STRESS CORROSION TESTING OF COPPER IN NEAR NEUTRAL SULFIDE SOLUTIONS

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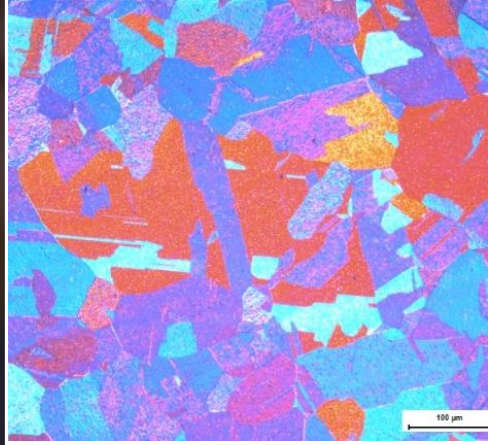


Background

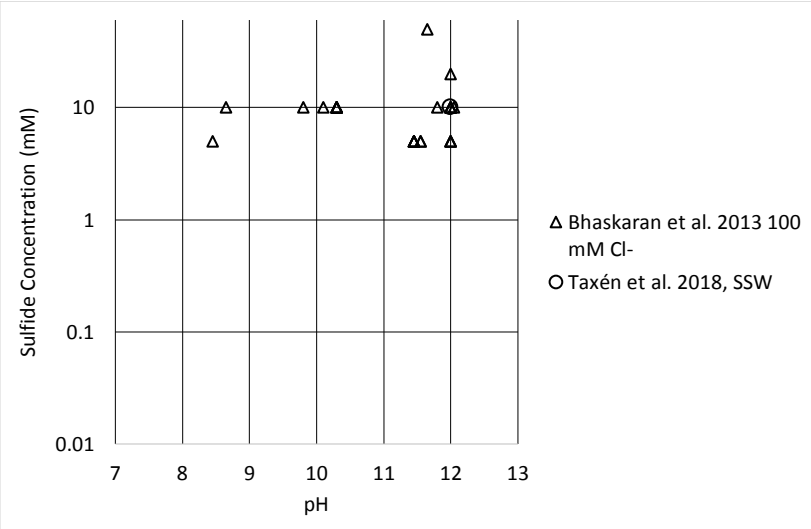
- Copper is the intended canister material for the disposal of spent nuclear fuel in Sweden.
- At repository depth the groundwater may contain dissolved sulphide
- Oxic stage immediately after closure
- **Anoxic stage** under geological time span

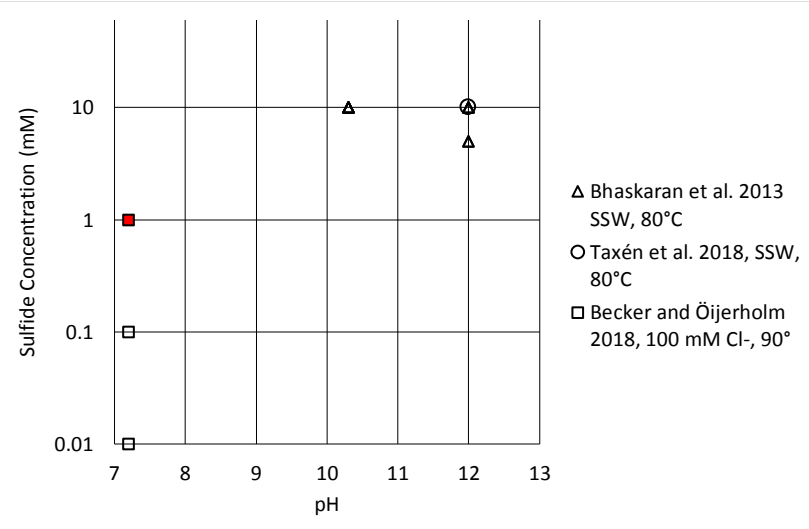
Sulfides cause corrosion of copper!

Can sulfide cause cracking of copper (EAC) ?

Previous studies of cracking of copper in sulfide

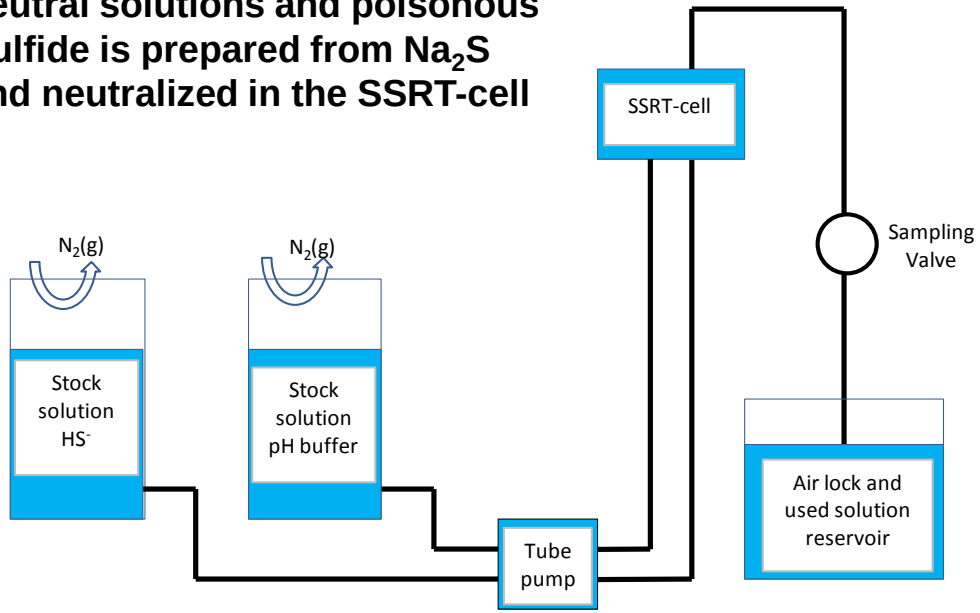
- Taniguchi and Kawasaki. 2008 YES
- Bhaskaran et al. 2013 NO SKB-Cu
- Becker R, Öijerholm J, 2017 YES SKB-Cu
- Taxén et al 2018 NO SKB-Cu





The experimental setup

- **Sulfide (HS^-) is volatile as H_2S in neutral solutions and poisonous**
- **Sulfide is prepared from Na_2S and neutralized in the SSRT-cell**



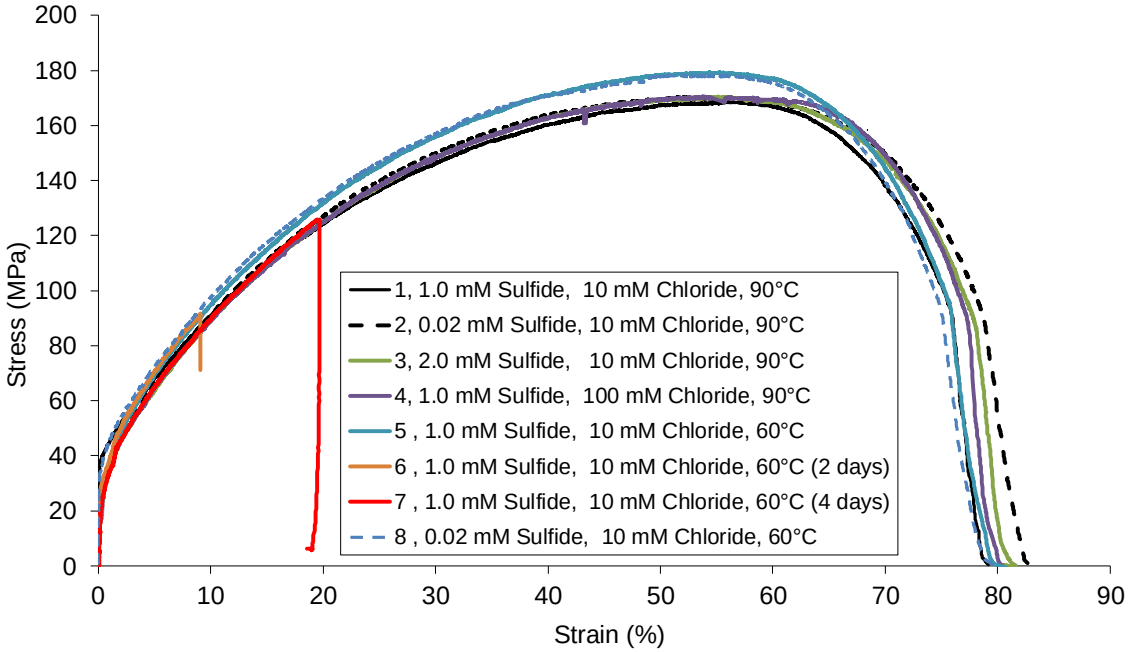
Summary of the test conditions

Run #	Temperature (°C)	Sulfide Concentration mM	Sulfide Concentration mg/l	Chloride Concentration (mM)	Duration (days)
1	90	1	32	10	Until rupture
2	90	0.02	0.06	10	Until rupture
3	90	2	64	10	Until rupture
4	90	1	32	100	Until rupture
5	60	1	32	10	Until rupture
6	60	1	32	10	2
7	60	1	32	10	4
8	60	0.02	0.06	10	Until rupture

Strain rate $5x10^{-7}$ s^{-1}
10 mM phosphate at pH 7.2

- Variations in
  - Temperature
  - Sulfide concentration
  - Chloride concentration
  - Duration

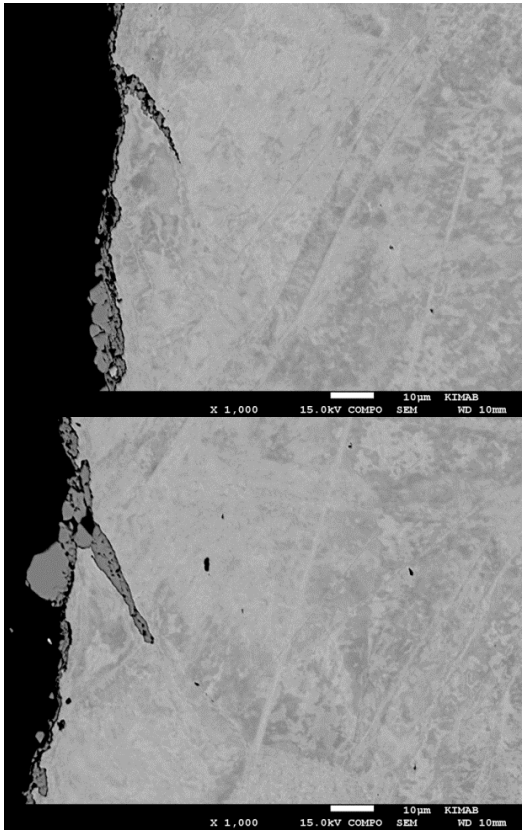
Results – Stress-strain



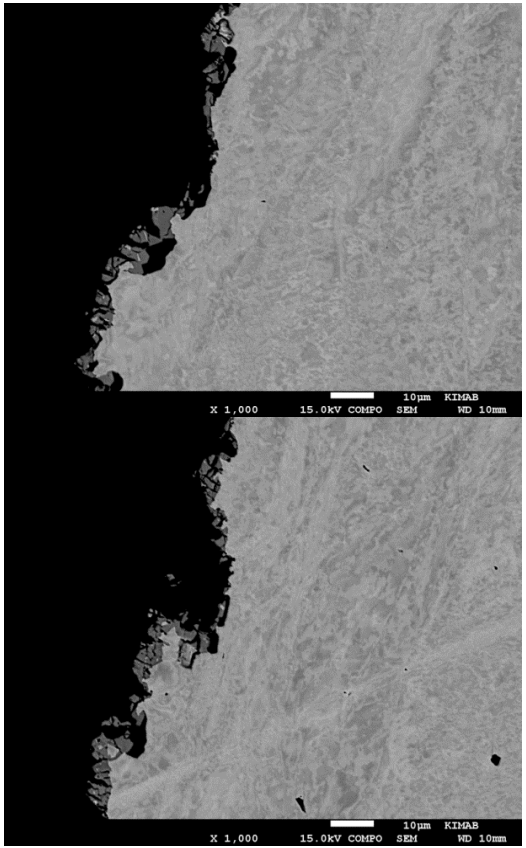
- Very ductile appearance
- No influence of sulfide
- Slightly lower Maximum stress at 90°C than at 60°C

Results – SEM

1 mM sulfide 90° (Run #1)



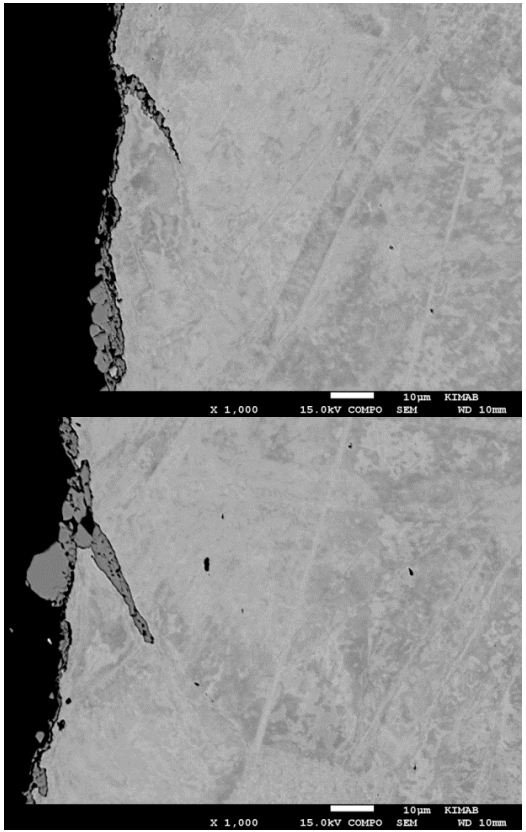
0.02 mM sulfide 90° (Run #2)



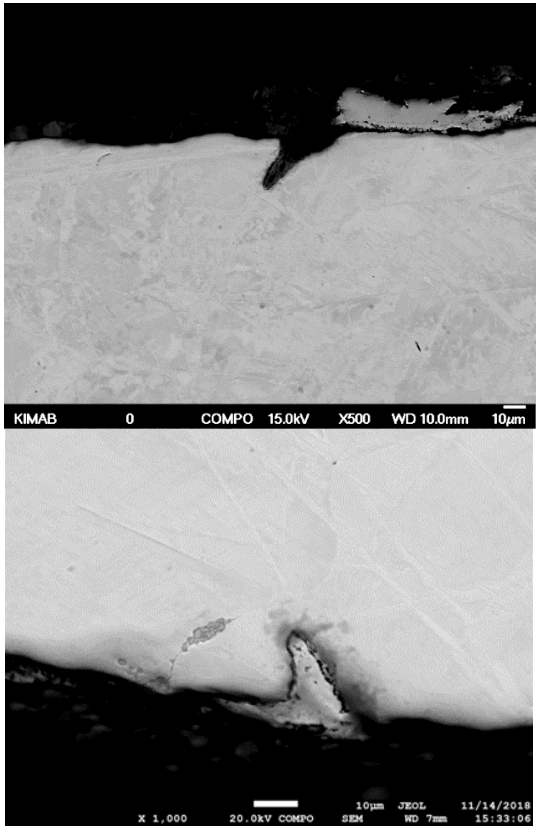
- Crack-like features are found after Run #1
- No such features are found after Run #2

Results – SEM

1 mM sulfide 90° (Run #1)



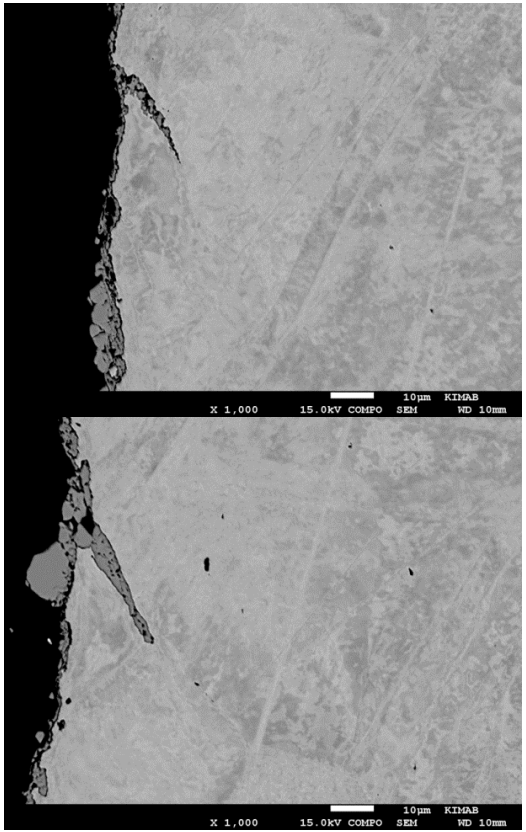
2 mM sulfide 90° (Run #3)



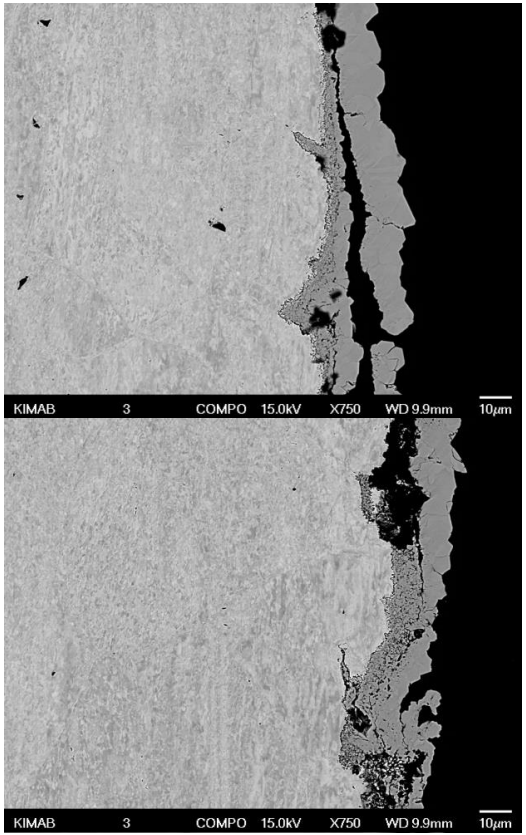
- Increasing sulfide concentration:
  - Generally wider and fewer cracks, similar depth
  - But – exceptions!

Results – SEM

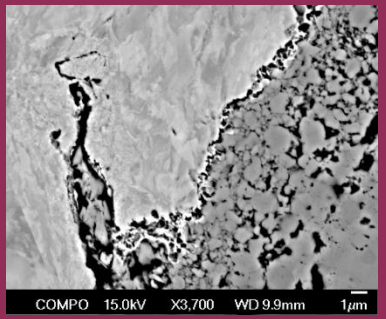
1 mM sulfide, 10 mM chloride 90° (Run #1)



1 mM sulfide, 100 mM chloride 90° (Run #4)



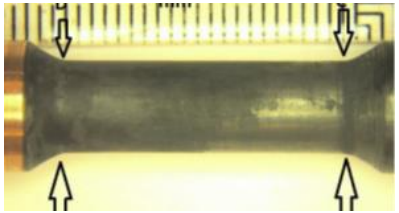
- Increasing Chloride concentration:
  - Cracks of similar depth
  - Larger amount of solid corrosion products
  - Fine structure

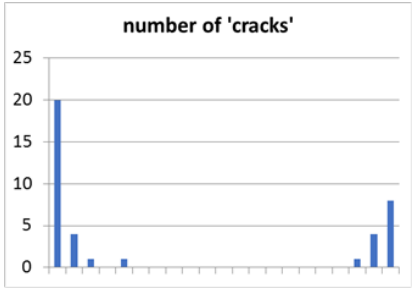


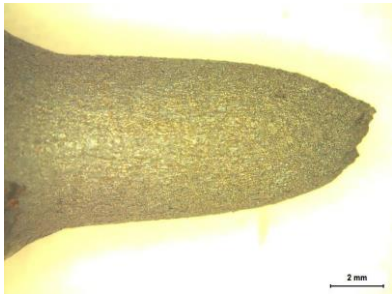
Location and number of cracks

- All crack-like features are intercrystalline
- More cracks were observed after test at 60°C than at 90°C.
- The initial cracks are preferentially located at the ends of the gauge sections of the test rods.
- Necking and final rupture occurs close to the middle of the gauge section.

After 2 days

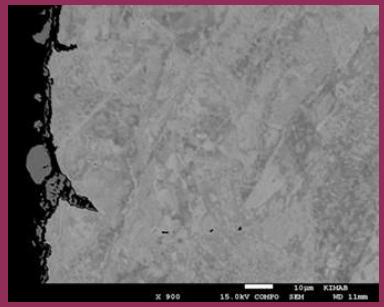


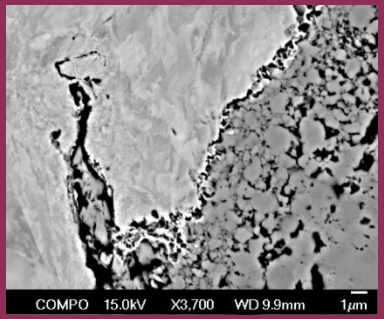




Interpretations/observations

- Cracks initiate easily
- The initial cracks do not lead to rupture
- Some cracks contain a fine structure of finer cracks
- The cracks follow the crystal structure, also the finer cracks
- Some cracks contain particles of corrosion product
- Crack walls seem to be bare copper



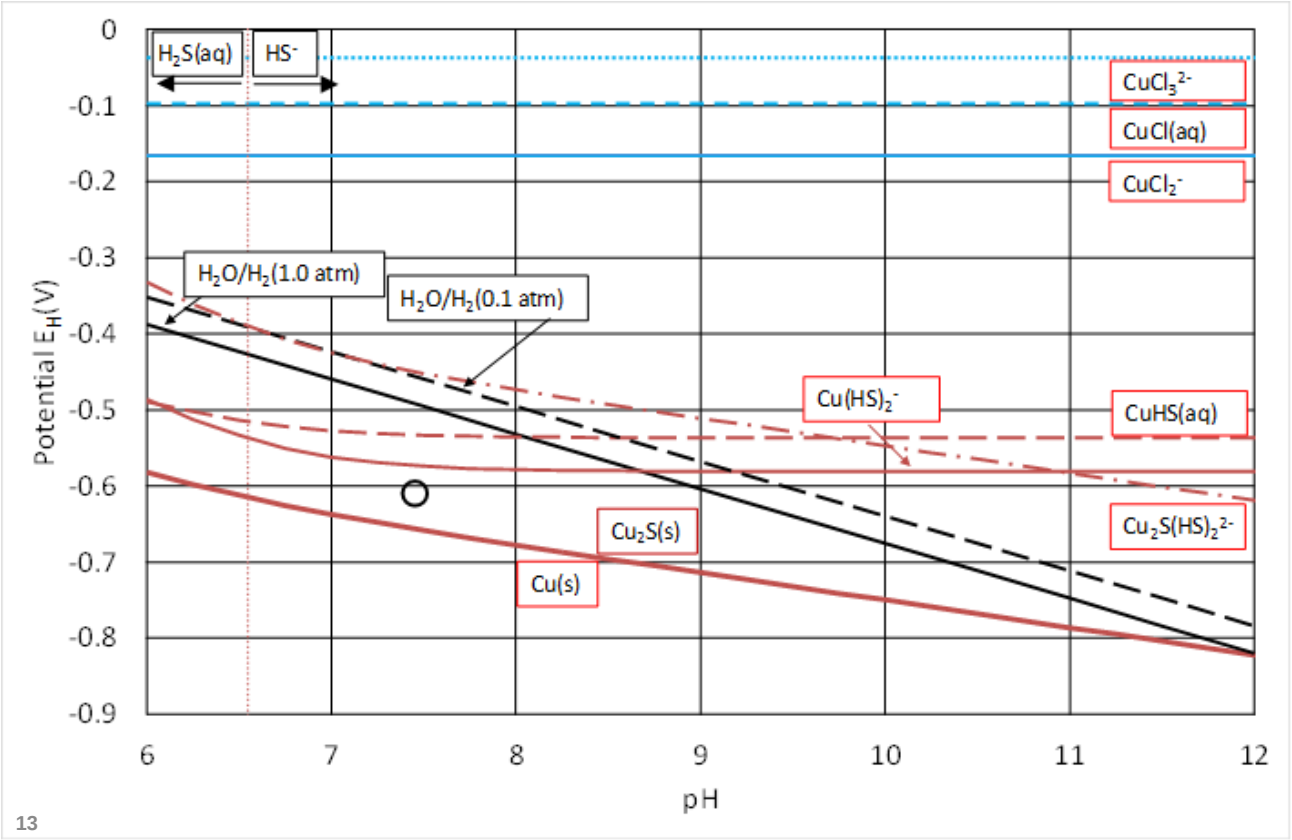


Hypothesis

Intergranular corrosion aggravated by strain

- Corrosion initiates at susceptible grain boundaries and produces small cavities. The intergranular corrosion is aggravated by strain that pulls apart the grains that form the flanks of the cavity.
- Grain boundaries (less noble) corrode and produce a concentration of dissolved Cu(I) so that grain bodies (more noble) appear as immune
- Precipitation (growth) of Cu2S decreases the concentration of dissolved Cu(I) preventing that also grain boundaries behave as immune
- Cu2S is a secondary corrosion product. The primary corrosion products are in the dissolved state
- Three forms of dissolved copper sulfide seem relevant: CuHS(aq), $Cu(HS)_2^-$, $Cu_2S(HS)_2^{2-}$

Representation in a E-pH stability diagram (90°C, 1 mM sulfide, 100 mM chloride 1µM limit)



- Grain bodies cannot produce 1 µM $Cu(HS)_2^-$ but a grain boundary might.
- Grain bodies would be immune.
- Supersaturation w.r.t. Cu_2S

Conclusions

- Intergranular corrosion in the shape of cracks observed at 1 mM sulfide at 60°C and at 90°C
- Identical conditions with 0.02 mM sulfide did not result intergranular corrosion but only an uneven surface.
- Stress-strain curves do not reveal any signs of stress corrosion cracking. The time to final fracture and the elongation at rupture are independent of the test conditions.
- Intergranular corrosion develops early during the test. Tests interrupted after 2 or 4 days reveal cracks preferentially located towards the ends of the gauge length.
- At final rupture of the test rods, 14 days, the cracks are more evenly distributed.
- Necking and final rupture occurs close to the middle of the gauge length.
- The maximum depth of the cracks is 20-30 µm after final rupture. Cracks after 2 or 4 days testing were estimated to be about 10-20 µm deep.

Summary

- Cracks observed in neutral 1 mM sulfide, not at pH 11
- Probable causes
  - Intergranular corrosion
  - Supersaturation wrt. Cu_2S
  - (Film fracture)
  - Temporary stage
- Projected development
  - Passive/immune cracks
  - HS^- cannot reach deeper grain boundaries
  - Cracks fill up with Cu_2S

Acknowledgements

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Thank You