Stress Corrosion Cracking of Stainless Steels in Chlorides Environments

Joint EFC NACE WORKSHOP September 10, 2007 Freiburg, Germany

Thierry Cassagne

TOTAL E&P France

Outline

- **What we want to avoid**
  - Examples of stress corrosion cracking field failures
    - Internal
    - External
- **What is known**
  - Short review on SCC of SS in chloride environments
- **What is unknown**
  - Missing or unclear answers

TOTAL

What we want to avoid …

Experience with internal SCC

- **22Cr duplex SS so far**

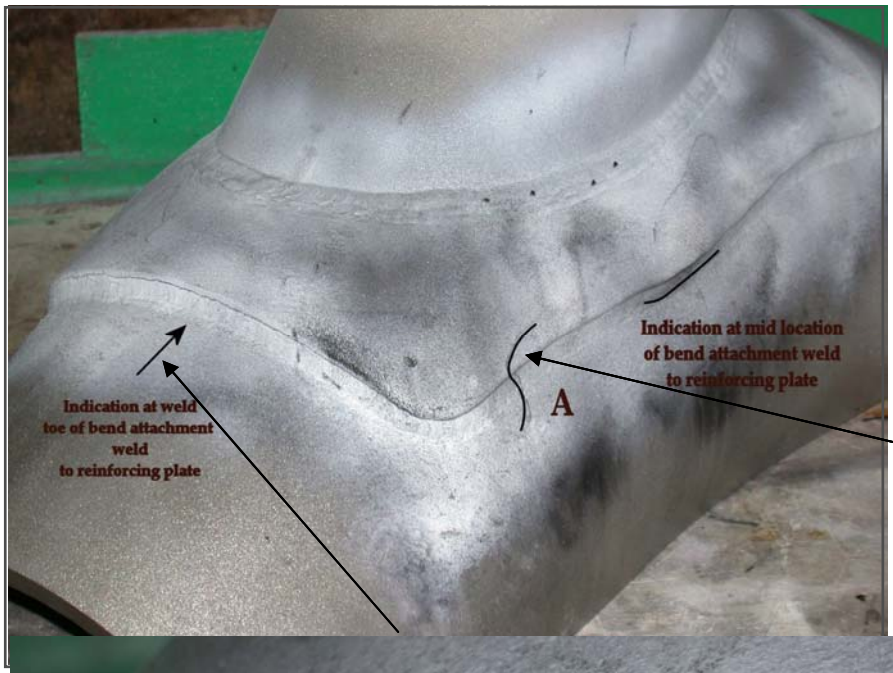
- **Environmental conditions**
  - High local chloride concentrations
  - High temperatures T>120°C
  - Oxygen content close to nil

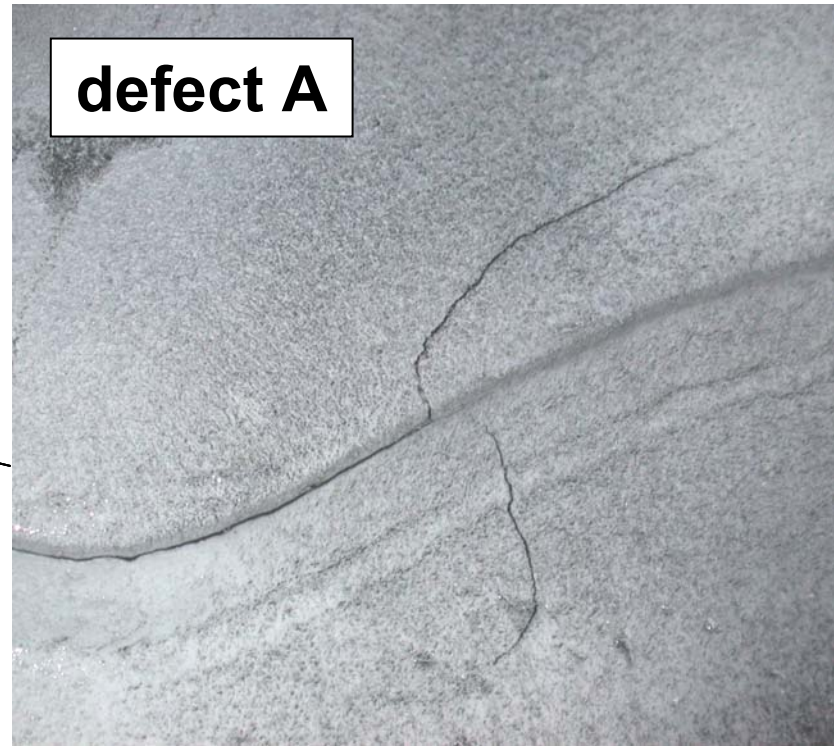
- **Residual stresses from welding or fabrication**

Only a few cases of internal SCC

TOTAL

Through wall internal SCC in 22Cr duplex

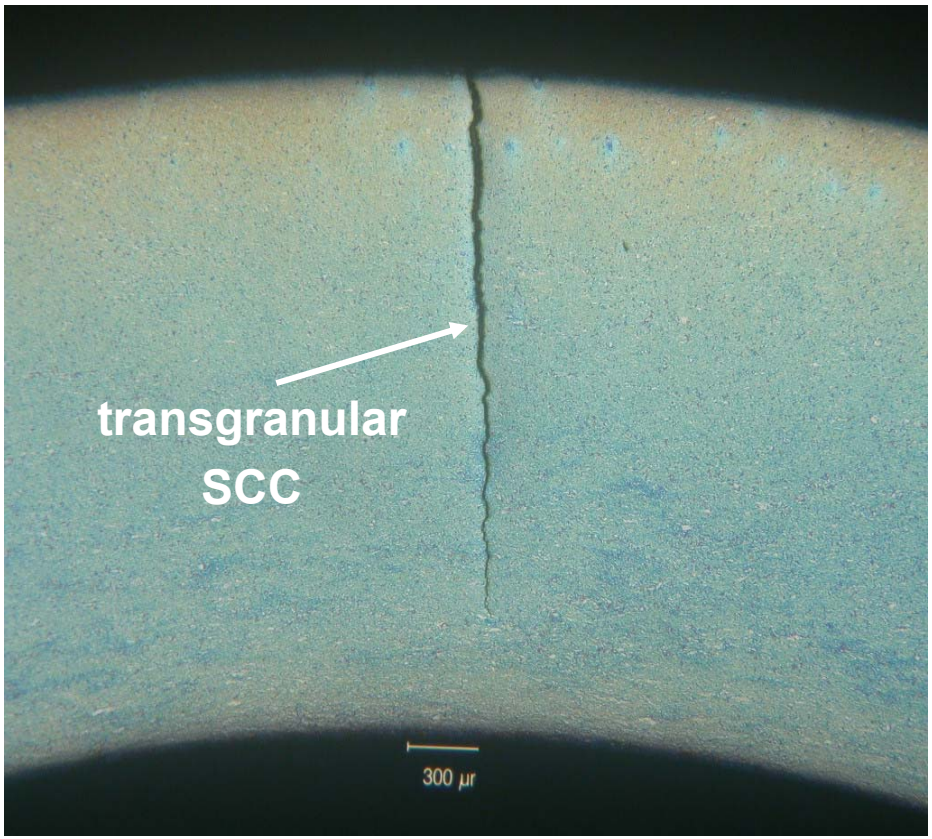




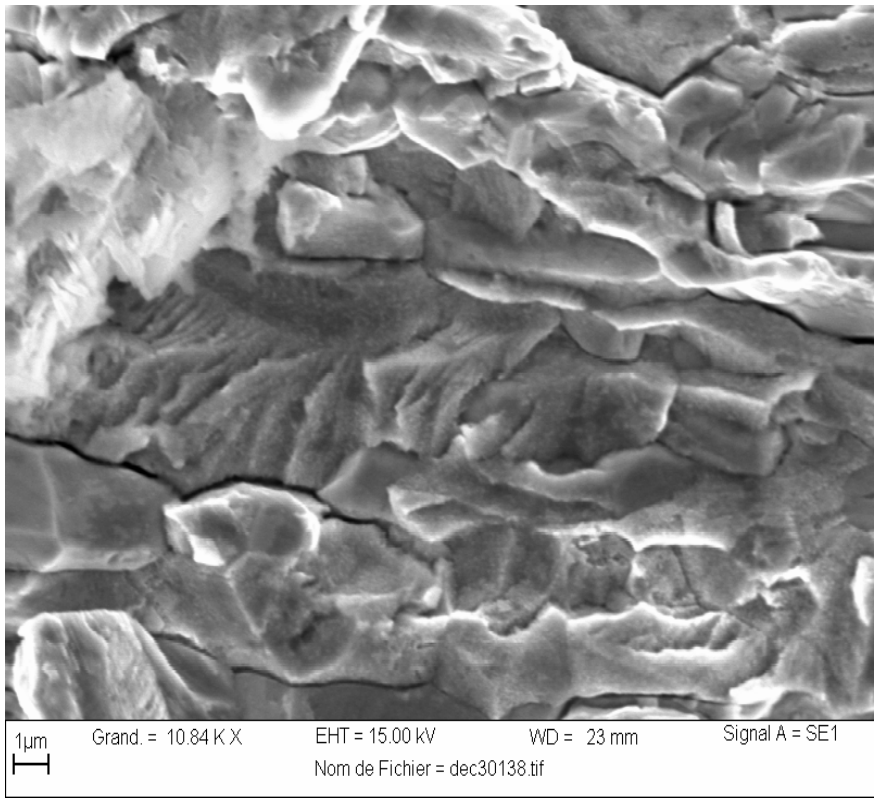
TOTAL

Internal SCC of duplex 22Cr heat exchanger tubes

External initiation (oil side)



Fracture surface



TOTAL

Experience with external SCC

- **Alloys involved have been:**
  - austenitic SS (304, 316L, 904L)
  - 22Cr duplex SS
  - martensitic SS (17-4PH)

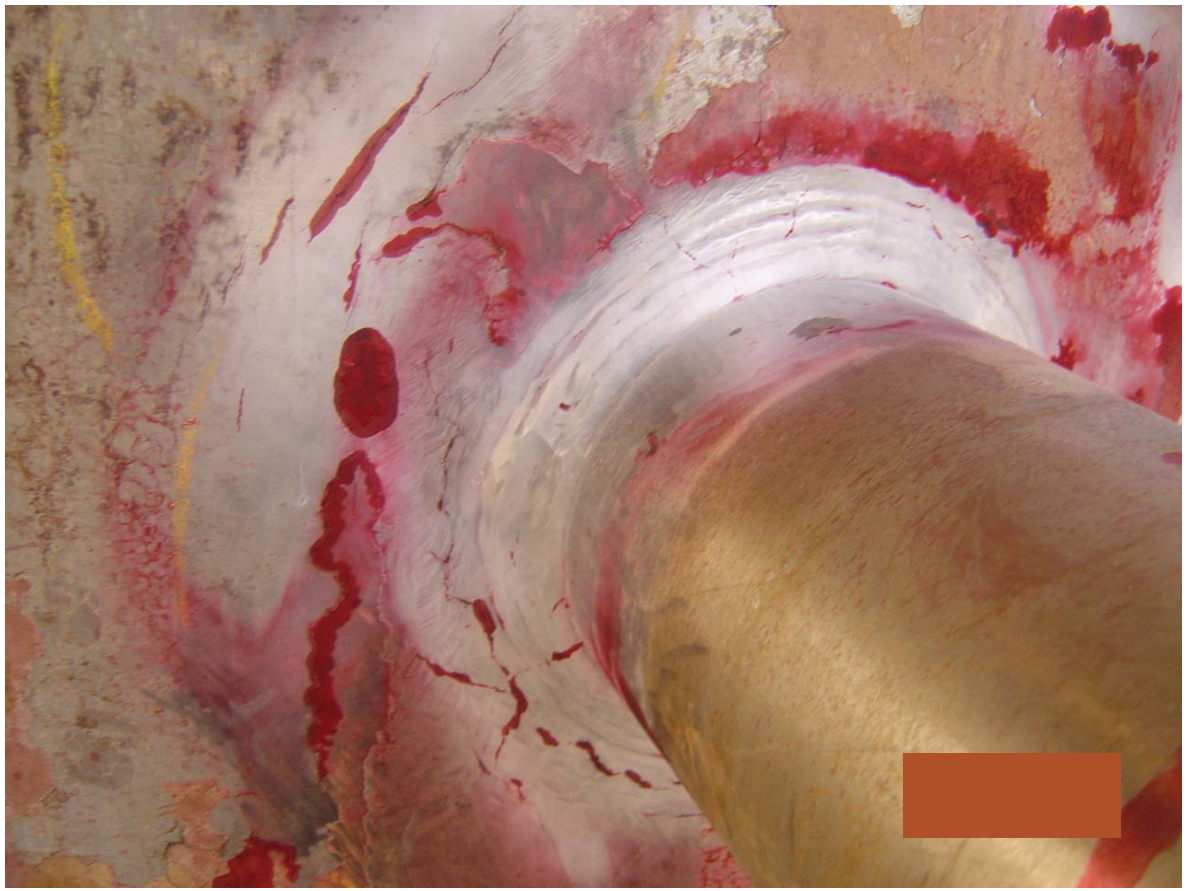
- **Environmental conditions**
  - No coating or damaged coating
  - Under insulation or not
  - High local chloride concentrations
  - Temperature of RT for austenitic and martensitic SS, >100°C for 22Cr duplex

- **Residual stresses are usually from welding**

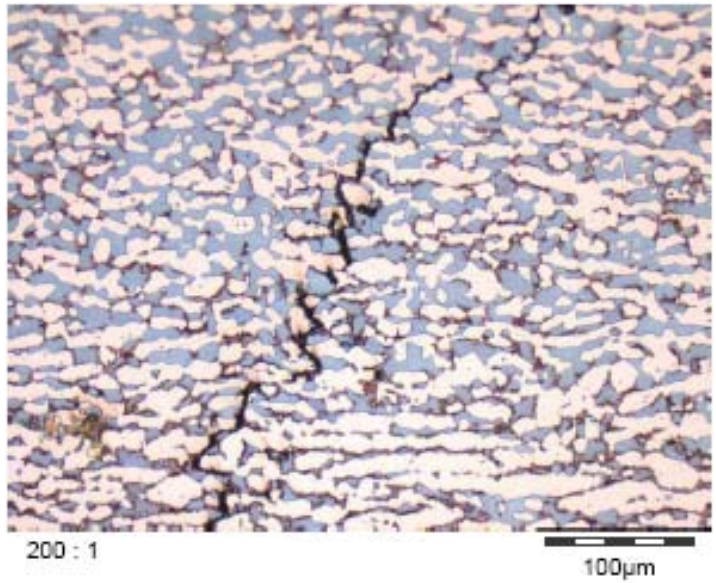
Some cases of external SCC

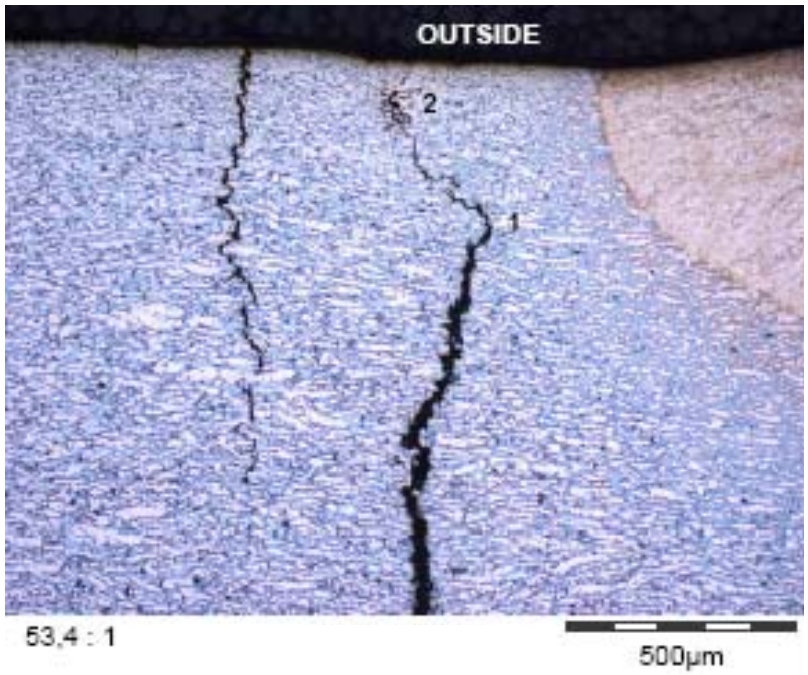
TOTAL

External SCC in 304 SS at welds

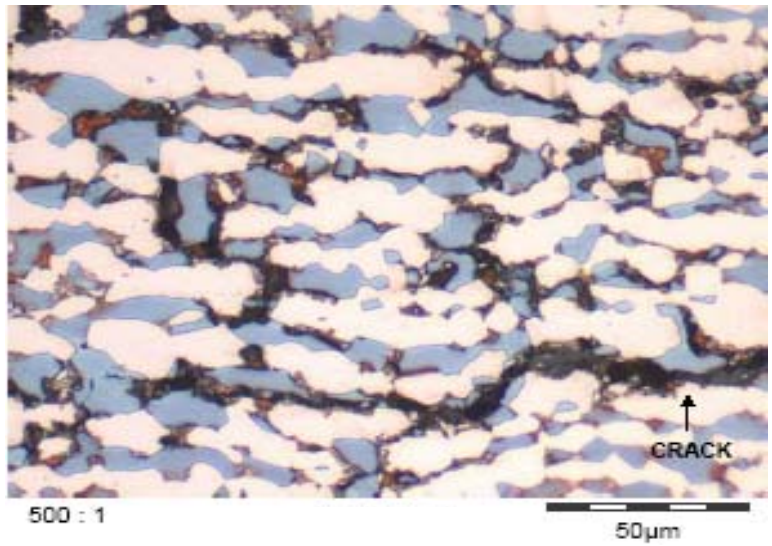


External SCC of 22Cr duplex + sigma phase





Up to 20% sigma phase



TOTAL

What is known …

Influence of environmental parameters

- **Major environmental parameters influencing SCC:**
  - Temperature
  - Chloride concentration
  - pH
  - Potential (oxygen, oxidizing species …)

- **SCC occurs ≤ RT (very acid) or ≥ 50°C in neutral concentrated chloride environments**

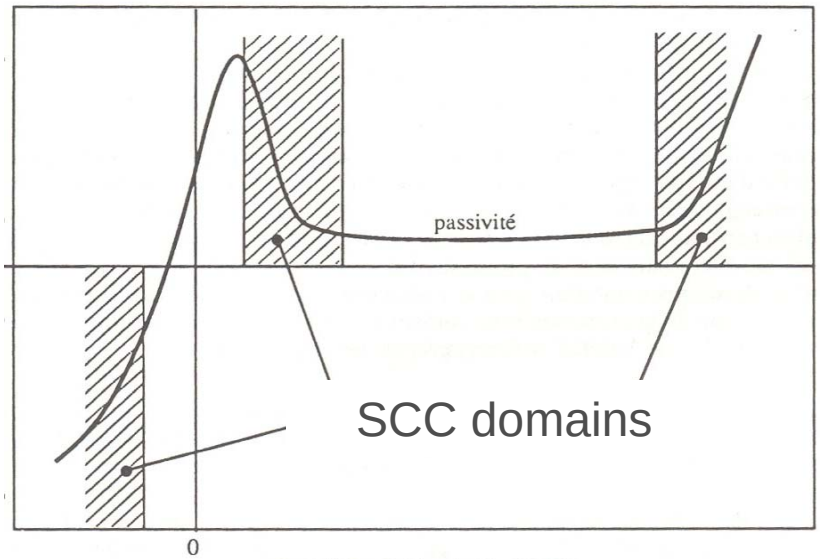
- **Pitting is necessary for SCC in neutral environments, not in acid environments**

- **Oxygen may not be necessary in concentrated acidic chloride environments (ex. boiling $MgCl_2$)**

Acid ≠ neutral environments

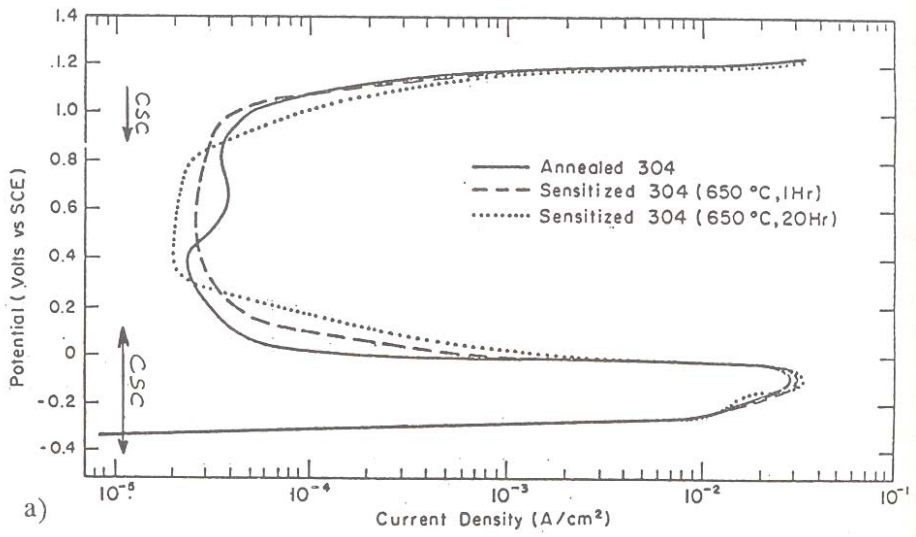
TOTAL

Influence of potential



Combrade CSC Bombannes 1990

10 N H_2S0_4 + 0.1 M NaCl solution at RT

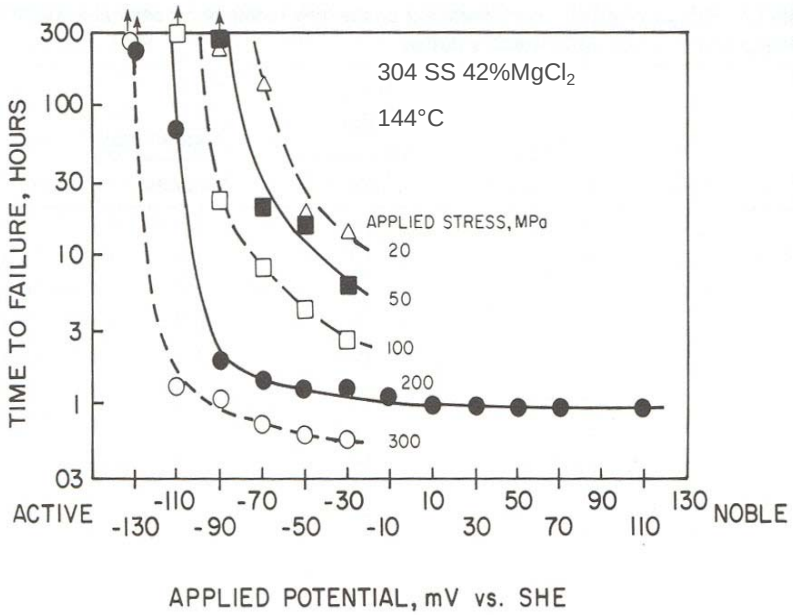


R. Staehle et al. 1979

Acid environments: SCC **when passive film is unstable**

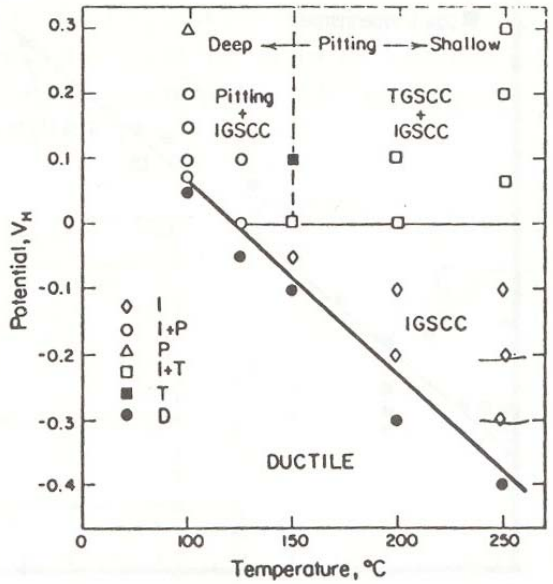
TOTAL

Influence of potential



Brauns W&K 1968

Sensitized 304 SS in 350 ppm Cl^- water

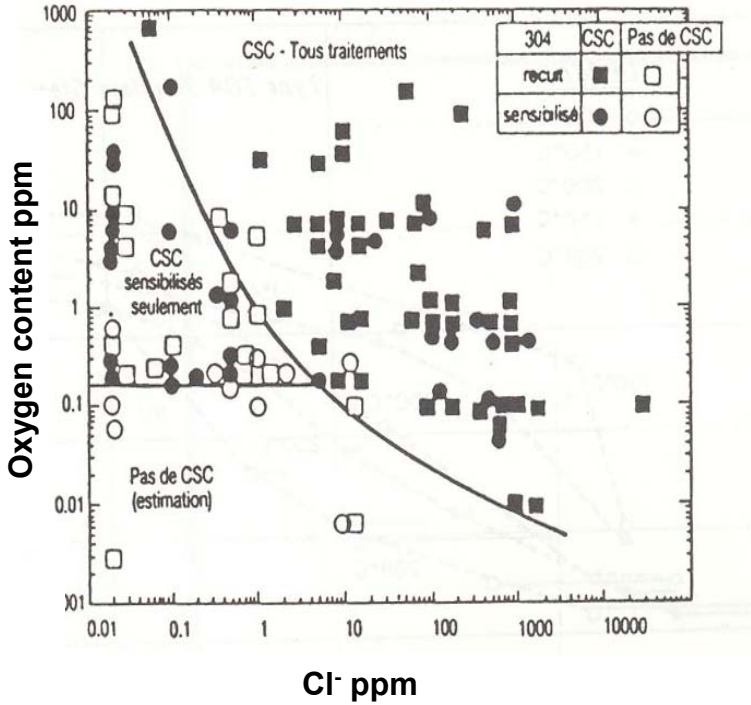


Lin et al. 1981

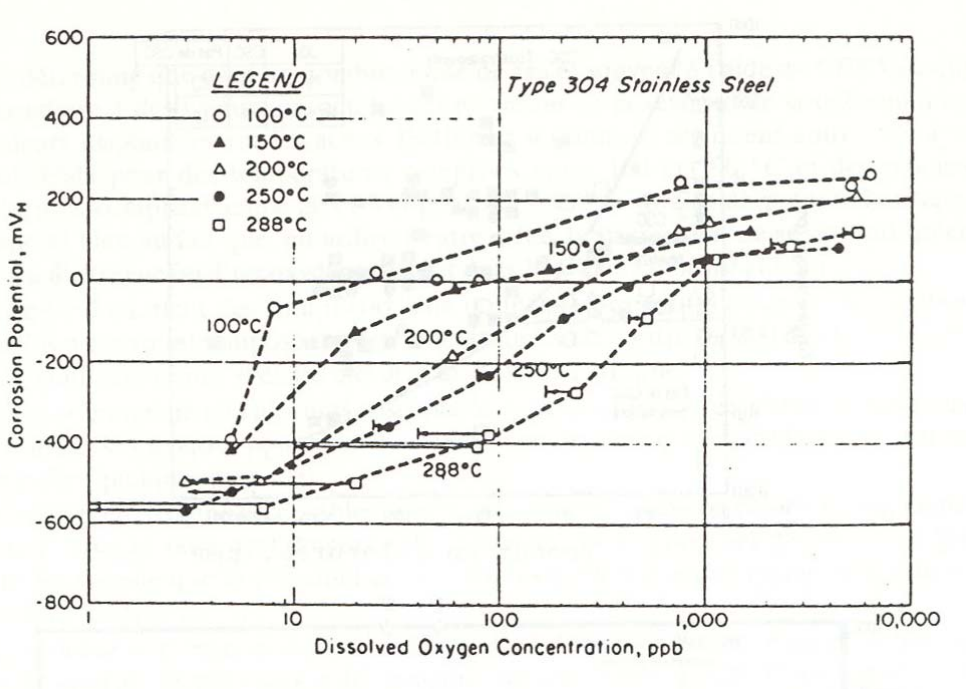
Necessity to be **above a critical potential** for SCC to occur in **moderately acid and neutral chloride environments**

TOTAL

Influence of oxygen and chlorides



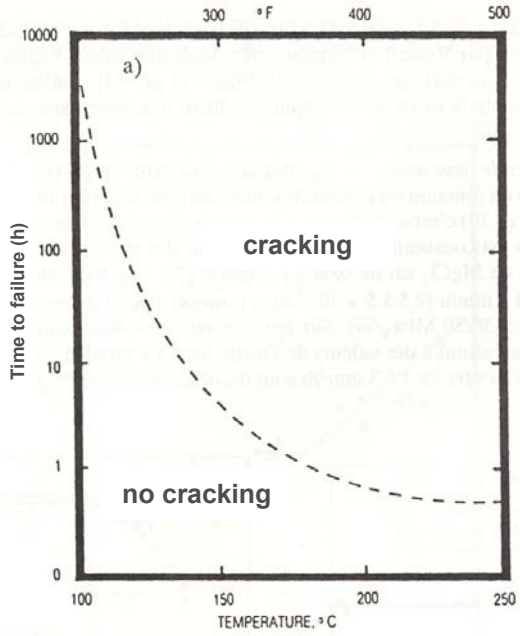
M. Speidel 1977

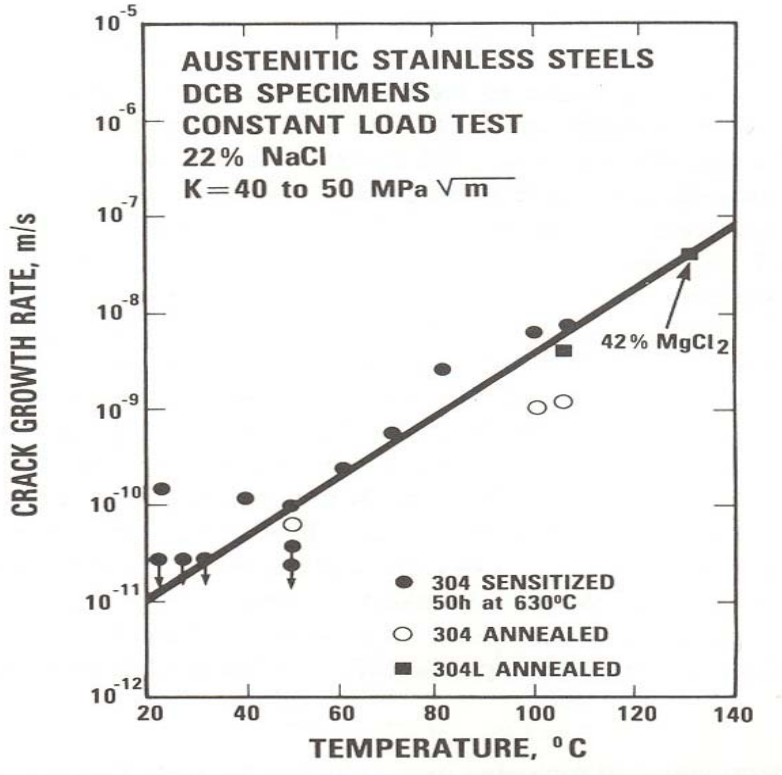


W. Huijbregts 1986

TOTAL

Influence of temperature

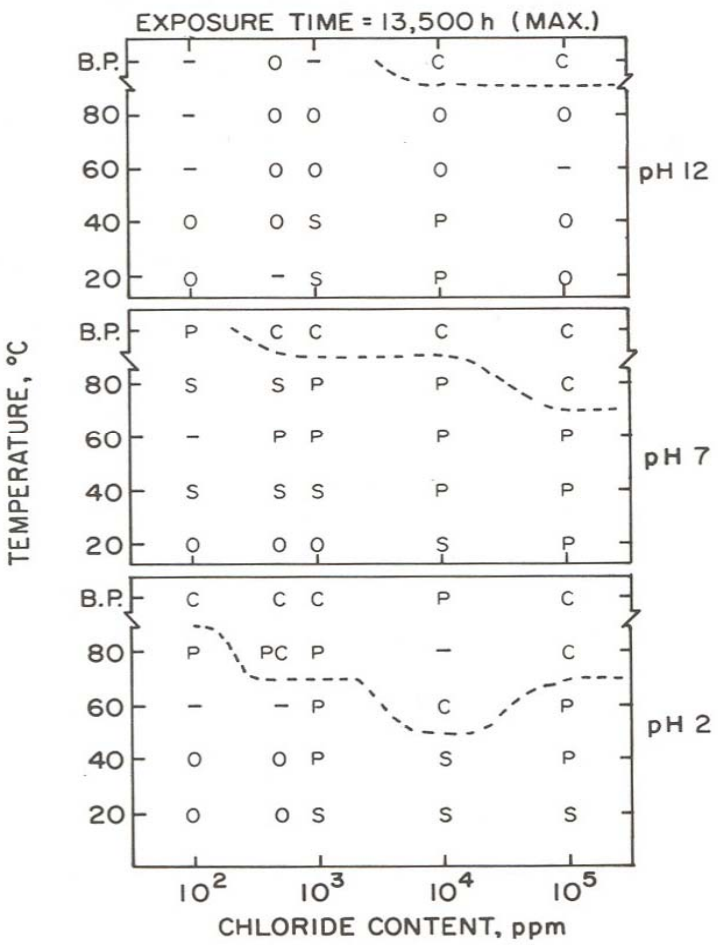




M. Speidel 1981

TOTAL

Influence of pH



J. Truman 1977

304 SS in NaCl

C: SCC, P: pitting, S: stains, O: no corrosion

Influence of mechanical parameters

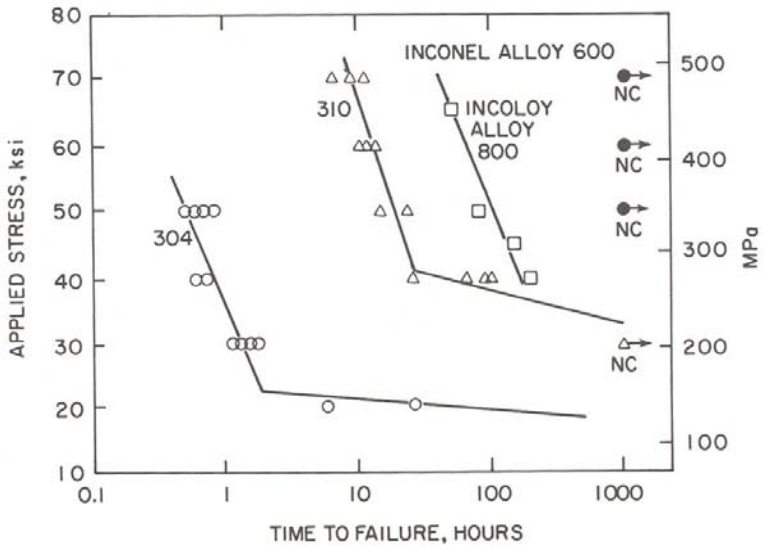
- **The major parameters influencing SCC are:**
  - Stress
  - Strain rate
  - Cold work

TOTAL

Stress

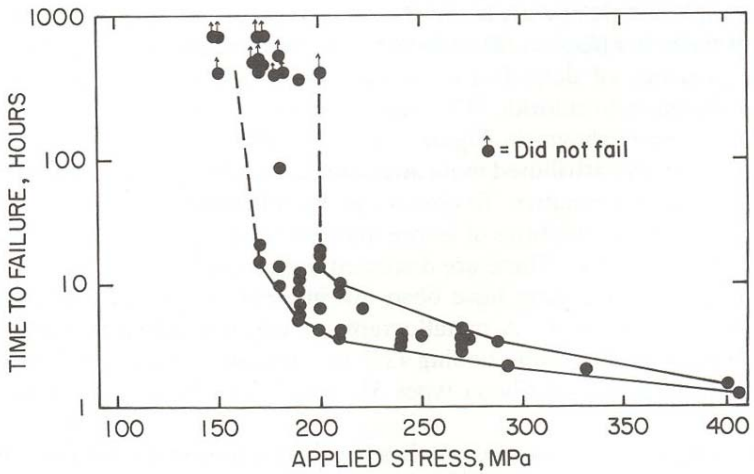
In 300 series austenitic stainless steels SCC occurs well below AYS

Boiling $MgCl_2$ 154°C



E. Denhard 1967

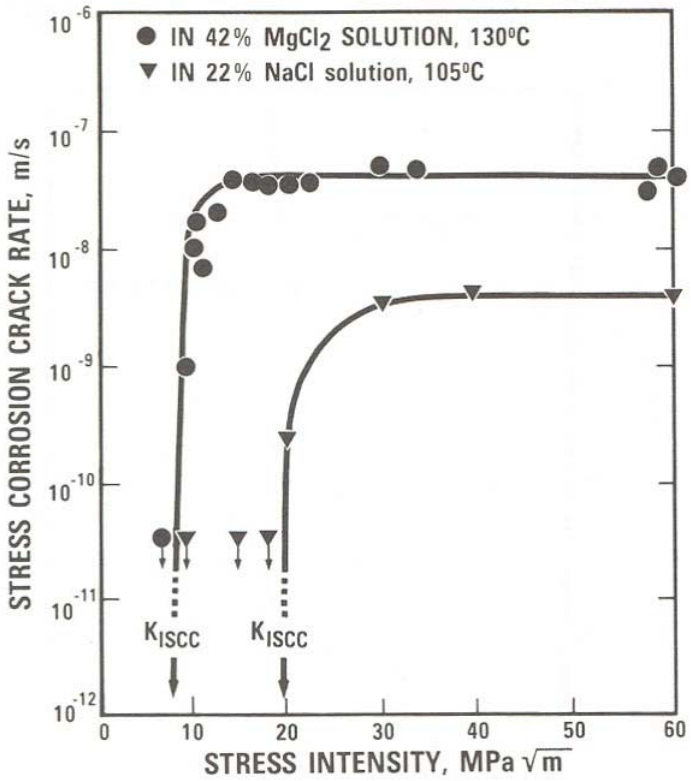
347 SS in boiling $MgCl_2$ 154°C



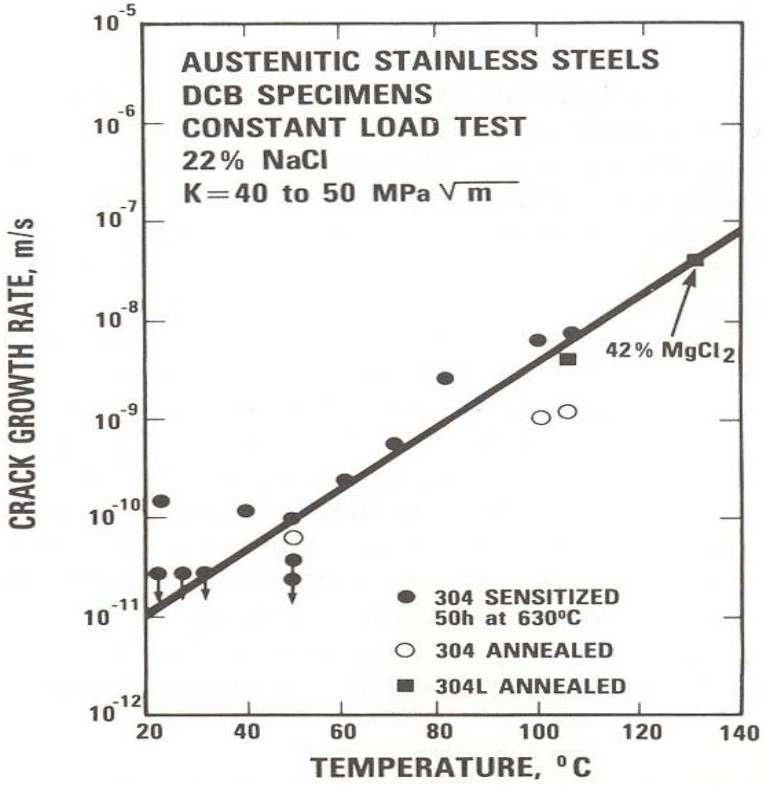
H. Spahn et al. 1973

TOTAL

Stress Intensity



M. Speidel 1981



M. Speidel 1981

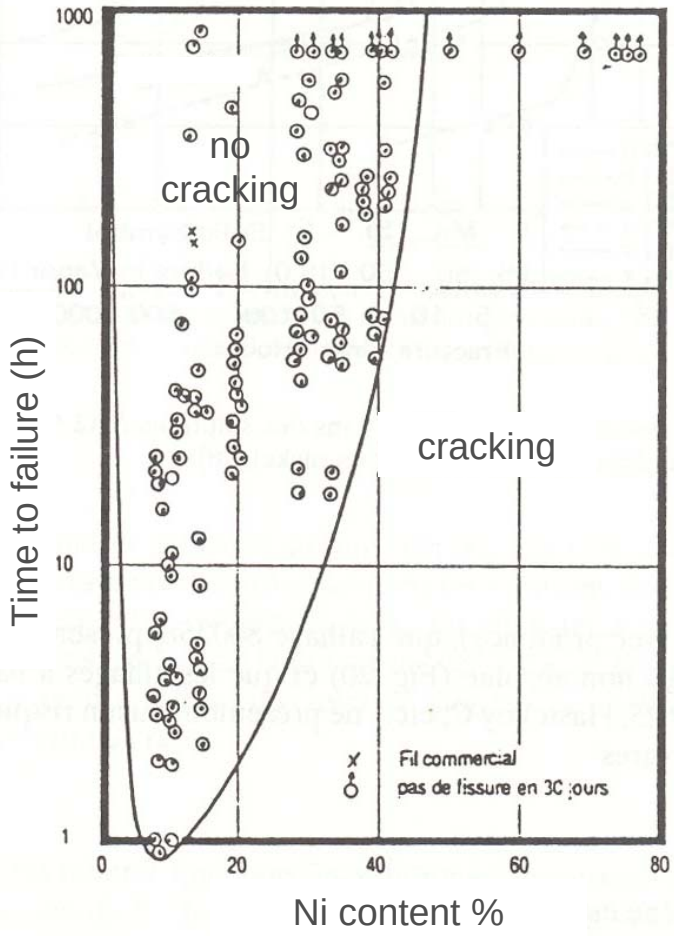
Influence of metallurgical parameters

- **The major parameters influencing SCC are:**
  - Chemical composition
  - Impurities
  - Microstructure (austenitic, duplex …)

TOTAL

Influence of composition

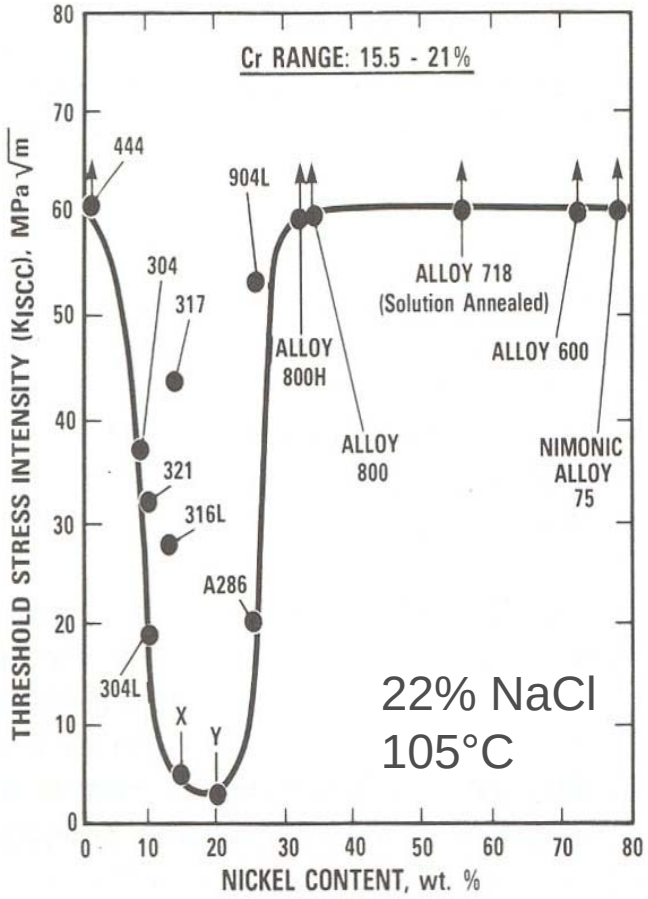
U-bends in boiling $MgCl_2$ 154°C



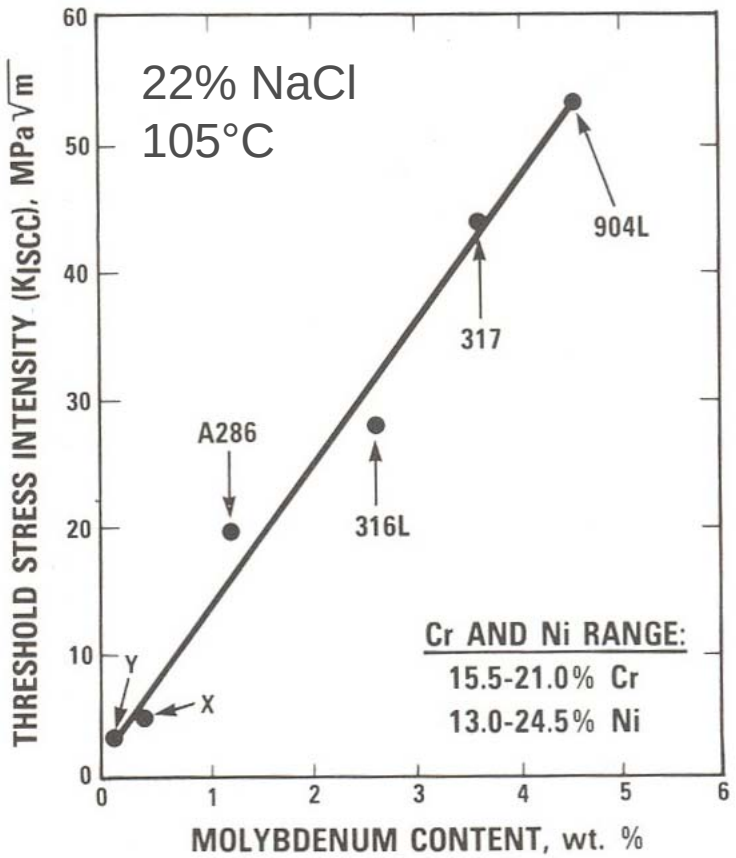
H. Copson 1959

TOTAL

Influence of composition



M. Speidel 1981

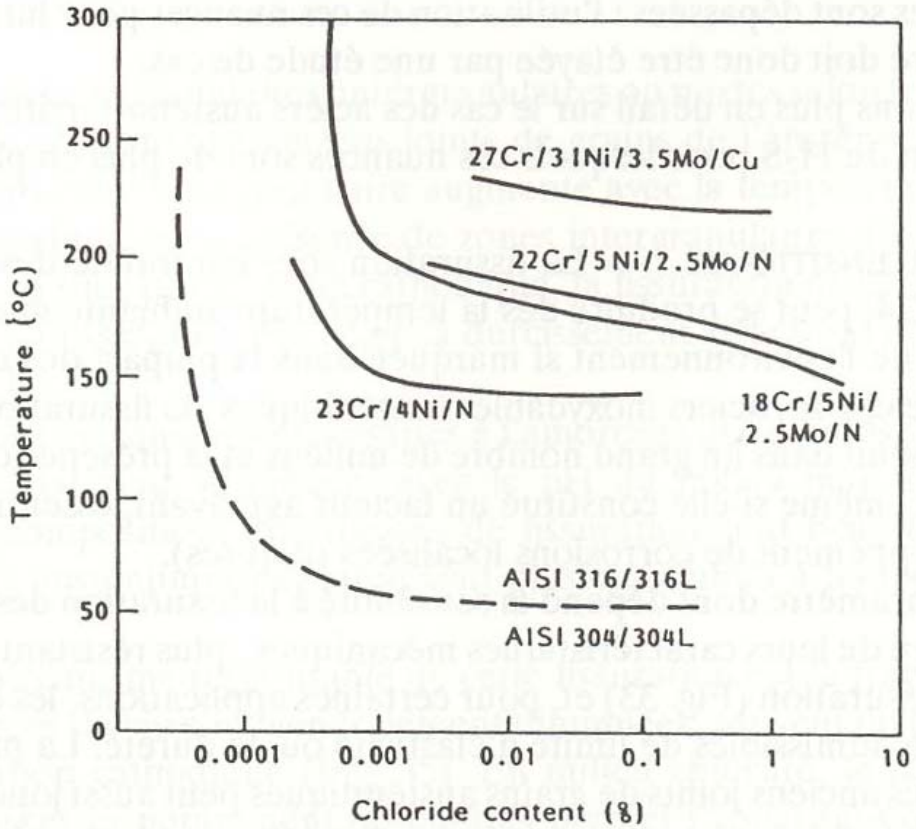


M. Speidel 1981

TOTAL

Influence of structure

Comparison between austenitic-ferritic (duplex) and 300 series austenitic stainless steels in neutral aerated chloride environments



S. Bernhardsson 1991

What is unknown …

- **SCC of stainless steels is well understood for external cracking but the temperature limit of the various grades is not so clear**

- **There are very few data available concerning SCC in concentrated chloride environments with “low oxygen”**
  - Internal SCC in concentrated production environments
  - External SCC in concentrated chloride environments (drop evaporation)

- **The limits of use of the various SS in concentrated chloride environments are not precisely known**

TOTAL

Unresolved practical questions

Internal SCC

- Can SCC occur in mildly acidic (pH 3-4) concentrated chloride environments in the absence of oxygen or low oxygen?
- If so, what are the threshold conditions in terms of temperature, chloride concentration and oxygen level for the various stainless steel families
- Results will depend on the nature of the salts (Ca^{2+}, Na^{+}, Mg^{2+}) and salt mixtures

External SCC

- What is the SCC resistance of SS when “degraded” by welding or else?
- What are the temperature limits of higher grade austenitic SS? 904L, 6Mo …

TOTAL

Questions?