# Surface Protection by Diffusion Barrier?

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- Motivation
  - Electricity production and environment
  - Next generation power plants
  - Corrosion in flue gases containing overwhelming $CO_2$
- Protection Systems
  - Requirements for steam power plant protective coatings
  - TBC or Cr-rich metallic coatings
  - $Al_2O_3$ Coatings
- Conclusions & Outlook

# Reliable electricity production and distributrion is necessary for an industrialised country

- Part of the infrastructure
- Electricity is the main form of energy for all techical machines.

Accidents caused by cracking steam pipes are known from chemical plants, waste incinerators and power plants.

# Combustion of carbon containing fuels produces $CO_2$

## Typical $CO_2$ values for different types of fuel

1 kg mineral oil for heating results in 3,1428 kg $CO_2$ and 4,4 MJ heat.

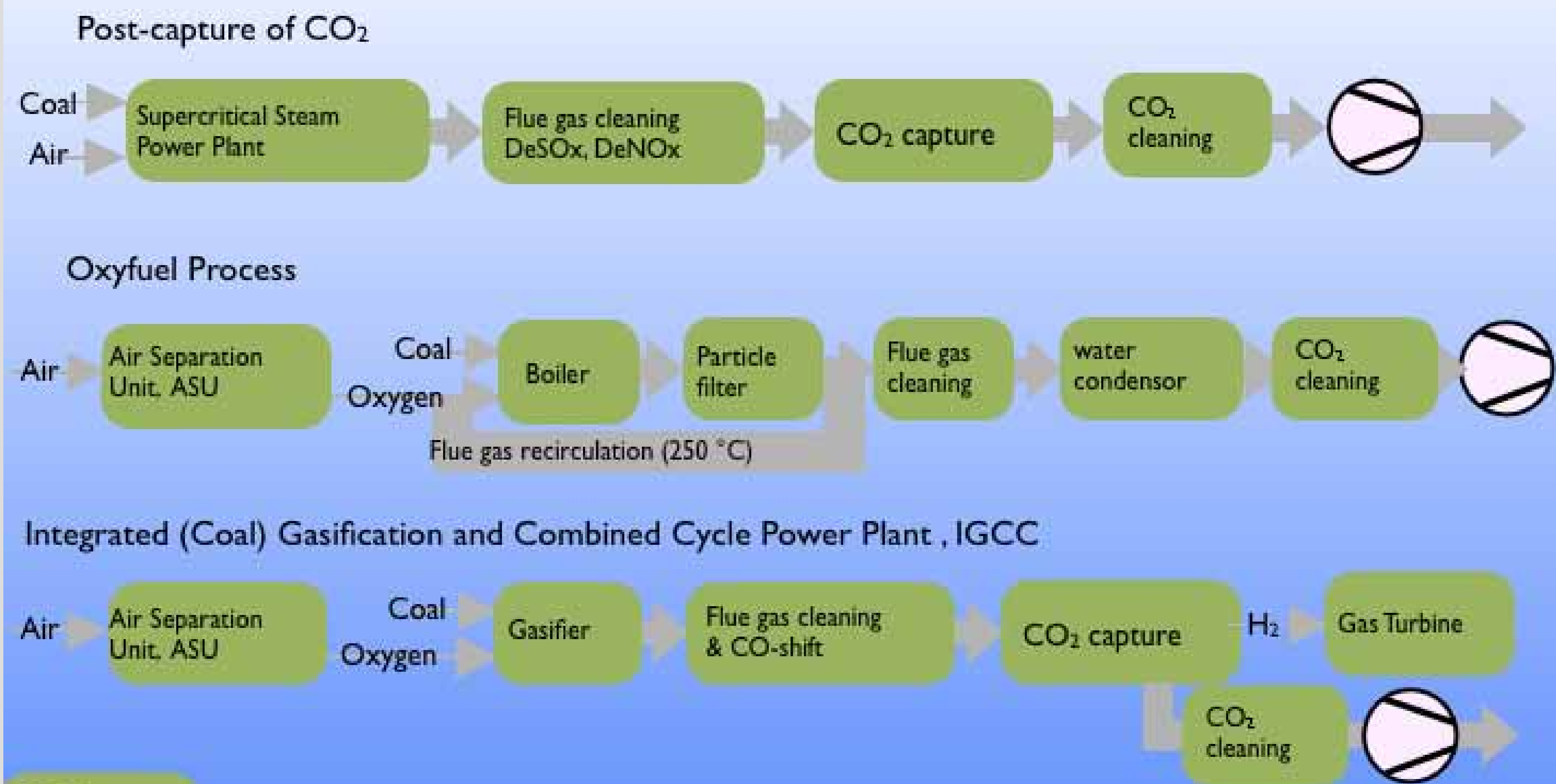
1 kg hard coal  results in 3,6164 kg $CO_2$ and 28,8 MJ

1 $m^3$ natural gas produces 2.2 kg $CO_2$ and 38,4 MJ

In Germany and world wide coal will remain an important fuel for electricity production.

Integration of $CO_2$ capture in the flue gas path of combustion steam power plants might be a potential technical route to avoid further $CO_2$ emission from electricity production.

# 3 cycles are in the focus of the German COORETEC Research Program.




**$CO_2$ cleaning** The effort to clean the $CO_2$ will increase investment cost end energy consumption within the plant.

- Any process has to be payed.
- The total efficiency will decrease
- The percentage of efficiency to pay cannot be calculated exactly but will not exceed 10 %
- A Capture Plant should offer a total efficiency of more than 42 % which is a typical level of efficiency for today technology.

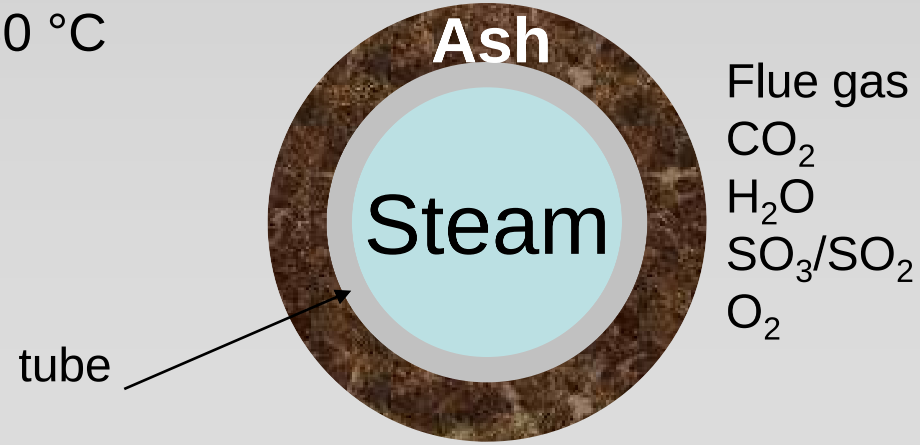
# Expectation for superheater tubes and water walls

- $10^5$ hours service life
- 650°C steam temperature
- 300 bar pressure
- Good heat transfer between flue gas and the water/steam inside
- Weldability (construction and maintanance&repair)
- Inspection (Typically ultrasonic thickness measurement)

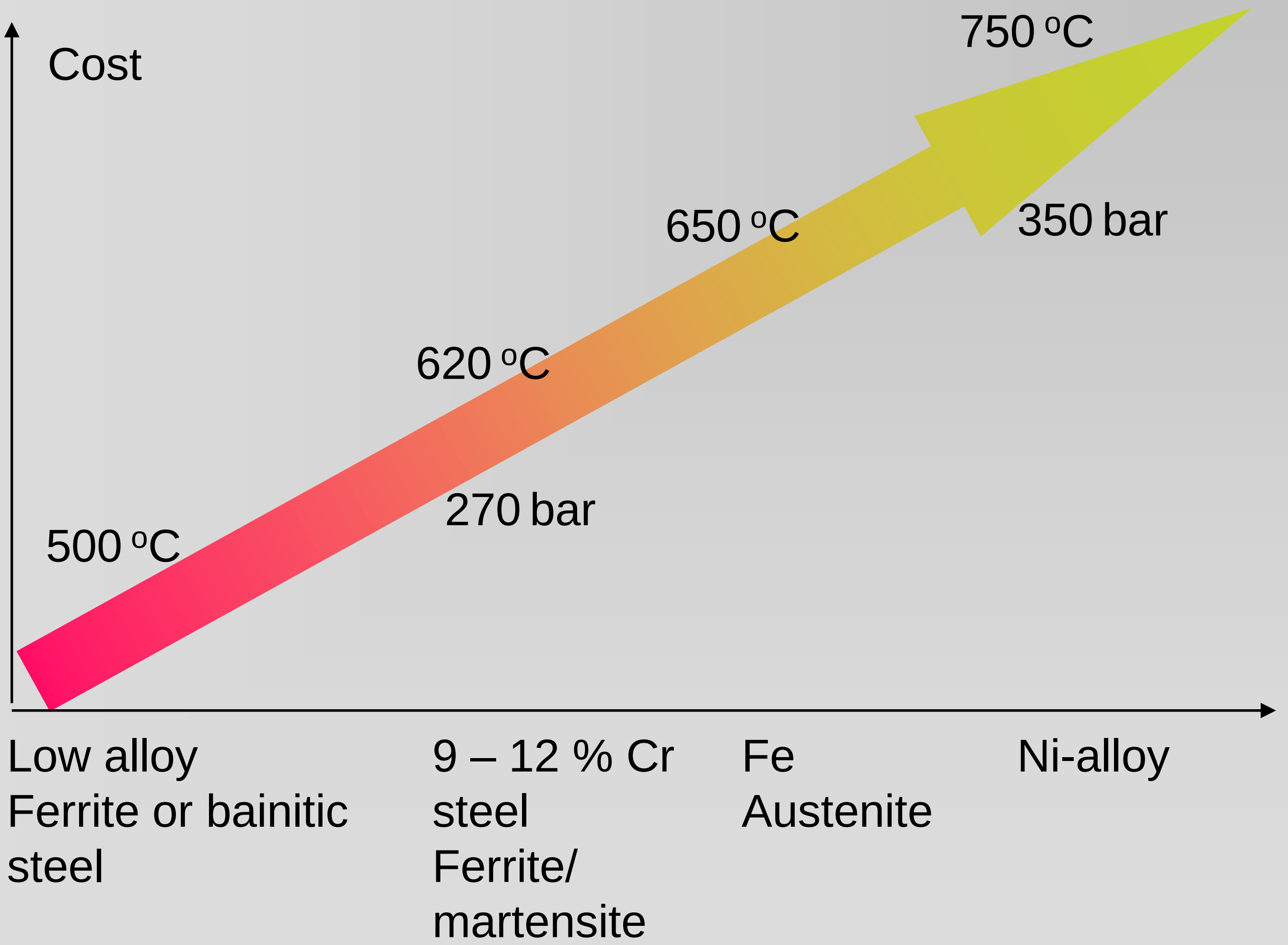
- Next generation steam power plants or steam cycles

+ Steam temperature up to 750 °C

+ Pressure 350 bar

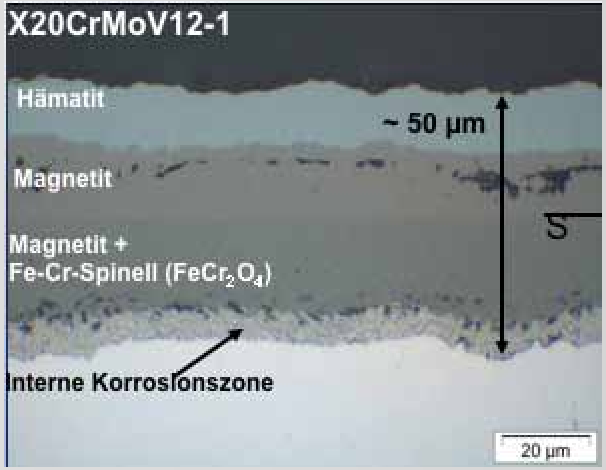


## Steels for steam power plants



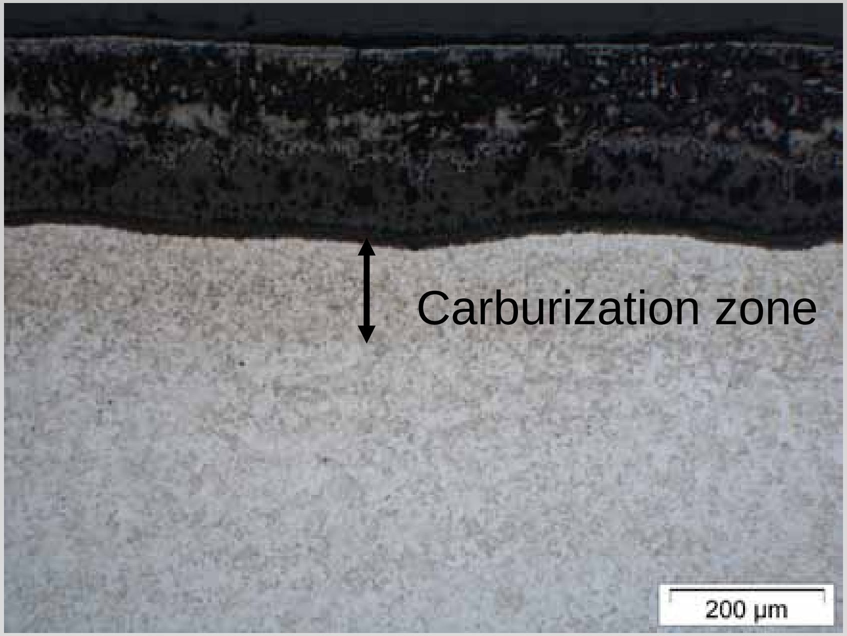
- The following discussion will focus on the conditions of the oxyfuel process
- Aim is to answer the question: Can current steels used in Oxyfuel Steam Power Plants? Only certified materials were included!
- How we have to adjust the working conditions to reach same lifetime as in conventional combustion systems?
- Flue gas
  - 68 $CO_2$ – 30 $H_2O$ – 1 $O_2$ – $SO_2$
  - Experimental simulation of the Vattenfall test facility in “Schwarze Pumpe”
- Material temperature max. T= 620°C

$CO_2$-$H_2O$-$O_2$, $p_{O2} = 9{,}94 \cdot 10^{-3}$ bar

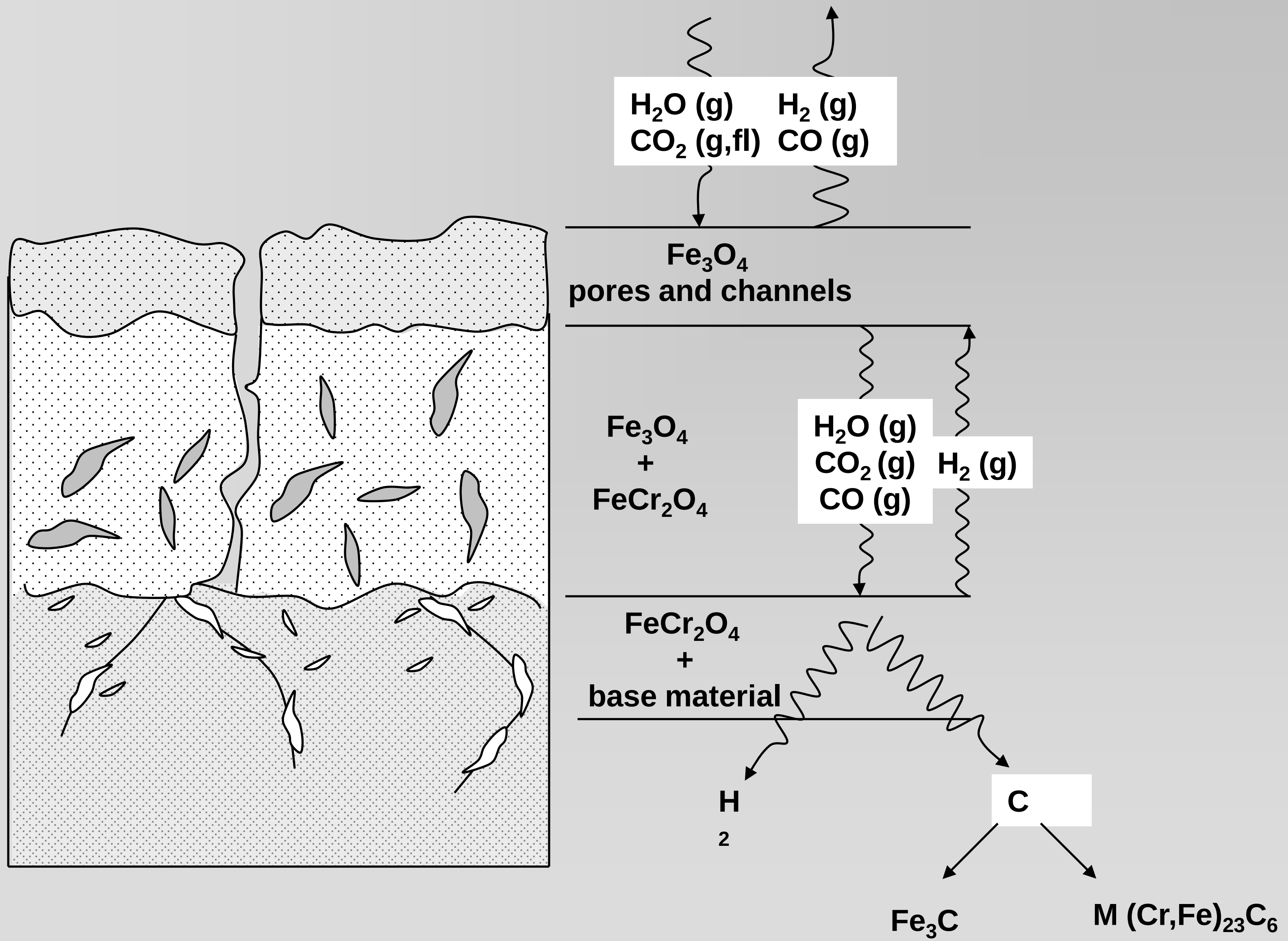


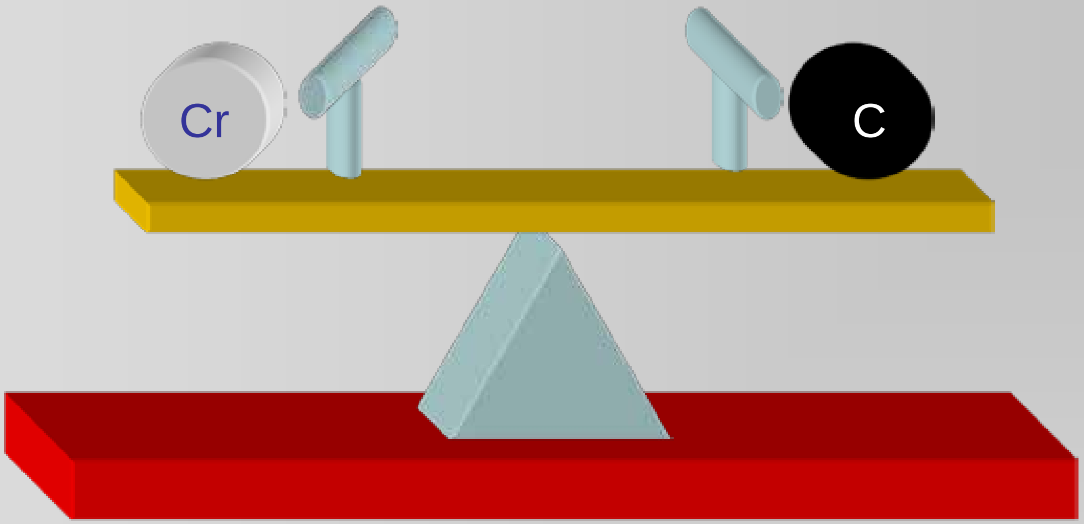


T92: carburization



# Motivation, Protective Systems, Conclusion






## Chromium:

- $FeCr_2O_4$ / $Cr_2O_3$ formation -> self protection
- Reduction of corrosion rate

## Carbon:

Fixing chromium and preventing of $FeCr_2O_4$ / $Cr_2O_3$ formation

-> Increasing of corrosion rate and carburization

# 3 Failure occured in laboratory


Local overtemperature < 75 °C
Internal load 270 bar steam
Time to failure < 24 hours

1. 13CrMo4-5 -> corrosion & carburization and volume expansion causes tensile stresses and crack growth from the outer surface towards the inside.
2. 9% Cr-steel.-> Corrosion and creep
3. 12% Cr steel. -> Corrosion

- Can current steels used in Oxyfuel Steam Power Plants? **Only with shorter life in the temperature window between 500 and 620 °C.**

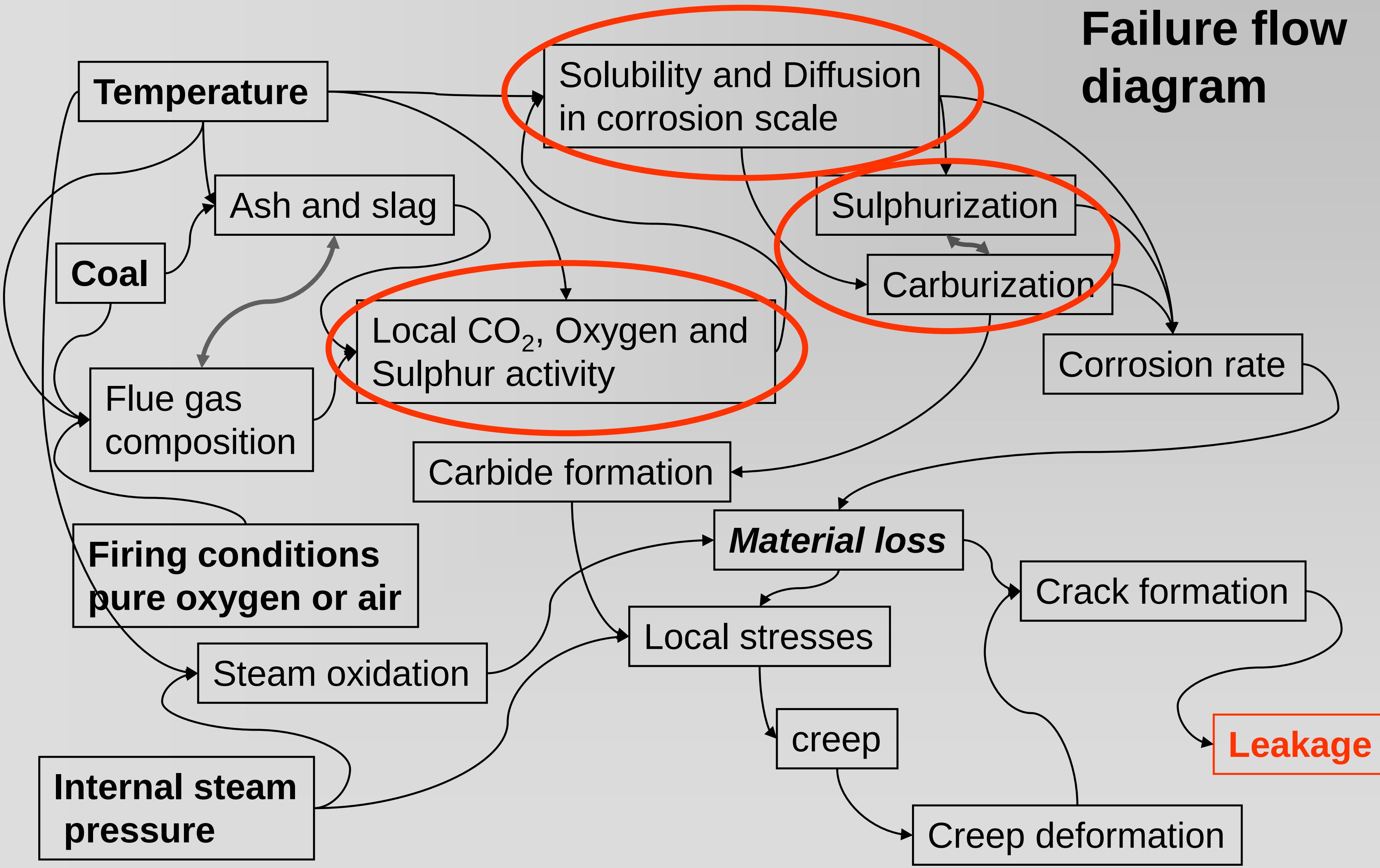
W. Schulz et al., “Comparison of the corrosion behaviour of 9-12 % Cr steels in H2O, H2O-O2 and H2O-CO2-O2”, NACE Corrosion, Atlanta, 2009 Paper No. 09264.

A.Kranzmann et al.: Reactions at the interface between steel and oxide scale in wet CO2 vontaining atmospheres, NACE Corrosion, Atlanta, 2009 , Paper No. 09265.

D. Hünert et al., “Corrosion behaviour of ferritic and martensitic power plant steels under conditions of dual atmospheres”, NACE Corrosion, Atlanta, 2009 , Paper No. 09263.

- How we have to adjust the working conditions to reach same lifetime as in conventional combustion systems? -> **Coating!**

## Failure flow diagram



## Requirements on a protective coating

- Chemical compatibility to metallic component
- Diffusion barrier for $O_2$, $CO_2$, CO, $SO_2$, S
- Low solubility of $O_2$, $H_2O$, $CO_2$, CO, C, $SO_2$, S
- Low wetting by slag
- Chemical stability in $SiO_2$-CaO-$Fe_3O_4$ lignite slag
- Chemical stability against $SO_2$ ans S
- Heat transfer equal or better than steel
- Easy to apply on boiler components
  - Spray technology or a paint
  - Atmospheric plasma spraying
- Repair and maintance

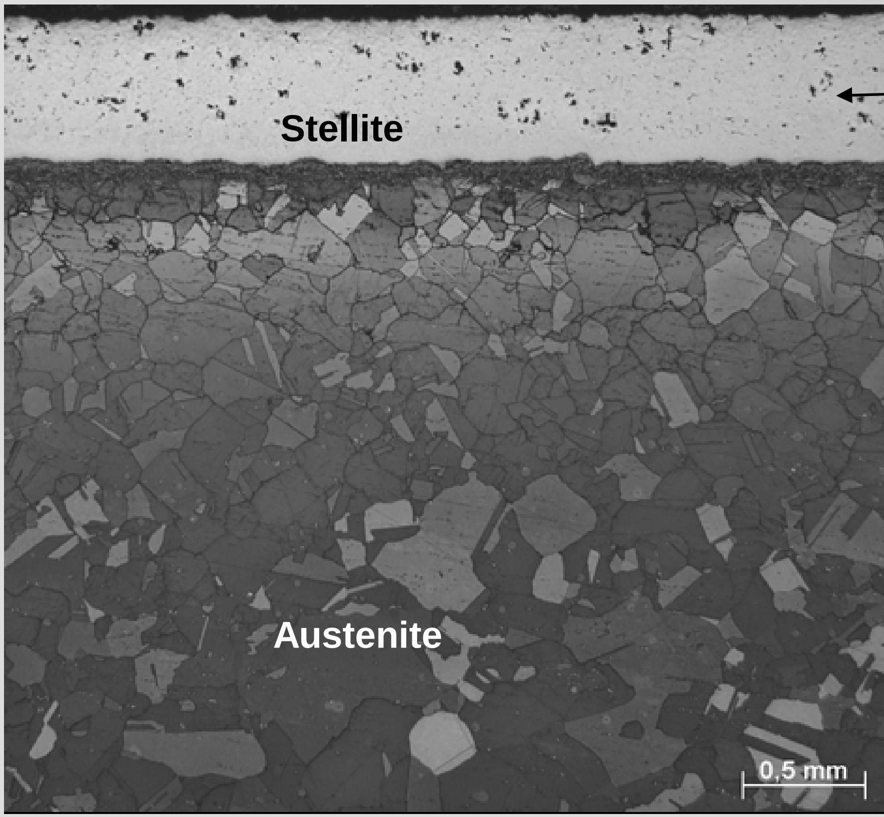
In power industry coatings are already applied

- Thermal protection -> Zirconia plasma sprayed ceramic
- Corrosion of Ni-base alloys -> MeCrAlY-coatings, Me - (Ni, Co)
- Steam corrosion protection -> Stellite

1. $ZrO_2$ used in gas turbine combustion atmosphere for component protection
   - In contrast to EB PVD or CVD techniques it can be applied outside of special chambers.
   - Proven technology
   - Several players on the market -> competition
   - No post heat treatment
2. Thermodynamic stability -> lowest eutectic temperature in important systems
   - $ZrO_2$-$SiO_2$, $T_{Emin}$ = 1685 °C
   - Al2$O_3$-$SiO_2$-$ZrO_2$, $T_{Emin}$ = 1556 °C
   - $ZrO_2$ – CaO, $T_{Emin}$ = 2141
3. Oxide Ion conductor -> **No diffusion barrier for oxygen**
4. Need for a bond layer
5. **Low thermal conductivity 3.2 W/mK** for dense material - Typical use for **thermal insulation**!
6. Good wettability for CaO-$SiO_2$-$Fe_3O_4$ based slags

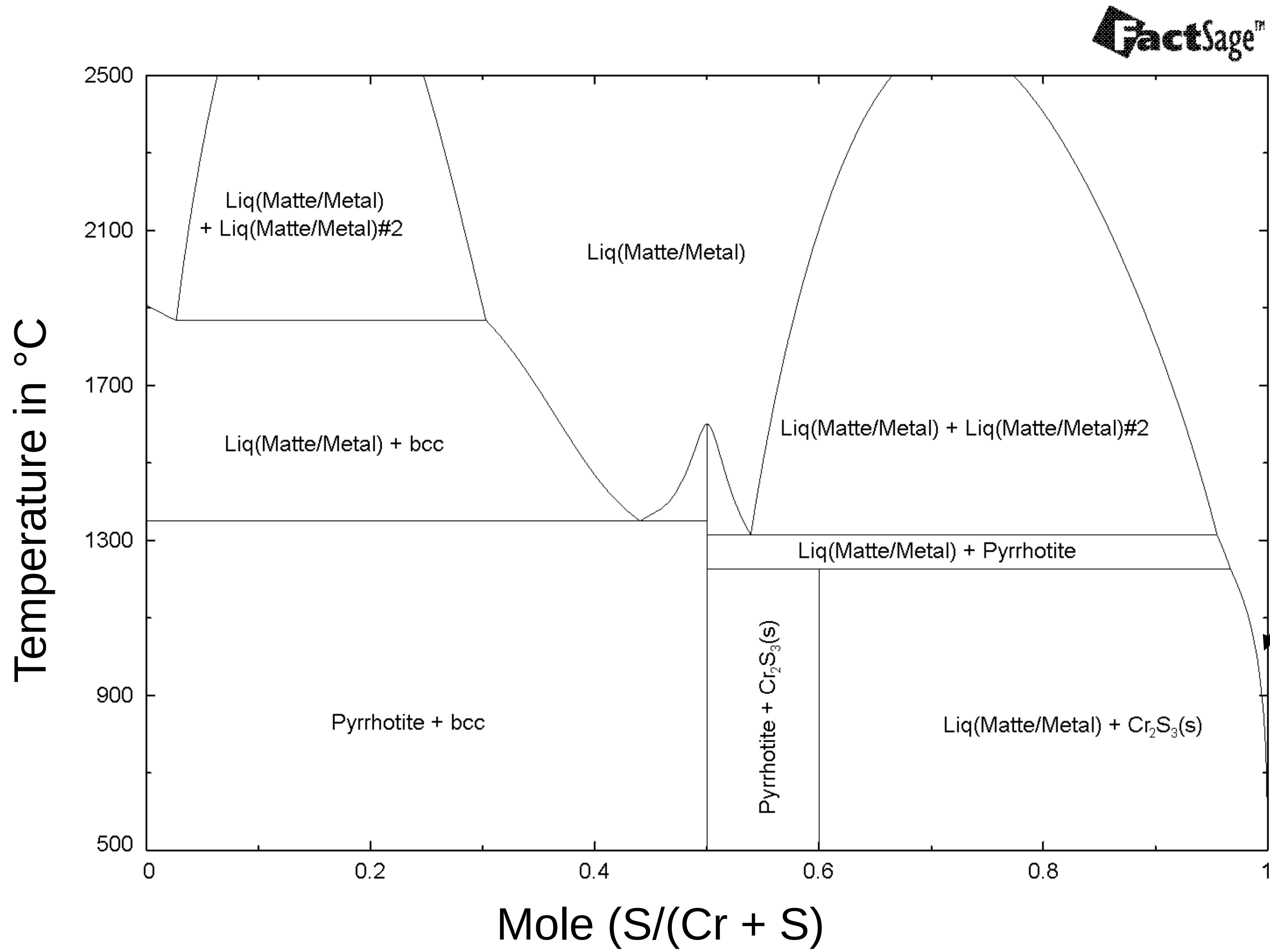
# Co-Cr based coating alloys for steam oxidation prevention

- Easy high velocity flame spraying is possible
- Typically need laser or thermal post-treatment to get a dense surface




Example
Stellite SF 6
52.3Co -19 Cr – 13 Ni – 3 Fe – 8 W – 2.5 Si – 1.5 B – 0.7 C

Cr can form a melt a low temperatures with sulphur




Melt below 700 °C

BAM

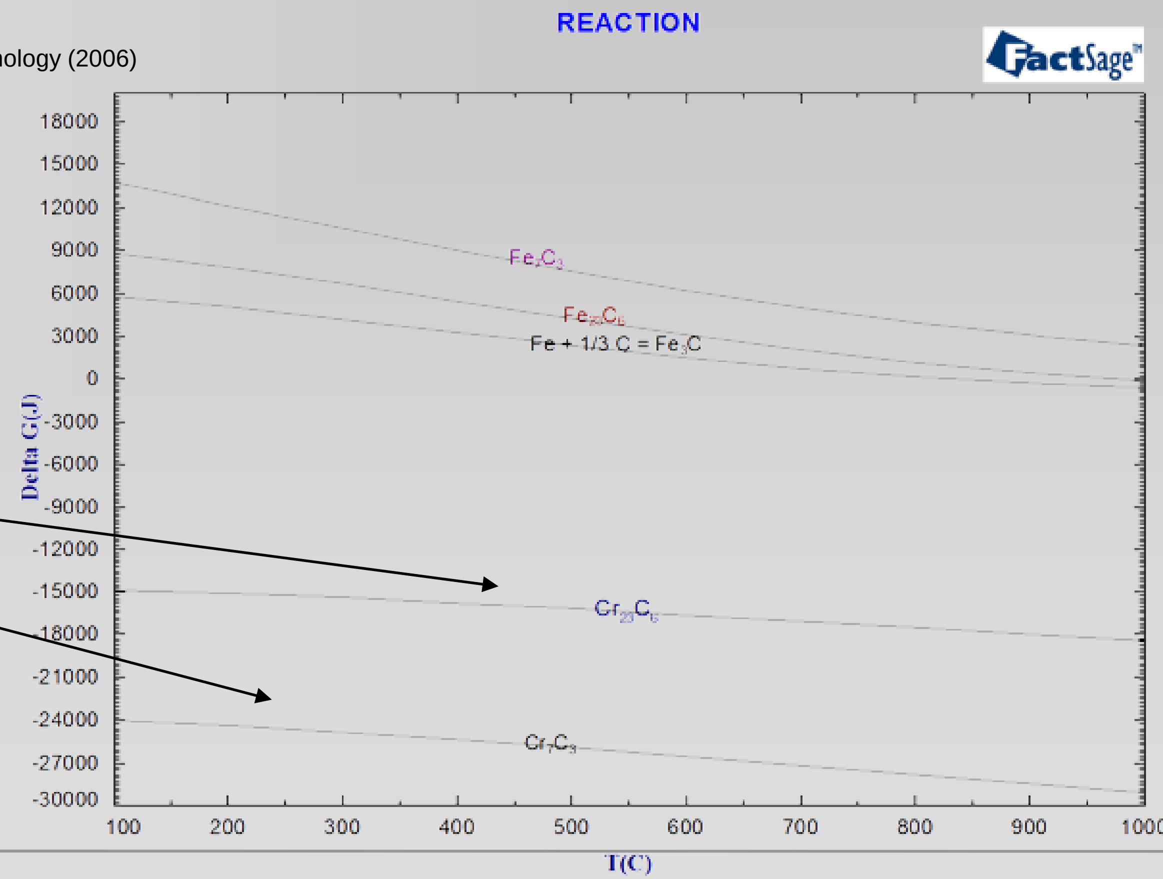
# Corrosion of Cr-alloys in $CO_2$-$H_2O$-$SO_3$/$SO_2$-$O_2$ environment

- Melt formation with S below 750°C -> sulphur corrosion
- Potential carbide formation and growth
- Further Carbide growth from preexisting carbides $M_7C_3$, $M_{23}C_7$ and $Co_6W_4C$,

U. De Oliveira et al., Surface & Coatings Technology (2006)

D. Hünert, A.Kranzmann, Corrosion (2011)

Stable $Cr_{23}C_6$ and $Cr_7C_3$



# Alumina

Low vacancy density on the oxygen sublattice -> good diffusion barrier for oxygen

Low Al selfdiffusion

Good resistance against aggressive gases

Thermal conductivity (30 W/mK) little better than alloyed steels at 700 °C.

# Goals

Dense layer

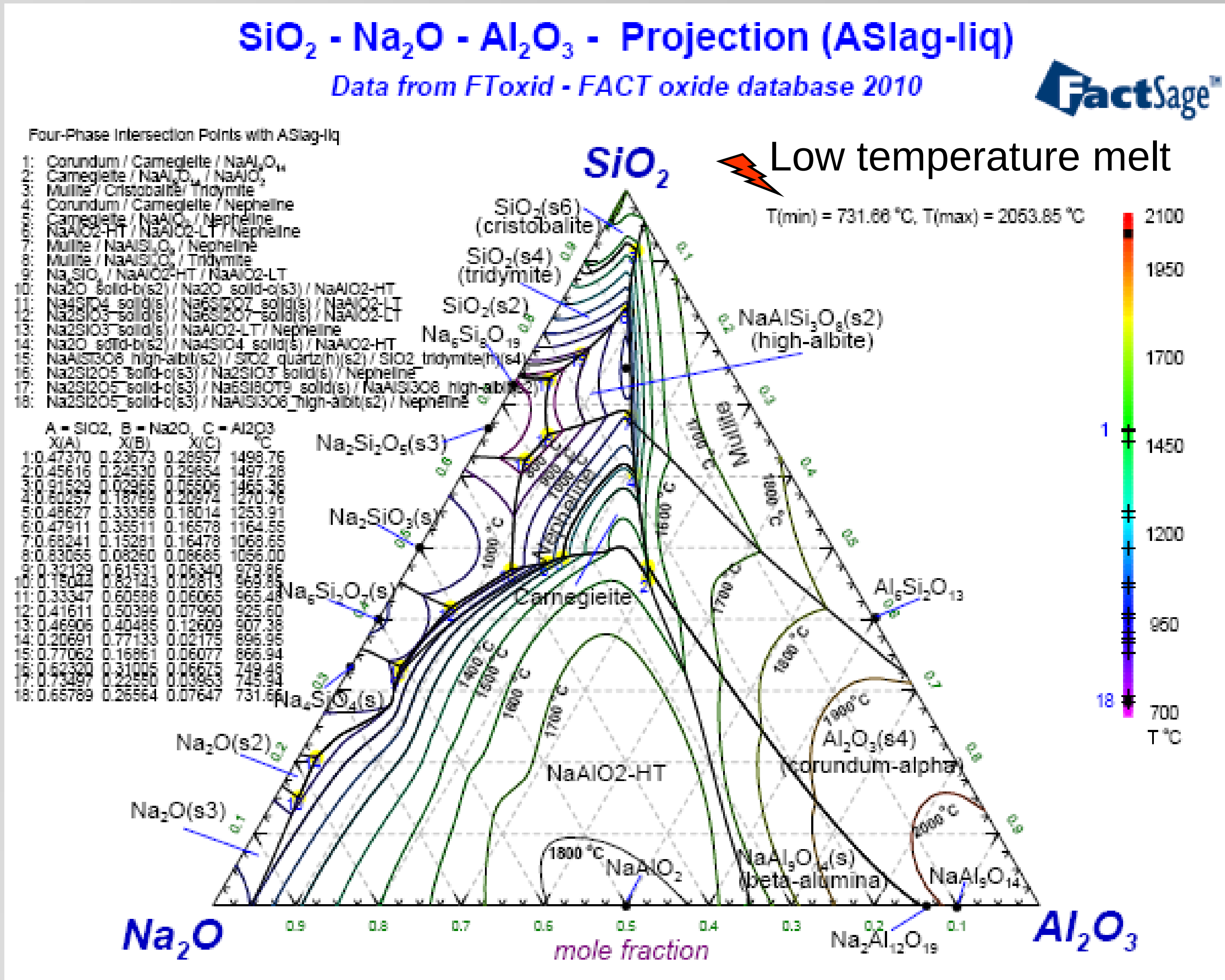
Crack free

Only very small (< 0.1 nm) or better no local defects

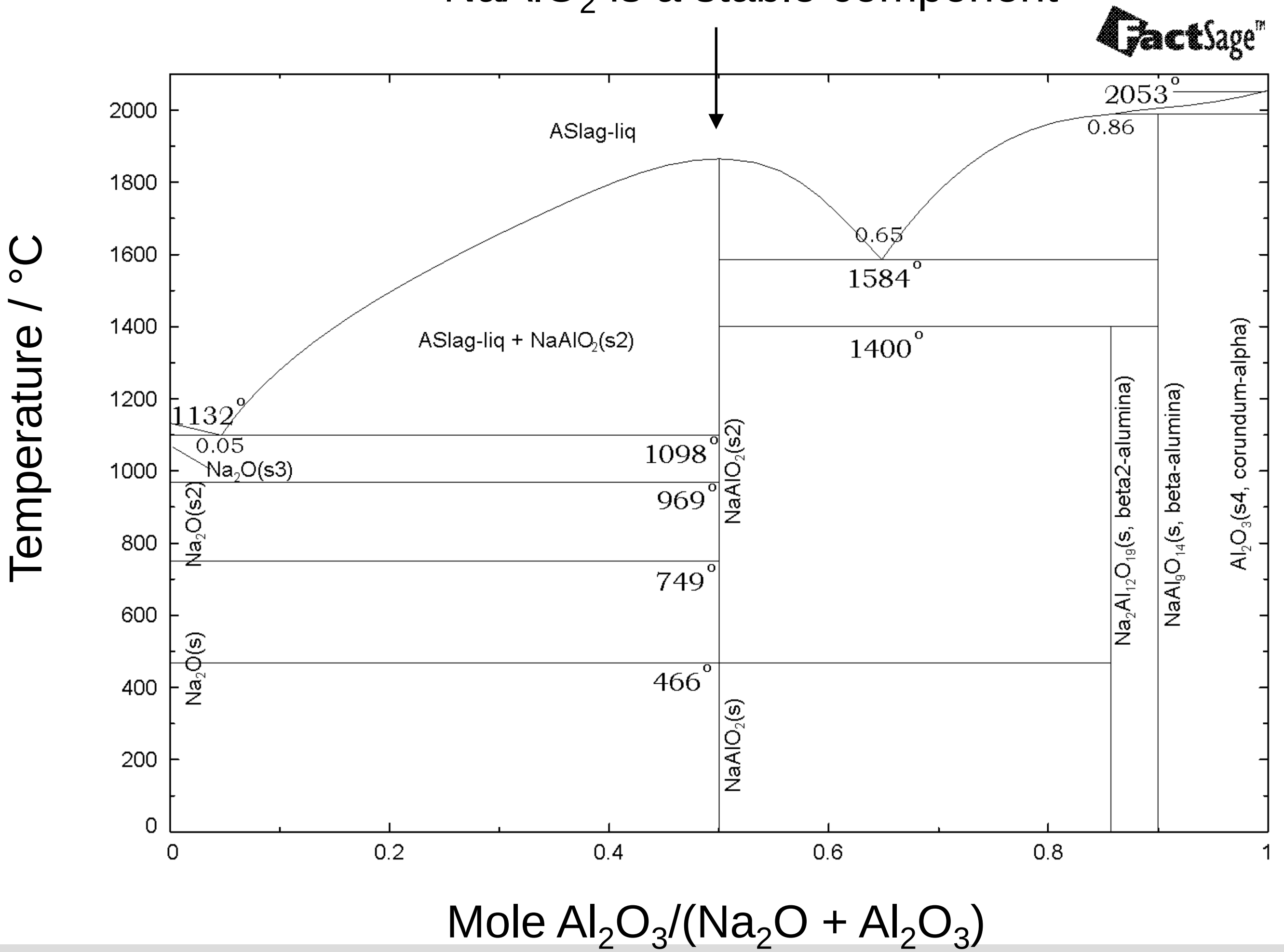
Applicable at low temperatures on technical surfaces

# Disadvantage

Less stable in Sodium rich ashes and slags



NaAlO$_2$ is a stable component



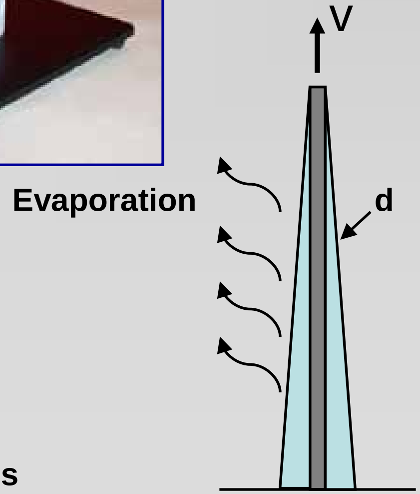
Alumina fullfills the chemical requirements

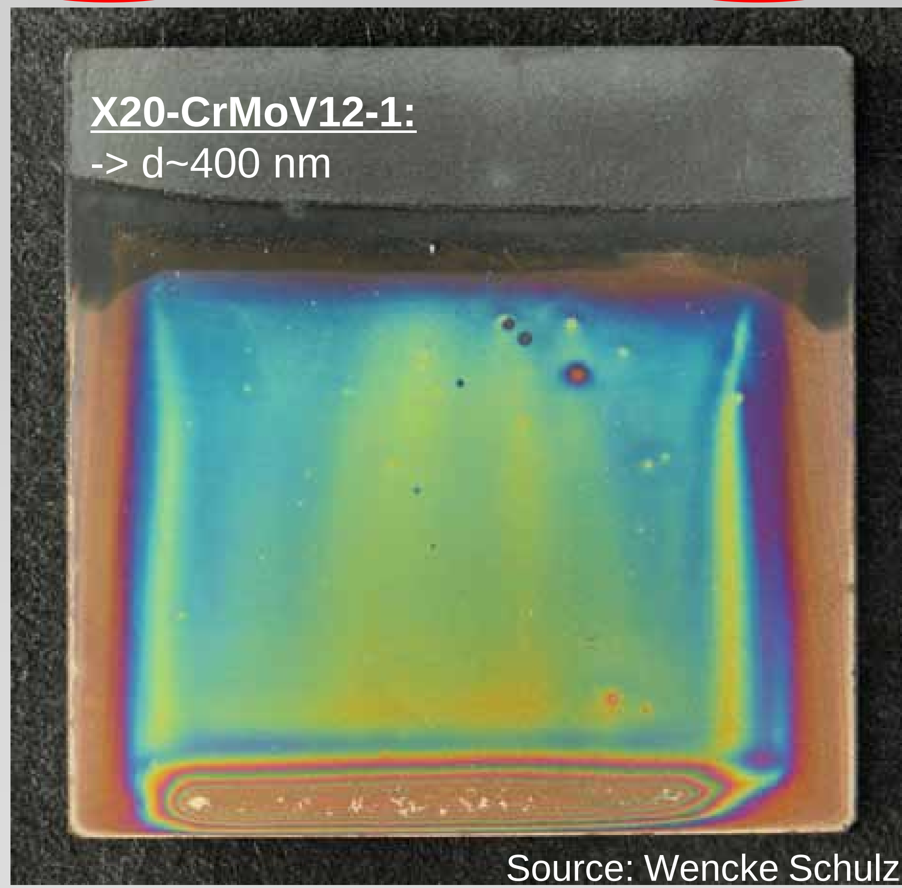
-> Two tasks

- Demonstrate the protective function!
- Think about a manufacturing technology!

# Prozess technology (tube manufacturer)

**Drying (350 ° C)** → **Heat treatment (600 ° C)**

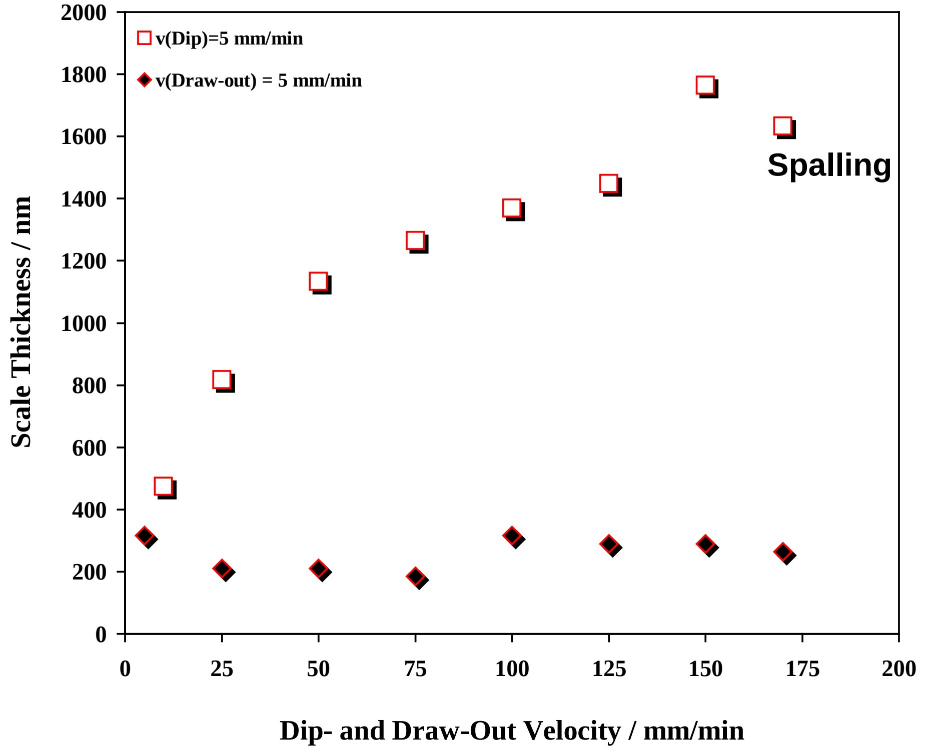



**v…velocity**
**d…coating thickness**

## Scale thickness of glass substrates after drying and heat treatment

$$d = \frac{Dm}{(2 \times G \times r)}$$




Source: Wencke Schulz

**Low Dip Velocity** → **Increasing Scale Thickness (Cracks after Drying)**

**Increasing Draw-Out Velocity** → **Homogeneous Coating Thickness**

- Advantage of thin coatings
  - Higher tolerance against strains than thick coatings
  - Lower interface stresses, less risk of spallation
  - Higher impact tolerance
  - Less lateral shrinkage in case of sintering effects

- Disadvantage
  - For a barrier against diffusion thicker is better
  - If reacts with slag or ashes fast dissolution expected

## Current process

**Goal**

**Transition Aluminas**

| | 500 ° C / 600 ° C | | 1050 ° C |
|---|---|---|---|
| **Al[6]** | **à g à d** | | **à q à a-$Al_2O_3$** |
| **$Al_{13}$-Ion** | **à Al[5] à h à** | (k/c) | **à (q) à a-$Al_2O_3$** |

**Xerogel**

Sol -> 120 ° C

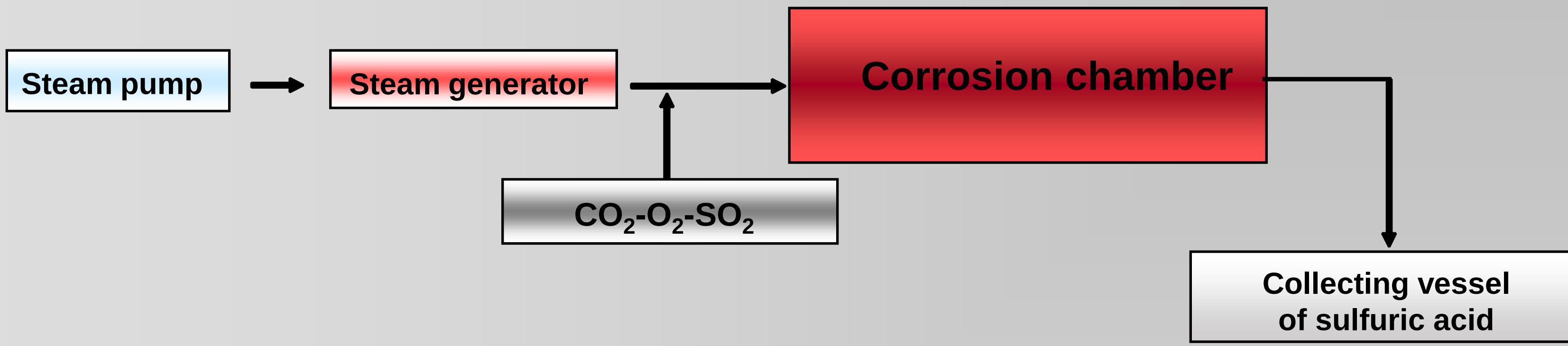
Heat treatment of steels offers to low temperatures to form a-Alumina

But

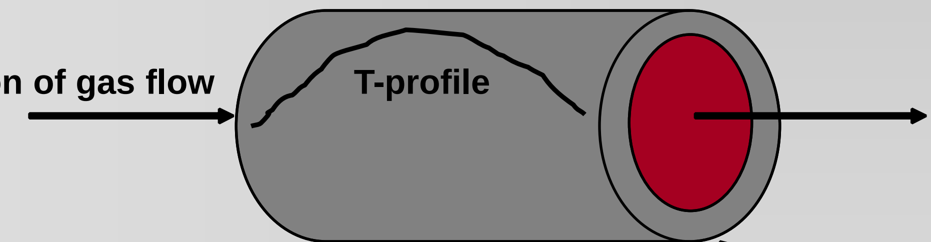
Formation of a-Alumina from natural Al-Hydroxide Minerals is possible.

Source: Wencke Schulz

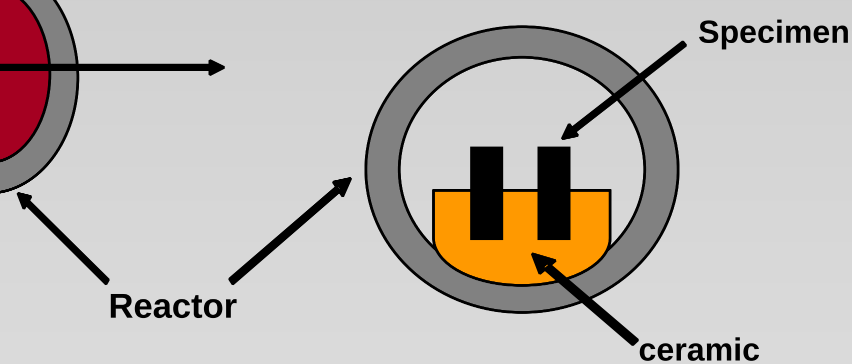
## Corrosion test facility testing plates in a reactor




### Corrosion chamber




### Specimen holder



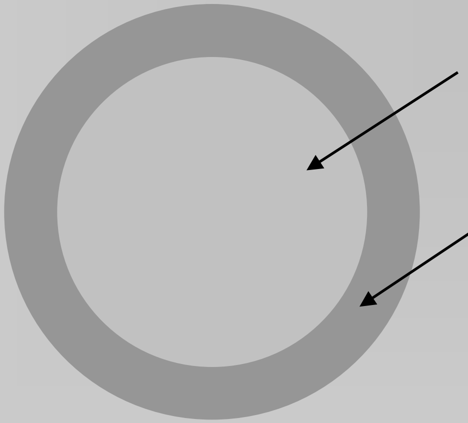

### testparameter:

| | |
|---|---|
| p: | atmospheric pressure |
| t: | 1000 h |
| T: | 600°C |
| gas: | $H_2O/CO_2/O_2/(SO_2)$ |
| | **(30 mol % / 67 mol % / 2mol % / 1 mol %)** |

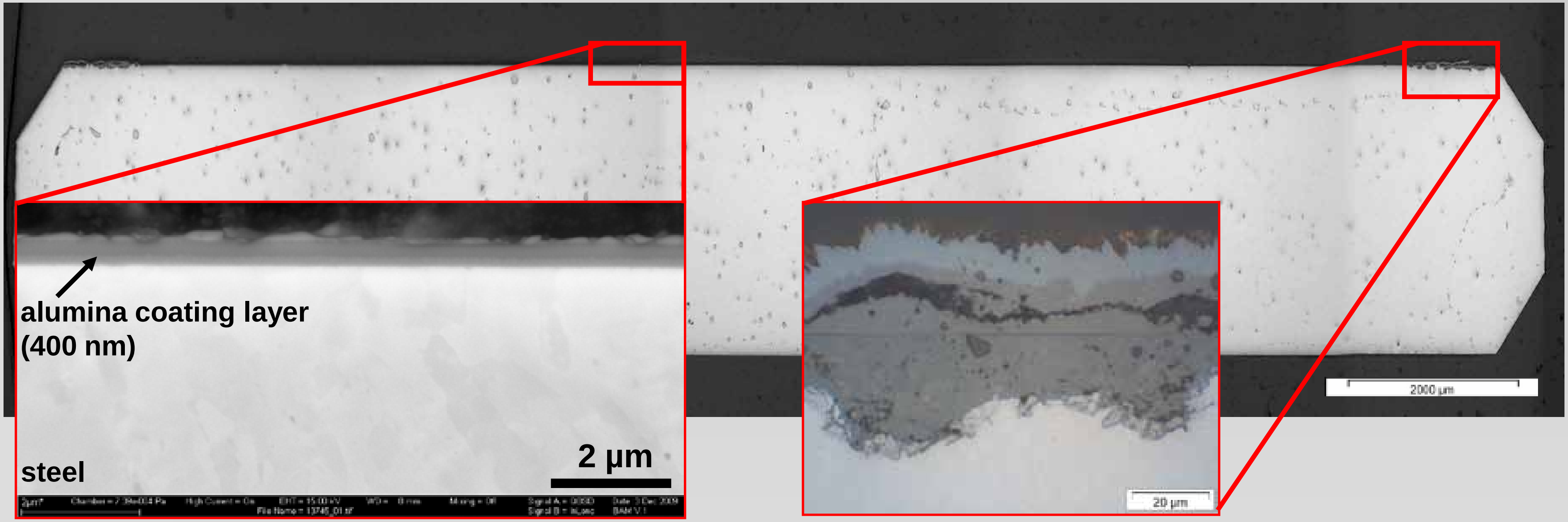
Source: Wencke Schulz

## Carburization protection

**Alumina layer tested in**
**-> $H_2O$-$CO_2$-$O_2$ / 1000 h / 600 ° C**



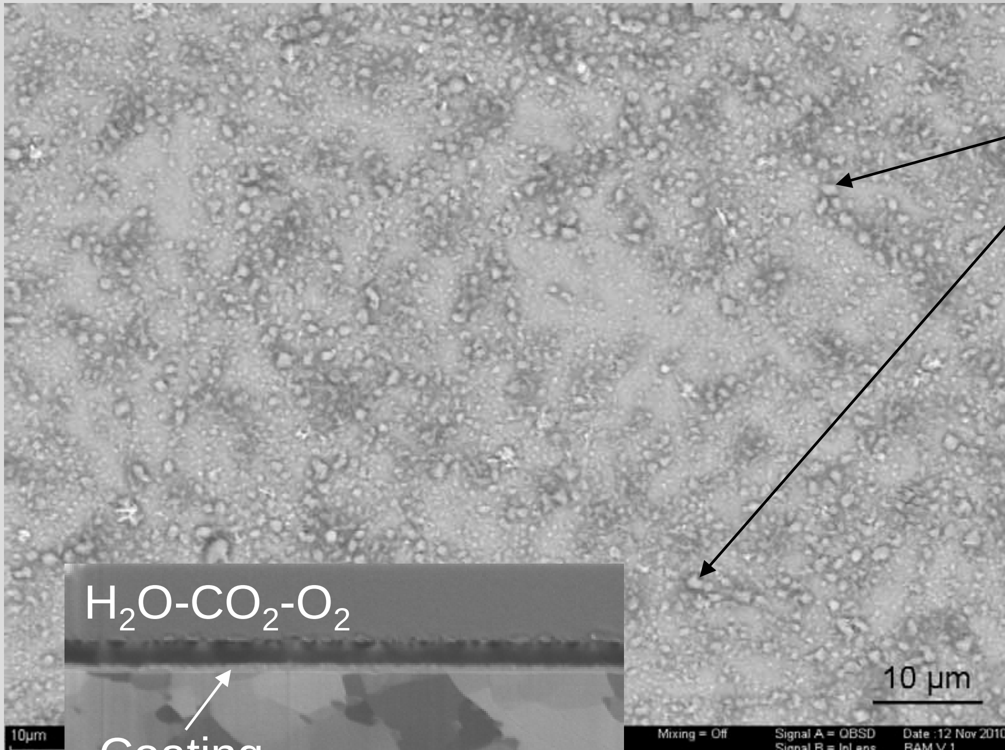

**X20-CrMoV12-1 / coated and uncoated**

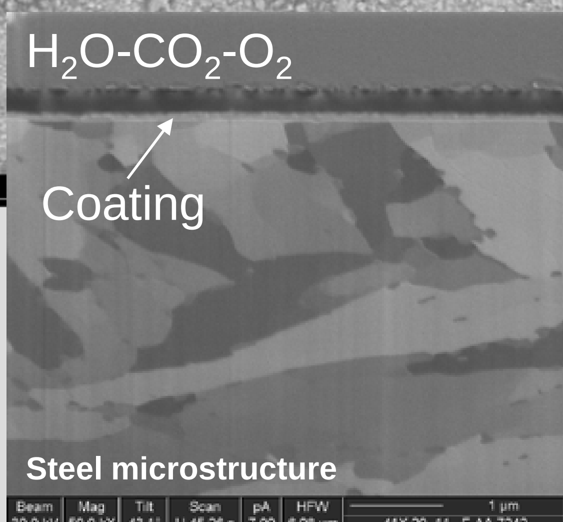



Below the $Al_2O_3$ layer carburization was not observed!

Source: Wencke Schulz

## Dip coated X20 after the corrosion in $H_2O$-$CO_2$-$O_2$-$SO_2$ for 1000 h at 600 °C

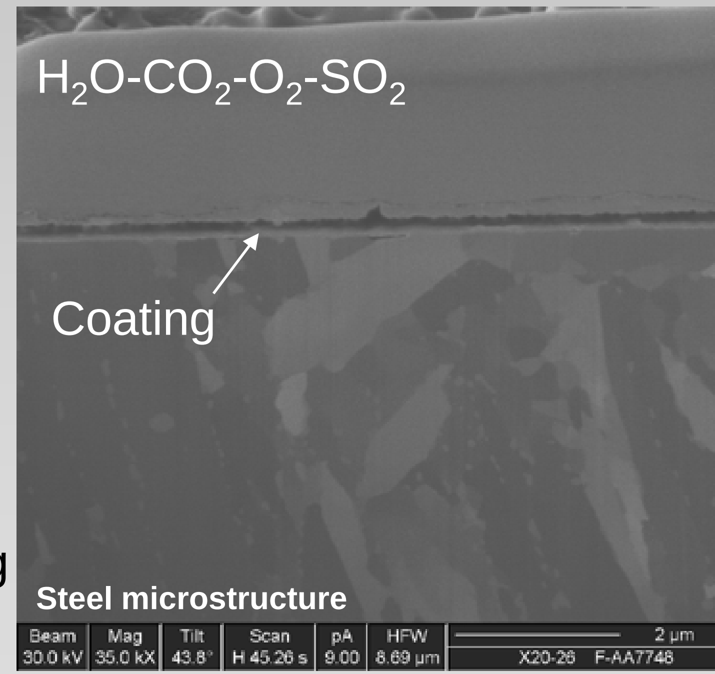



Sulfur, Manganese, Oxygen

-> manganese sulphur phase

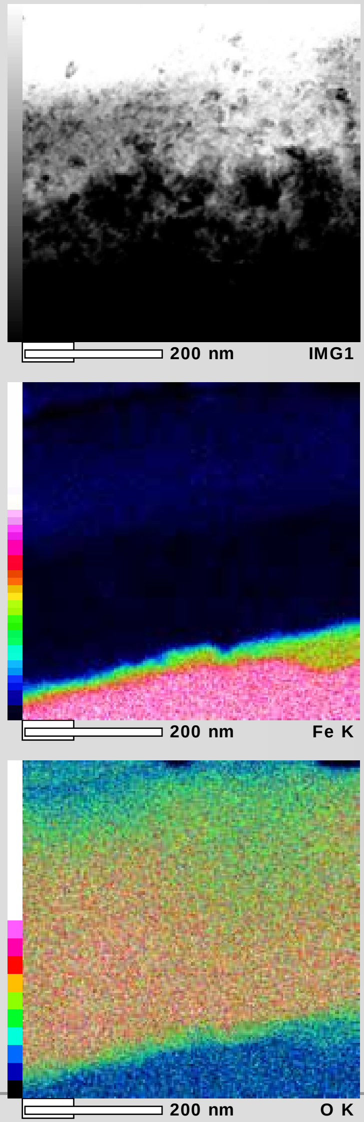
Only on the outer surface

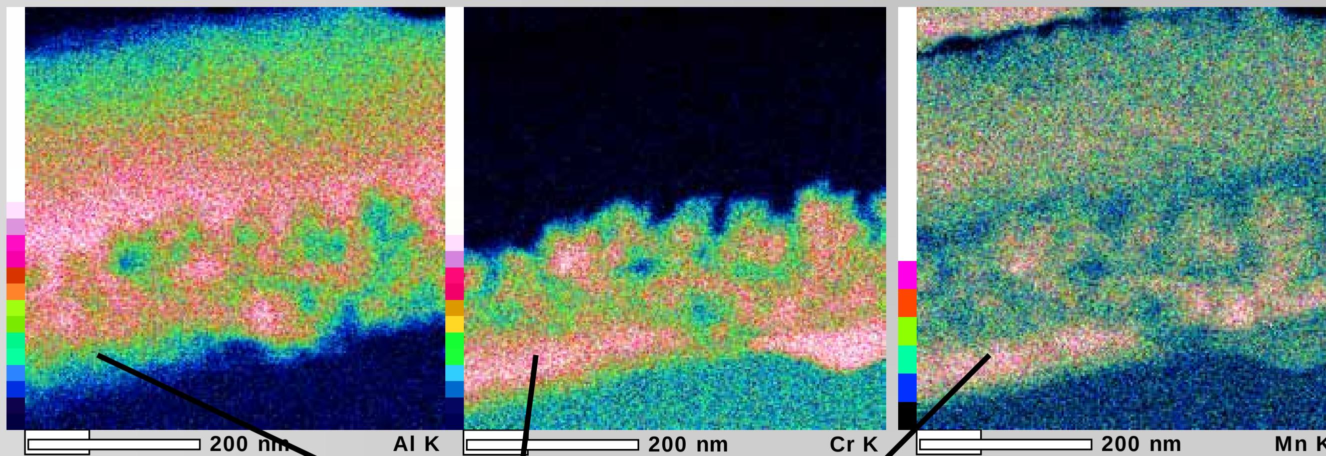



No Sulphur
In the bulk coating
material.

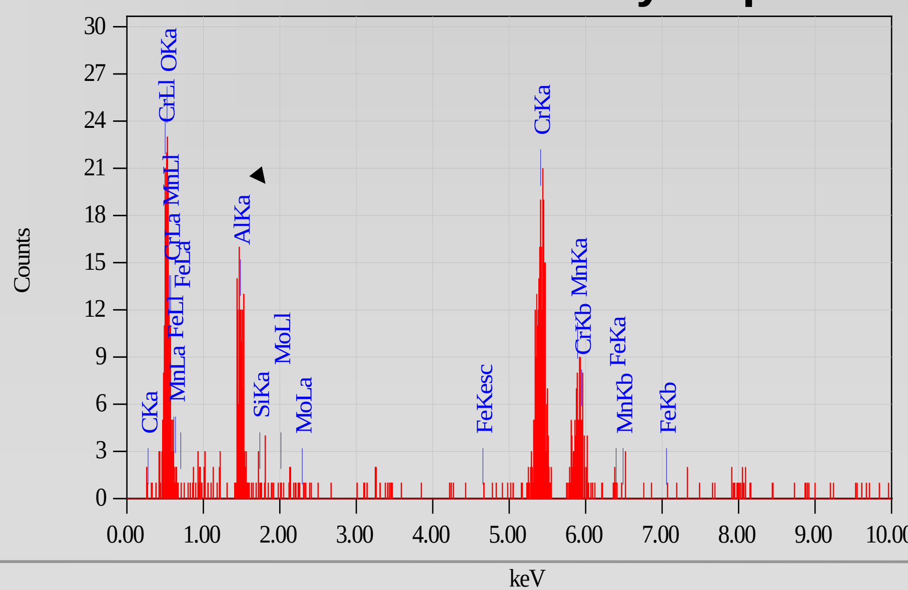
Source: Wencke Schulz

## Corrosion tests in $H_2O$-$CO_2$-$O_2$ of a spin coated X20 after 1000 h at 600 ° C




**Potentially a spinel layer**




**Possible phases:**

**δ-$Al_2O_3$**
**δ-$(Al,Cr)_2O_3$**
**δ-$(Al,Mn)_2O_3$**
**δ-$(Al,Cr,Mn)_2O_3$**
**$Cr_2O_3$**

Source:
Ilona Dörfel,
Wencke Schulz

Alumina coating in SO2 containing oxyfuel atmosphere

1. No degradation or reaction because of $SO_2$ influence
2. Again no carburization
3. Some development of the coating microstructure indicated by the distribution of Al, Cr, Mn were observed. The consequences on the long term reliability are not clear now.

- Alumina coatings were tested in an Oxyfuel Coal Power Plant Flue gas test.
- As expected alumina coatings produced at BAM by Dr. Nofz and Wencke Schulz demonstrated high resistance against reaction with $CO_2$ and $SO_2$ in combination with high water vapour partial pressure.

- DIP coating is a method qualified for industrial processes
- Self-healing effects will be part of the next development step.

# Acknowledgement

Our coating team

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- Dr. Marianne Nofz, coating chemistry
- Dr. Ilona Dörfel, TEM work
- Romeo Saliwan Neumann, SEM

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