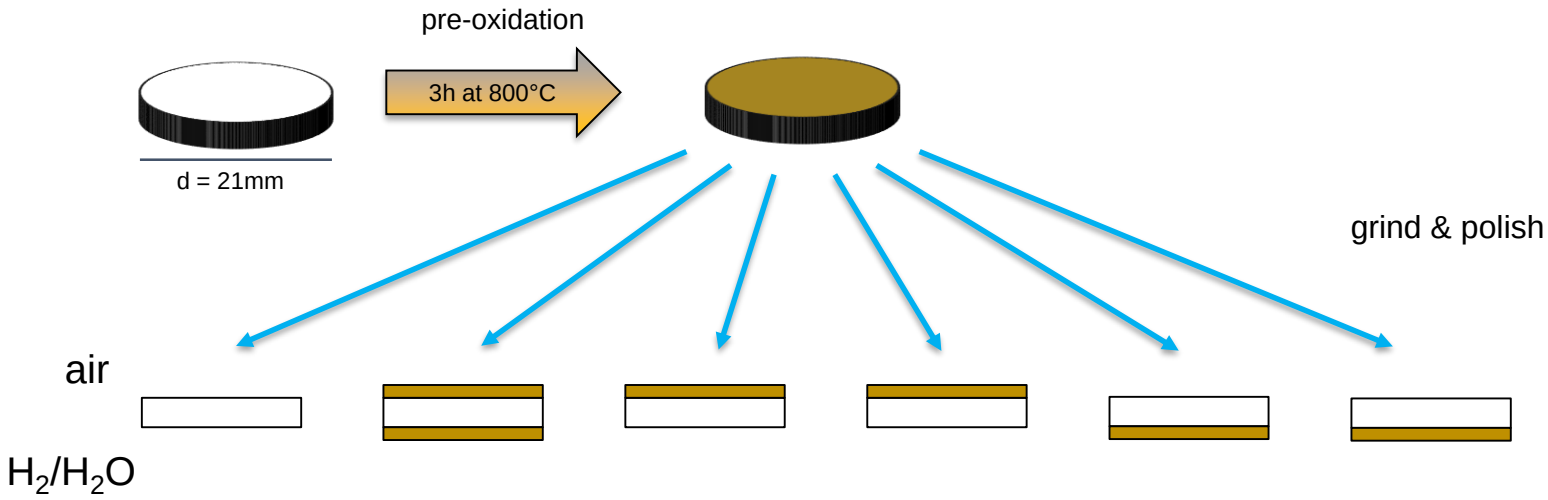


Pre-oxidation helps because…

…of the presence of an already protective scale on the air side?



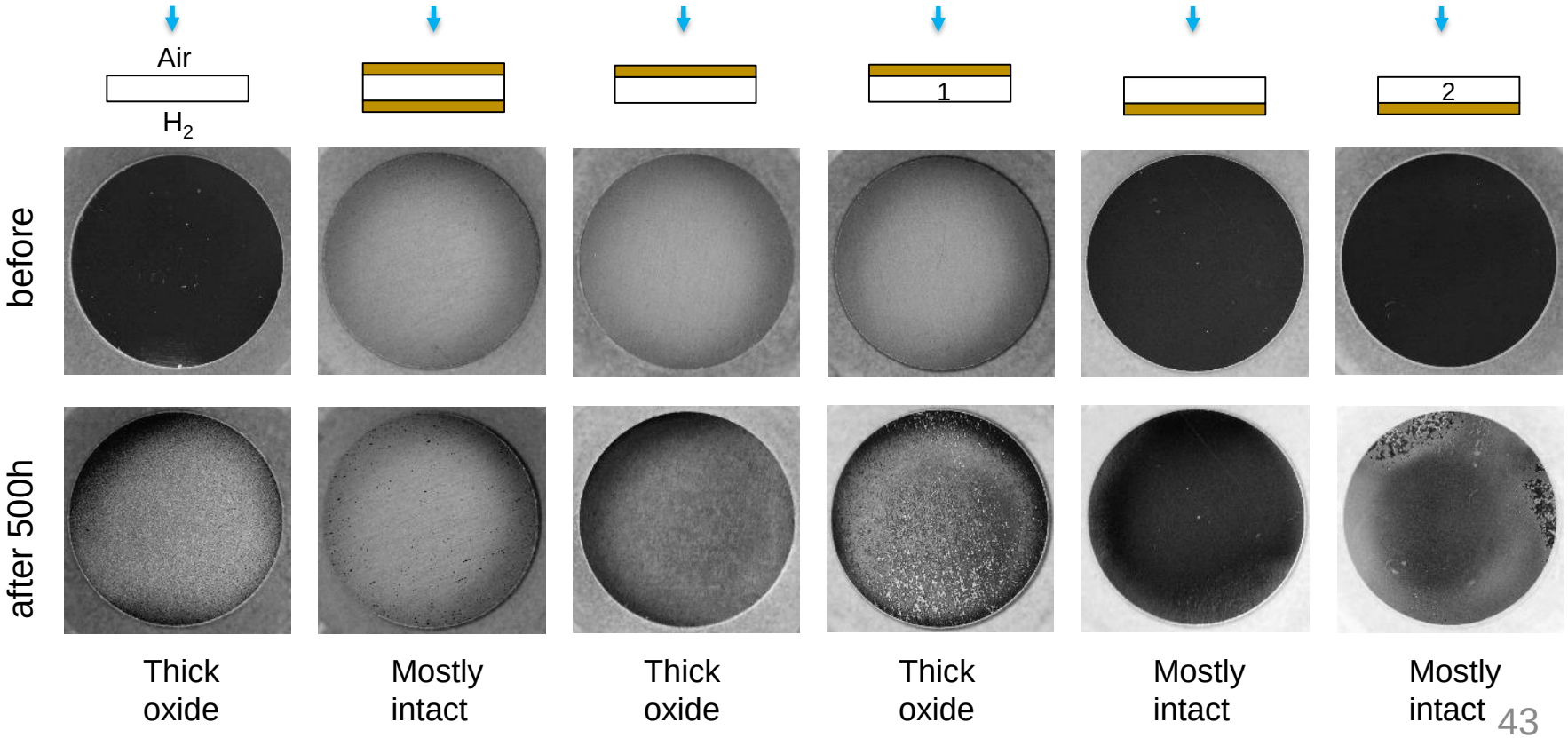
Sample Preparation



Exposure

441, 500h, 600°C, Dual atmosphere, Air-3%H_2O // Ar-5%H_2–3%H_2O

Visual Inspection (Air side)



Summary (2)

- Pre-oxidation is beneficial.
- There is a strong correlation between the length of pre-oxidation and the onset of breakaway corrosion.
- The fuel side pre-oxidation layer is most detrimental.

Better materials

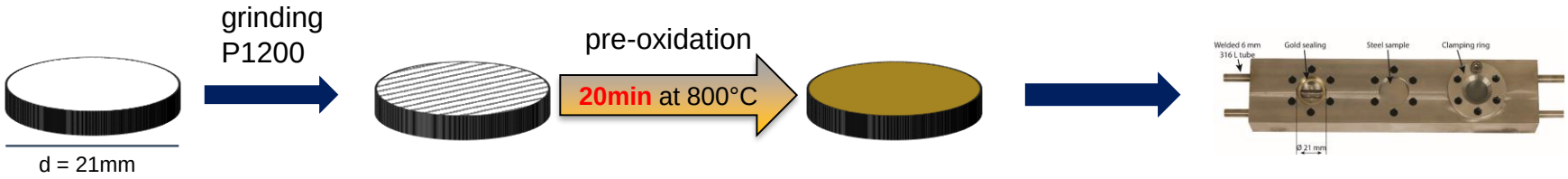
- AISI 441 is cheap but a marginal chromia former under these conditions.

- Solution: Higher alloyed steels ?

	EN code	Fe	Cr	Si	Nb	Mn	Ni	Ti	C
AISI 441	1.4509	Bal.	**17.74**	**0.55**	**0.37**	0.30	0.192	0.148	0.015
1.4622	1.4622	Bal.	**20.8**	**0.45**	**0.25**	0.38	0.2	0.12	0.019
Crofer 22APU	1.4760	Bal.	**22.7**	**0.02**	**-**	0.44	-	0.07	0.003
Crofer 22H	1.4755	Bal.	**22.9**	**0.2**	**0.5**	0.4	-	0.07	0.007

All materials with ground surfaces

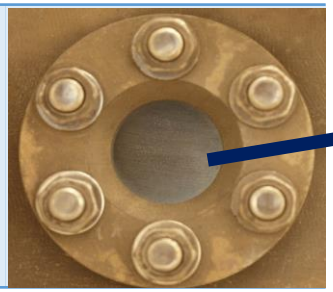
Sample Preparation

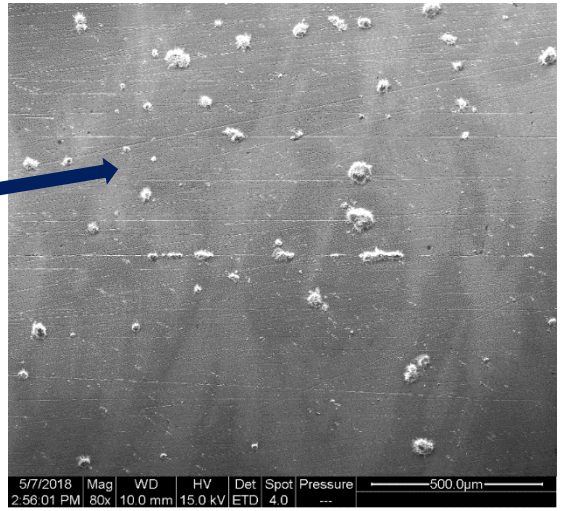


Exposure

441 vs Crofer 22 APU vs Crofer 22 H VS 1.4622
Dual atmosphere, Air-3%H_2O // Ar-5%H_2–3%H_2O

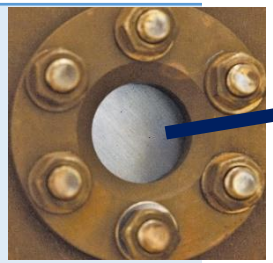
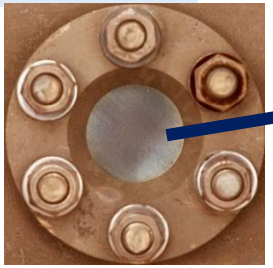
336h, 600°C

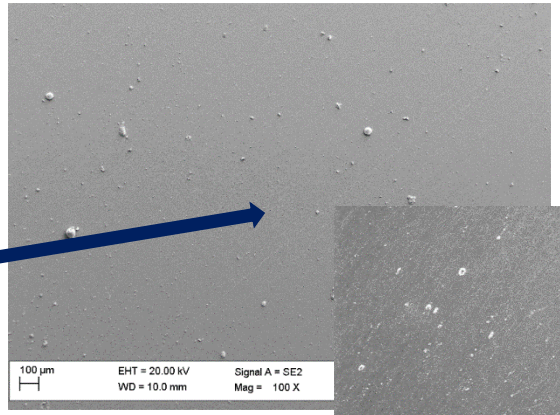
Material	168h exposure	336h exposure
AISI 441		

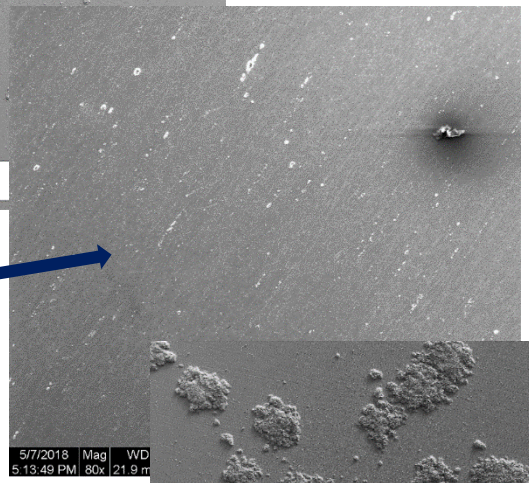


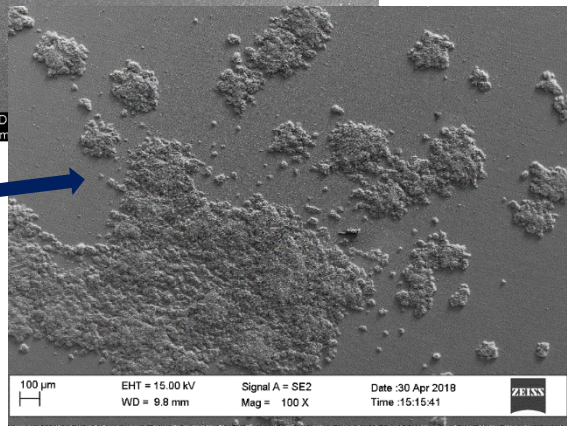
Few oxide nodules, but much better behaviour than *as received* material

→ Grinding has a beneficial effect

Material	168h exposure	336h exposure
Crofer 22APU		
Crofer 22H		

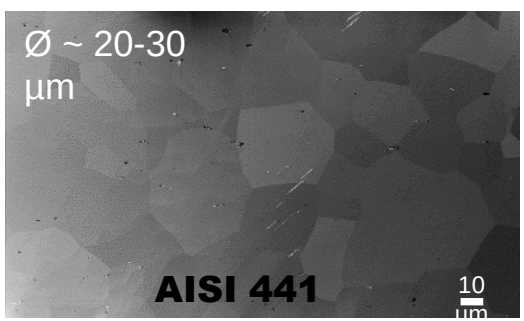


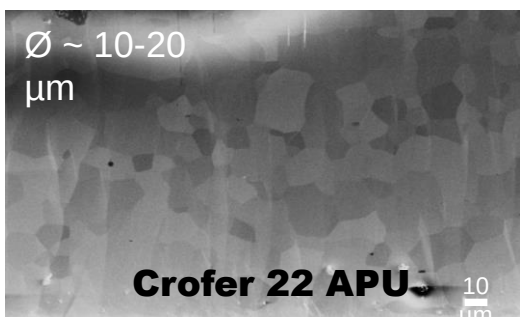


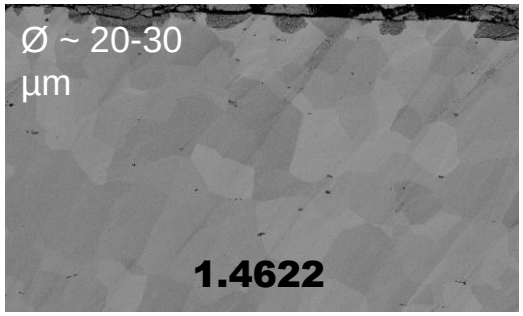


Summary (4)

- Ground Crofer 22 APU, Crofer 22 H and AISI 441 perform ok. 1.4622 shows severe attack.
- Higher Cr content does not result in significantly increased corrosion resistance.
- Pre-oxidation helps. For a while…
- Fuel side more relevant.







Conclusions

- The Co/Ce nano coatings give excellent surface properties.
  - Low Cr evaporation
  - Low corrosion rate
  - Low ASR
- Although very thin Co/Ce coatings work for 40 000h @800 C with minimal degradation.
- Dual atmosphere conditions pose new challenge.
  - Most pronounced at low tempertures
  - Pre-oxidation is beneficial due to limited ingress of hydrogen