

Sicherheit in Technik und Chemie

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COMPARISON OF EQUILIBRIUM CALCULATIONS AND REAL CORROSION SCALES. USELESS OR NECESSARY?

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Outlook









A number of flue gases contain Sulfur. Sulfur is known for its potential to

enhance the corrosion kinetics. If melts can be formed with other phases

hot corrosion can happen. Sulfur diffuses into the alloy microstructure.

All can be observed in parallel.

We discussing here Fe-alloys including less than 14 % Cr by mass and

focus on the time at high temperature!

Working conditions of water/stream tubes and water walls



Example: Simple tube with inner pressure



DROXISIM – High pressure test simulation



Designed for testing of tubes



A: gas mixtures $(SO_2, CO_2, H_2O, O_2, N_2, CO, ...)$ with up to 5 components B: Pressure(air, N₂, CO₂, H₂O (steam))

- pressure: 1 bar 320 bar
- Temperaturr: RT 800 °C





Our experiments



Coupon test according ISO-Standard 21608:2012





TC156 - ISO SO 73801986 ISO 7539-6:2011

ISO 9225:2012 ISO 13573:2012 ISO 14802:2012

ISO 17224

General requirements Stress Corrosion testing – precracked specimen Corrosivity of atmospheres Thermal cycling corrosion Guidelines for applying statistics to analysis of corrosion data application of deposits...



Dual-Gas Coupon Experiment





All experiments demonstrated here were performed under the conditions below

550 °C (823 K) \leq T \leq 650 °C (923 K) Heating and cooling in flowing Ar (ISO 21608 test conditions flue gas T \geq 300 °C and Ar T \leq 300 °C) Heating rate typical 10 K/min – in case of infrared heating around 100 K /min.

Ambient pressure

Gas:

- I. Ar plus (0.0025 0.01) SO_2 fraction of mol
- II. (0.6 0.7) CO₂ (0.20 0.25) H₂O 0.02 O₂ 0.01 SO₂ + N₂ fraction of mol

Local elliptic nodules





Steel > 0.09 Cr mass fraction

T = 550 °C 99,5 Ar + SO₂

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Corrosion in Ar/SO₂





Steel < 0.02 Cr mass fraction

T = 550 °C 99,5 Ar + SO₂

Oxyfuel flue gas (2000 h)



Ash coating







12 % Cr steel, 610 °C/1000 h, Oxyfuel





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Some observations (analytical STEM, grazing incidence x-ray)

Scale starts to grow

Metalloxide, no sulfur detectable! A volume fraction near the interface is amorphous

Only under ISO 21608 standard test conditions Sulfates become visible.









Literature data indicate Fe-Sulfate instability



 $\begin{array}{cccc} Fe_2(SO_4)_3 & -> & FeSO_4 & -> & Fe_3O_4 + SO_2 \\ & 450 \ ^\circ C & & 750 \ ^\circ C \end{array}$

Wet oxygen, Start T > 530 °C: $4FeSO_4 \rightarrow Fe_2O(SO4)_2 - \alpha - Fe2O3 + 2SO_2/1/$ Wet Oxygen: T > 600 °C: $Fe_2O(SO4)_2 \rightarrow \alpha - Fe2O3 + 2SO_2 + \frac{1}{2}O_2$ In dry air the reaction at 210 °C.

Dry Nitrogen: Decomposition of Fe2(SO4)3 starts at 553 °C /2/ Air, heating rate 2K/min: The decomposition of $Fe_2(SO_4)_3$ starts at 507 °C /3/ Flowing dry Nitrogen: The decomposition of FeSO₄ starts at 537 °C /4/

For TG experiments it was shown, that the oberved decompositon temperature is lower as lower the heating rate.



Equilibrium calculations ?

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Stability diagramm Fe-S₂-O₂





Ftdemo and FactPS both possible.

Sulfate Phases excluded







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Phase diagramm module (FactPS) Idea: SO_2 can cross the scale – contact with alloy.





The observed phase Fe_7S_8 was not calculated.

Fe_7S_8 becomes present if S_2 is considered.





Sulfide formation in the inner oxidation zone.





Wuestite will be consumed by SO_2 .

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Iron oxides reacting with S₂ (g)









If SO₂ can be transported in the inner oxide scale Sulfate should

be observable in our experiments.

Classical idea of SO₂ decomposition below $pO_2 < 10^{-14}$ bar, SO₂ can not be transported in the gas phase.



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BAM



Model – SO₂ decomposition -> O^{2-} and S₂



FeO in contact with S₂(g)





Considering the experiments and the calculations



- The entrance remark is black versus white and is not useful
- The calculations were helpful and indicate rather the reaction with S_2 then the reaction with SO_2 .
- Calculated phase diagrams can very frequently support the understanding of the possible corrosion mechanisms.
- In case of metal sulfate phases the decomposition should better included in corrosion mechanism discussion.
- Observation of sulfates indicate direkt contact to gases like SO₂ or O₂.

Literature



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