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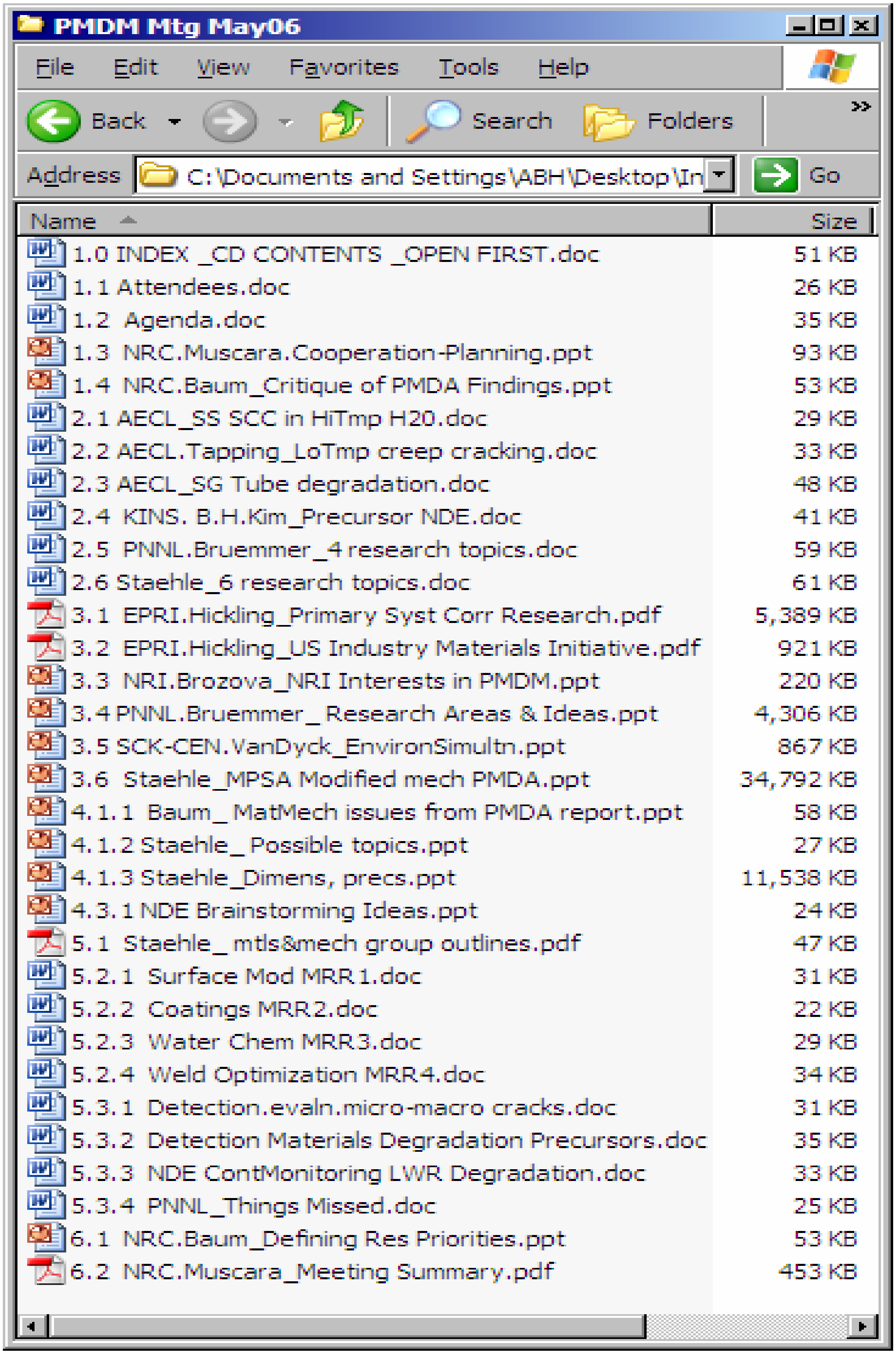

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Third Planning Meeting for the International Cooperative Group and Research Program for Proactive Materials Degradation Management (PMDM)
May 11 - 13, 2006
Mills House Hotel, Charleston, South Carolina, USA

Attendance List

Name	Organization
Arioka, Koji	INSS
Ballinger, Ron	MIT
Baum, Allen	NRC
Brozova, Anna	NRI REZ
Bruemmer, Steve	PNNL
Doctor, Steven	PNNL
Hickling, John	EPRI
Hull, Amy	NRC
Karwoski, Ken	NRC
Kim, Beok Hum	KINS
Kim, Hak-Joon	Sungkyunkwan University
Lu, Zhanpeng	Tohoku University
Muscara, Joe	NRC
Pinhero, Patrick	INL
Poruks, Peter	AECL
Roney, Tim	INL
Staehle, Roger W.	Consultant
Van Dyck, Steven	SCK-CEN
Wang, Li H.	ITRI
Yeh, Tsung-Kuang	National Tsing Hua University
Yonezawa, Toshio	Tohoku Univ.

Third Planning Meeting for the International Cooperative Group and Research Program for Proactive Materials Degradation Management - May 11 – 13, 2006

Mills House Hotel, Charleston, South Carolina, USA

Agenda

Thursday, May 11, 2006		
9:00 am – 10:15 am	Welcome , Overview of PMDM International Cooperation , and Q&A	Joe Muscara, USNRC
10:15 am – 10:30 am	Break	
10:30 am – 12:00 am	Short 10 minute Presentations by Participants	
12:00 am – 1:00 pm	Lunch	
1:00 pm – 5:00 pm	Three Break Out Groups: Material Degradation and Mechanisms Mitigation and Repair NDE and Monitoring Write Brief Research overview Papers	All Attendees

Friday, May 12, 2006		
8:30 am – Noon	Break Out Groups Continue to Develop Research overview Papers	All Attendees
Noon – 1:00 pm	Lunch	
1:00 pm – 5:00 pm	Break Out Groups Continue to Develop overview Papers	All Attendees

Saturday, May 13, 2006		
8:30 am – 9:15 am	Summary Presentation of Break Out Group on Materials and Degradation Mechanisms	Co-Chairs
9:15 am – 9:45 am	Summary Presentation of Break Out Group on Mitigation and Repair	Co-Chairs
9:45 am – 10:15 am	Summary Presentation of Break Out Group on NDE and Monitoring	Co-Chairs
10:15 am – 10:30 am	Break	
10:30am – Noon	Discussion of Break Out Group Reports, Summary of Meeting and Future Actions	Joe Muscara, USNRC

Planning Meeting on International Cooperative Research Group and Program for Proactive Materials Degradation Assessment and Management

May 11-13, 2006
Charleston SC

Dr. Joseph Muscara
Senior Technical Advisor for Materials Engineering Issues
US NRC Office of Nuclear Regulatory Research
Email: jxm8@nrc.gov Phone: 301-415-5844

Proactive Materials Degradation Assessment
Motivation

- Several unexpected materials degradation incidences have occurred in the recent past
- Regulators and industry have concluded that a proactive approach to materials degradation assessment and management is desirable
  - Develop a foundation for appropriate actions to keep materials degradation from adversely impacting component integrity and safety and avoid safety significant surprises

Proactive Materials Degradation Assessment
Scope

- **What is proactive with respect to materials degradation management?**
  - Predict and prevent or mitigate
  - Predict, monitor, and repair/replace in a timely manner
- **Prediction is a critical aspect of PMDM**
  - Proactive research allows us to manage the issue before it becomes safety-significant
  - Thousands of components need to be considered
- **Consider risk importance of components susceptible to degradation**
  - Prioritize research efforts
  - Develop regulatory guidance
- **Roles**
  - The industry develops methods
  - The regulator confirms their effectiveness
  - These roles can share the same research

Proactive Materials Degradation Assessment

Approach

- First step is to identify materials and locations where degradation can reasonably be expected in the future, and determine the risk significance

- Next step is to organize an international cooperative research program for the components and degradation of interest that will address:
  - Inservice inspection and continuous monitoring techniques for the detection, characterization, and evaluation of degradation
  - Materials and degradation mechanisms
  - Techniques to ameliorate stressors for mitigation or prevention of expected degradation
  - Repair and replacement materials and techniques
  - Post-repair and fabrication inspection techniques

Proactive Materials Degradation Assessment

Identify Susceptible Components and Knowledge level

- Three activities to accomplish the first step
  - Conduct Phenomena Identification and Ranking Table (PIRT) process to identify plant components susceptible to future degradation
    - Study has been completed; identified susceptible components and assessed level of knowledge
  - Use existing information to identify components that have experienced degradation
    - Input for evaluation of inservice inspection effectiveness
  - Recognize risk significance of component failure
    - This work is ongoing
    - First approach is to assume safety related components and reactor coolant pressure boundary are risk significant

Proactive Materials Degradation Assessment

Susceptible Components and Knowledge (Cont.)

- Hundreds of components with medium-to-high susceptibility to future degradation were identified
  - To be discussed during “break-out” session
- PMDA PIRT includes forward thinking with respect to time related aging phenomena and changing conditions
  - Ex. 1: Accumulation of chloride on the exterior of piping at seaside plants
  - Ex. 2: PWR operation at end of fuel cycles with practically zero boric acid in the primary coolant
    - Potential for lithium hydroxide accumulation in crevices without buffering effect of boric acid which could lead to stress corrosion cracking (pressurizer heater sleeves?)

Proactive Materials Degradation Assessment
Susceptible Components and Knowledge (Cont.)

- **PMDA PIRT includes "what-if" exercise**
  - **Used to brainstorm non-component specific scenarios that could lead to degradation not previously seen**
    - **Pb SCC, particularly for Alloy 690**
      - **Laboratory observations**
    - **Does IGSCC of LAS/CS imply a new and/or faster SCC degradation mode? (Point Lepreau)**
    - **Issue of high CGR in nickel-base HAZs and application to other materials**
    - **Validity of K_{IC} values, air versus environment**
    - **Lack of predictability of thermal fatigue due to complex TH and FEM in unanalyzed lines**
    - **Corrosion events under slow-evolving deposits and changing composition of metal surfaces**
    - **Low-temperature sensitization**

Proactive Materials Degradation Assessment

International Cooperative Research Group

- To accomplish the second step, an international research group and program will be assembled
- Technical experts and sponsoring organizations
- Together develop a broad-based research program plan
  - Materials and degradation mechanisms
  - Mitigation
  - Repair and replacement
  - Nondestructive examination and monitoring techniques
- Through cooperative agreement, sponsor, implement, and share research results
- Meetings to develop program plan and cooperative agreement:
  - USA, Europe, Japan

THE INTERNATIONAL COOPERATIVE GROUP AND RESEARCH PROGRAM FOR PROACTIVE MATERIALS DEGRADATION MANAGEMENT

Planning and Coordination

- **Implementation of PMDM programs for components and degradation of interest will require an extensive technology base and new research**
  - No one organization alone can accomplish
  - Feasible through international cooperation
  - We need to think, plan, and act together beyond our individual every day interests and responsibilities
- **Success in PMDM will require the support and commitment of the reactor community, while recognizing industry's and regulators' roles**
  - Regulators, Industry, Sponsoring Organizations, Laboratories, Universities

Planning and Coordination (Cont.)

- Develop a broad-based research program plan, conduct the research, and share the results through a cooperative agreement
  - Materials and Degradation Mechanisms
  - In-service Inspection and continuous monitoring (regulator verifies)
  - Mitigation, repair, and replacement (regulator verifies)

Planning and Coordination (Cont.)

Examples of Research Topics

- **Materials and degradation mechanisms**
  - Quantitative treatment of microcrack initiation, coalescence followed by short crack propagation
  - Mechanistic understanding of crack growth and quantitative evaluation of important variables and interactions
  - Definition of “corrosion system” parameters that control the kinetics of EAC
  - Effects of cold work and hardening
  - Low temperature crack propagation
- **NDE and monitoring**
  - New inspection technology
  - Continuous monitoring – additional validation
- **Mitigation, repair, and replacement**
  - Validation of evolving mitigation methods/fixes
  - Study of fabrication parameters to optimize microstructures and residual stresses

Planning and Coordination (Cont.)

- Approximately 3 working meetings in the USA, Japan, and Europe
  - Begin by identifying the broad-based research needed and assemble the research plan
  - Review and identify appropriate ongoing research work that participants are willing to share
  - Identify additional new research and possible sponsors
  - Discuss and agree on Agreement language and conditions
- Introductory meeting held at Snowbird, UT (8/05)

Planning and Coordination - Japan Meeting (Cont.)

- First working meeting held in Tokyo, Japan (11/05)
  - Obtained input for the broad-based plan
  - Expressions of intent to participate from several organizations
  - Discussed a model for cooperation
- Participant can be a single organization or a consortium
- Participant provides value in kind research of 3 person-year per year during the cooperation
  - Less for countries with small nuclear power programs
- Model for cooperation is not fixed
  - Other suggestions are welcome
  - Flexibility to allow widest participation possible

Planning and Coordination – Japan Meeting (Cont.)
Summary of Materials and degradation Discussion

- SCC of non-sensitized stainless steels
- Cold work effects on low alloy steels, stainless steels, and high nickel alloys
- Lead effects on Alloy 690
- Fracture toughness of welds at low temperatures as affected by environments
- Capacity to predict long term performance of Alloys 800 and 690
- Long term aging effects on alloy properties including especially grain boundaries
- SCC of dissimilar metal welds
- Modeling environmentally affected fatigue
- Integrate the materials behavior in BWR and PWR for mutual benefit

Planning and Coordination – Japan Meeting (Cont.)
Summary of NDE Discussion

- General consensus that improvements in NDE and monitoring are needed in order to manage degradation
- On-line monitoring, validation
- Identify those components and degradation processes where NDE/ISI is not effective at managing
  - Develop better ISI methods: Detection, Length and Depth Sizing
  - Coarse grained materials
- NDE methods for directly measuring material properties, especially radiation embrittlement
- Better NDE methods for wall thinning measurements
- More effective loose part monitoring techniques- Including AE

Planning and Coordination – Japan Meeting (Cont.)
Summary of Mitigation, Repair, Replacement Discussion

- Fundamental research in this area is more feasible for the cooperation since there will be a reluctance to share commercial “know-how”
- Validation research methodology for new mitigation, repair, and replacement technology should be conducted with world wide consensus
  - Emphasis placed on Development of guidance to provide the criteria

Planning and Coordination (Cont.)
Post – Japan Meeting

- Based partly on discussions at the Japan meeting, a number of short overview papers on research issues and needs were written
  - Initiation and propagation of SCC in cold worked stainless steel and Alloys 600 and 690: Fundamental assessments of crack tips
  - Measurement of accumulation of Pb, as well as S^{y-} in line contact crevices of steam generators
  - Reduction of high valence sulfur species to lower valence species
  - Long term LPSCC of Alloy 690TT
  - SCC and mitigation for Alloy 600TT and 690TT in Pb^{-} and S^{y-} contaminated solutions
  - Scaling of Alloy 690 TT in Pb-containing environments

Planning and Coordination
Post – Japan Meeting (Cont.)

- Establishing and updating recommended ECP/pH zone for minimizing SG tube degradation
- Determine factors controlling the SG tube degradation initiation and propagation
- Assess local chemistry conditions under SG conditions
- Factors affecting effectiveness of SG inspection
- SCC of welds and cold worked stainless steel in high temperature water
- Investigation of metallurgical variables affecting the low temperature creep cracking of carbon steel piping
- New nondestructive testing techniques for precise detection and evaluation of early stage materials degradation

Planning and Coordination (Cont.)
Charleston Working/Planning Meeting

- Participate in one of three focus groups
- Continue technical discussions of research issues and needs
- Continue development of overview papers for the broad research program plan for the cooperation
- Discuss approaches for collaboration (one type has been presented)
- Take away– Intent to participate e-mail to Dr. Jennifer Uhle jxu1@nrc.gov AND Dr. Joseph Muscara (jxm8@nrc.gov)
- Future discussions with interested parties will establish the type of collaboration used for PMDM research

Topics for Proactive Materials Degradation Assessment

May 2006

Allen Baum

Develop Plan by Combining Two Approaches

Recognition of Technology Development Needs

(Section 3.4)

Ranking of Component Degradation Mechanisms

(Appendices B and D)

PMDA Panel Technology Development Recommendations

- Damage Assessment
- Fracture Assessment
- Margin Assessment

Damage Assessment

- Establish requirements for crack propagation, given initiation by pitting, IGA, general corrosion
- Develop understanding of conditions responsible for initiation and propagation after long operating times
- Quantify statistical variation in initiation times and propagation rates
- Quantify the threshold conditions for initiating SCC and the crack propagation kinetics
- Define the ranges of the independent variables used to specify the supporting tests
- Characterize additional degradation modes

Define the Ranges of the Independent Variables for Test Specification

- Improve characterization of local stress and its effect on crack tip strain rate
- Improve metallurgical characterization
- Improve definition of environmental conditions

Improve Characterization of Local Stress and Its Effect on Crack Tip Strain Rate

- Effect of high R (ratio of max to min) loading on EASCC (in oxidizing environments)
- Quantify anomalous residual stress effects at welds
- Quantify change in stress intensity factor with crack length (dK/da)
- Quantify effect of thermal loads and flow-induced vibration on SCC at socket welds

Quantify Anomalous Residual Stress Effects at Welds

- Quantify inter-related effects of residual stress and strain profiles
- Experimentally verify calculated residual stress and strain profiles
- Quantify irradiation assisted stress relaxation
- Quantify effect of weld repair
- Quantify effect of surface cold work

Improve Metallurgical Characterization

- Characterize weld metallurgy, particularly for replacement nickel-base alloys subject to hot shortness during welding
- Quantify SS grain boundary composition changes from irradiation
  - Consider dose rate effects as well as cumulative dose
- Improve specification of selected alloying elements, such Al and N in low-alloy steels
  - More susceptible to SCC & fatigue in oxidizing environments

Improve Definition of Environmental Conditions

- In PWR SG crevices, particularly relating to lead and low-valence sulfur
- In annulus between CRDM penetration tube (nickel alloy) and pressure vessel head (low-alloy steel)
- At crack tips, because of chloride transients in low-alloy steels under oxidizing conditions

Characterize Additional Degradation Modes

- SCC of some nickel-based alloys at low potentials below 150°C (302°F)
- Accelerated flow-accelerated corrosion at welds, possibly associated with galvanic effects
- Biological fouling and corrosion in service water systems
- Synergistic effects of multiple corrosion processes
  - e.g. H_2 absorption with FAC promotes SCC of CS
- Slow compositional or microstructural changes over long term

Slow Compositional or Microstructural Changes Over Long Term

- **IGSCC, rather than TGSCC, of low-alloy steel in high-temperature water**
- **Near-surface composition changes, such as depletion of A690 surface chromium in high-temperature water promoting crack initiation**
- **Kinetics of sulfate reduction to sulfide by hydrazine in SGs and turbine blades**

Fracture Assessment

- Characterize fracture resistance reduction in water compared to air
- Quantify dissolved hydrogen effect on low-temperature fracture resistance of nickel-base alloys
- Characterize hydrogen embrittlement of duplex stainless steels and thermally aged higher ferrite content cast austenitic stainless steel

Margin Assessment

- Quantify aging effects and incorporate into probabilistic risk assessment evaluations
- Develop and validate improved inspection capability

Categorization of Degradation Phenomena

- Stainless
- Inconel
- Steels

Stainless Steel Degradation Phenomena

- SCC of sensitized and non-sensitized SS SCC, including weldments
- Irradiation induced SCC
- Thermal aging and embrittlement of cast stainless steels
- Stress corrosion cracking and pitting: contaminating external environments

Inconel Degradation Phenomena

- SCC of Ni alloy 600 and Alloy 182 and 82 weld metals in BWR water
- SCC of Alloys 600, 690, 182, 82, 152 and 52 in PWR primary water
- Corrosion of steam generator tubes
- Degradation of fracture resistance: low-temperature crack propagation (LTCP)

“Steel” Degradation Phenomena

- Stress corrosion cracking of carbon and low alloy steels
- Environmental degradation of high strength materials
- Boric acid corrosion (BAC)
- Microbiologically influenced corrosion (MIC)

Key Components & Mechanisms

SCC	Socket welds (and HAZ) Nozzle welds CRDM housing welds Pressurizer components Core internal components Steam generator tubing Main steam line (BWR)
Fatigue	Socket welds Dissimilar metal welds Nozzle welds Steam dryers
General	PV boric acid corrosion SG tubing wear FAC of steam plant piping Service water system MIC and pitting Baffle bolt swelling

AECL Proposed Topics for PMDM Program --Regarding SCC of Stainless Steel in High Temperature Water

There are concerns over the use of austenitic stainless steel piping where cold work and welding procedures could lead to increased susceptibility to stress corrosion cracking. Obvious precautions have been taken to minimize the risk of SCC by avoiding the use of sensitized, and/or cold worked materials, which are known to be particularly susceptible to SCC. These precautions include restricting the carbon content of the material within the low carbon grade (C< 0.035%) and optimizing weld procedures to minimize sensitization, and ruling out the use of cold bends, for instance by using techniques such as induction heating. However, there is still some work needing to be done regarding SCC assessments of welds and cold worked stainless steel. This work will benefit the nuclear industry in degradation management of stainless steels.

1. Characterization of small diameter stainless steel welds
   - Confirm the sensitization status even though it is minimized.
   - Measure residual stress by neutron diffraction to optimize weld procedure and improve residual stress at inside surface.
   - Measure localized plastic strain (cold work) close to the fusion boundary by orientation imaging microscopy technique.

   The results from the relatively small diameter pipe welds will be compared to those of large diameter pipe welds and shroud welds.

2. Characterization of dissimilar metal welds
   Measurements identical to those on stainless steel welds above will also be performed on dissimilar metal welds with Alloy 82/182 and their alternatives.

3. Characterization of induction bends
   Induction bending process is currently proposed to reduce the effects of cold work in pipe bends. Sensitization status and the stress/strain conditions of induction-heated bends will be measured.

4. SCC growth rate tests

   SCC growth rate will be measured on welds and cold worked stainless steel under well-controlled water chemistry and mechanical conditions to quantify and benchmark crack susceptibility. The possibility of a mitigation effect of high pH (about 10) operation is of particular interest.

AECL Proposed Topics for PMDM Program

1. Investigation of Metallurgical Variables Affecting the Low Temperature Creep Cracking Susceptibility of Carbon Steel Piping

Low temperature creep cracking is an established, although relatively uncommon, degradation mechanism in low carbon steels used in the power generation industry. Unexpected, and sometimes catastrophic, failures of piping in fossil power generation plants occurred during the 1970's and the 1980's in both Europe and the United States. The failed pipes typically operated at ~ 360°C and internal pressures of ~18.5 MPa. Failure times of 1,000 to 10,000 hours were commonly reported, however some failures occurred after 100,000 hours of operation. Failure investigations revealed a 100% intergranular fracture with little to no microstructural damage away from the crack. Laboratory investigation into these failures led to the recognition of a new degradation mechanism, low temperature creep cracking. The temperature at which this process is active is below that previously thought to be necessary for creep process to occur at meaningful engineering rates in carbon steels. Subsequent research has established the occurrence of creep cracking in cold worked pipe material to temperatures as low as 340°C in carbon steel, and as low as 320°C in a low alloy steel heat treated to simulate a coarse grained heat affected zone. This latter work has been spurred by interest from the Swedish nuclear regulator.

The CANDU industry has experienced a small number of externally initiated cracks in carbon steel piping in the primary heat transport system. Metallurgical failure investigations have discounted a role of pure mechanical fatigue, or stress corrosion cracking in these failures. It is hypothesised that low temperature creep cracking may play a role, either in total or in combination, in causing these cracks. As a result AECL-CRL has initiated an experimental program to test creep cracking in representative carbon steel material. The cracked pipes are manufactured from SA 106B and contain cold worked bends that are not stress relieved.

The samples used in the current tests come from one heat of SA 106B, which is also the same heat of steel used to manufacture archive bends during the construction of a CANDU station. Additional archive bends duplicating the original bends have been produced. The test samples are machined from the extrados of the bend, which has been cold worked approximately 30%.

The current tests utilize this starting material and test low temperature creep cracking by dead weight load machines. Currently the only variable being studied is temperature. Tests have been conducted at 380, 370 and 360°C. Tests will continue to lower temperatures as the program continues.

Metallurgical variables of interest are:

a) The temperature. Testing should continue to the temperature of interest to the CANDU industry, 310°C.
b) The level of cold work. Material from the flank of the bends, which has only been cold worked approximately 15% should be tested.

c) Alloy composition, especially trace impurity levels. Steels from other heats should be tested that comprise a range of chemistries within the SA 106B specification. Special attention should be given to the levels of Phosphorous and Sulphur and if there is any enrichment of these species at the grain boundaries.
d) Free nitrogen content. Free nitrogen is known to promote dynamic strain aging at reactor operating temperatures. Heats of high and low free nitrogen steel should be tested to evaluate their susceptibility to cracking.

The current scope of testing involves progressively reducing the test temperature. This seeks to resolve the question of whether creep cracking as a mechanism can occur under CANDU conditions (310°C). However the confirmation of the occurrence of creep cracking in CANDU steels is not a final end in itself. Rather the susceptibility to creep cracking is viewed as a screening tool to evaluate various heats of steel.

2. Microscopic Characterization of Low Temperature Creep Cracks

The microstructural features controlling creep cracking susceptibility and crack growth rates are unknown. A review of the literature reveals that few nucleation sites for these cracks are found. Indeed as the temperature is reduced the occurrence of microstructural damage away from the crack becomes progressively less. At temperatures less than 340°C no features in the micron scale are associated with the cracking which is purely intergranular and follows one well defined crack path with no branching. Transmission electron microscope work is virtually non-existent with regards to studying this mechanism.

A project of detailed SEM and TEM has been concluded studying cracks in failed ex-service piping. The results of this investigation did not reveal any new insights into the microstructural parameters associated with cracking.

The production of creep crack samples in the laboratory allows material for detailed microscopic examination at the optical, SEM and TEM scales. Cracks of known history in well characterized materials will be available for study. Examination of such material offers a much higher possibility of identifying the relevant microstructural parameters than studying failures from the field.

3. Investigation of the Role of Hydrogen in Enhancing Low Temperature Creep Cracking of Carbon Steels

The presence of a flux of hydrogen through the walls of carbon steel piping in CANDU has been well established. The hydrogen is produced due to corrosion of the piping in the PHT water and enters the steel.

The level of hydrogen is below that required for classical hydrogen embrittlement of steel. Indeed no microstructural evidence of hydrogen damage has been observed in failed pipes. However hydrogen levels below that necessary for hydrogen embrittlement are known to effect cracking susceptibility in carbon steel.

The symbiotic role of a low temperature creep cracking mechanism and the presence of a continuous hydrogen flux should be investigated. While creep cracking alone may explain the initiation of cracks on the outside surface of CANDU feeders, it is believed that a hydrogen flux would significantly enhance a steel's susceptibility to cracking.

AECL Proposed Topics for PMDM Program

1. Establishing and Updating Recommended ECP/pH Zone for Minimizing SG Tube Degradation

Steam generator (SG) tube materials are susceptible to corrosion degradation under some plausible non-standard operating chemistry conditions. Determining the boundary conditions that lead to tube degradation is of vital importance to minimize SG tube degradation and extend the service life.

AECL Chalk River Laboratories has been carrying out high-temperature electrochemical studies as well as accelerated corrosion and SCC tests to examine the crevice corrosion/SCC susceptibility of SG tube alloys under a variety of CANDU SG conditions under COG and nuclear platform funding. To date, the chemistry regimes with minimum tube degradation have been defined for all major SG alloys including Alloy 800, Alloy 600, Alloy 400 and Alloy 690.

The recommended chemistry regimes for SG tube alloys allow plant operators to avoid conditions that are hazardous to the alloys through appropriate SG water chemistry management. The Electrochemical Corrosion Potential (ECP) is a measure of the driving force for oxidation/corrosion determined by the overall reactions of oxidizing and reducing species on the surface of SG tubing. The ECP of SG tubing can be correlated to SG blowdown chemistry. The corrosion kinetics of SG alloy is a function of ECP under specific pH and concentration of aggressive species conditions. Using the recommended ECP/pH zone developed under plausible SG conditions, the status of an operating SG could be assessed and decisions for maintaining the SG under its optimum conditions could be made.

Future work will consider the interactions between the most common SG impurities such as lead, chlorides, sulphates, reduced sulphur and copper etc. on SG tube degradation and updating the existing ECP/pH zones for SG tube Alloys based on new data.

The recommended ECP/pH zone for SG alloys could be extended to SGs other than CANDU reactors in the world based on the assessment of the aggressive local chemistry conditions developed in the crevice or under deposit areas in the SG.

2. Determine Factors Controlling SG Tube Degradation Initiation and Propagation

In recent years the detrimental effect of lead in the degradation of steam generator (SG) tube alloys has raised great deal of concerns in the nuclear industry, where the presence of lead has been implicated as a primary contributor to the premature stress corrosion cracking failure of SG tubing material. Field data and laboratory studies have confirmed that SG tubes are susceptible to lead-induced SCC, even at low lead concentrations. As summarized by a number of investigators, several issues are critical in considering lead-induced SCC of SG tubing. AECL is proposing to perform the following work on lead induced SG tube degradation:

2.1. Study the key factors leading to the PbSCC initiation and propagation of SG tube Alloys under plausible secondary side SG crevice chemistry condutuions.

The current status is that the envelope of environmental, material and mechanical conditions required for SCC, particularly in the presence of lead for the nickel base Alloys (Alloys 400, 600, 800, and 690) are still poorly defined and some times are controversial. This is especially true for near-neutral high-temperature pH conditions where most SGs operate and where non-lead secondary side SCC is suppressed. With only a few exceptions, most testing has been performed with unrealistically chemistry conditions differe from the plausible SG secondary side chemistry conditions.

Mechanistic studies are required to study the key factors leading to the passivity breakdown and the initiation of pitting/crevice corrosion/SCC under realistic SG crevice chemistry conditions. The studies will include:
1). Study the detrimental effect of Pb on SG tube degradation as functions of potential and pH of the solution.
2). Characterize the effect of lead and other impurities on the electronic structure and the composition of the passive films formed on SG alloys.
3). Determine the effect of stress in the migration and incorporation of lead in passive films
4). Determine the effect of Pb-contamination on mechanical properties of passive films

Following the study on the SG tube degradation initiation, key factors leading to the propagation of pitting/crevice corrosion/SCC are to be determined. The eventual objective for this study is to establish a model to determine the rate of SCC and other mode of degradation and predict service life of the SG tube alloys.

2.2. Evaluate the lead enhanced scaling for Alloy 800 and Alloy 690 as a function of ECP under plausible SG crevice chemistry conditions.

Lead enhanced scaling on high nickel alloys has been observed on Alloy 690TT and Alloy 800. As Staehle suggested that the scaling process becomes important both from denting types of processes in tube supports and TTS geometries and in the acceleration of crack growth via the wedging action inside growing scales.

The chemistry and ECP conditions that leading to the Pb-enhanced corrosion scaling on Alloy 800 and Alloy 690 will be studied under plausible SG crevice chemistry conditions at different ECP levels. This information will be used to assess and update the recommended ECP/pH zone for Alloy 800 and Alloy 690.

3. R&D work to assess the local chemistry conditions under SG conditions

3.1. Verify the local chemistry under the SG crevice conditions including under the line contact crevice conditions.

AECL currently has one of the only working line of contact crevices (at this time) for this type of work. It is not currently instrumented to measure all of the temps that Roger suggests, but could possibly be modified. It is a very small space and there is a limit for these measurements in the current design. The low valence sulphur species during hideout/hideout return was observed in our packed cup crevice design- there should be no problem re-creating this in the line of contact crevices.

3.2. Solubility of lead compounds

Knowledge of the regions of thermodynamic stability and solubility for lead species are necessary to determine lead mobility. It will also provide insights into the possible mechanism of SCC.

Currently, there is lack of high-temperature, pH-dependant experimental solubility data of lead compound possibly existing under secondary side SG conditions.

AECL has the capability to experimentally determine the solubility of lead compounds under a range of conditions relevant to SGs.

With funding from COG, AECL is currently measuring the solubility of:
- lead oxide
- lead sulphate
- lead chloride

AECL also plans to measure the solubility of:
- lead carbonate
- lead silicate
- metallic lead
- lead sulfate in the presence of chloride.

With solubility data, it is expected that the following will be learned:
- Pb species most likely to precipitate in SG and crevice environment
- Pb species most likely to cause/promote Pb-assisted corrosion/cracking
- a simple model to simulate the migration of lead species towards to the metal alloy can be developed and verified.

3.3. Identification of the stable phases of lead under SG conditions

The thermodynamically stable lead phases under selected sets of steam generator operating conditions will be determined experimentally through autoclave tests.

3.4. Lead mobility

Literature survey is planned to complete a practical set of equations describing lead mobility (dissolution, precipitation, and transport by diffusion, convection and advection) in the steam cycle and inside the SG. In conjunction with the solubility data, a model will be developed to elucidate how lead is drifted towards the metal deposit interface and induces tube degradation. It is anticipated that this will provide insight as to the water chemistry under which lead will unlikely to cause SCC.

3.5. Sulphur chemistry under SG conditions

Sulfate ion (SO_4^{2-}) is one of the most common impurities in the SG secondary side chemistries. It can be reduced to lower valence sulphur species (e.g., sulfide, elemental sulphur, thiosulfate, or tetrathionate). Little work was done up to date on abiotic conversion of SO_4^{2-} to the low valence sulphur species under SG conditions.

A critical literature survey should be performed and a set of simple equations assembled to predict the conditions leading to the formation of aggressive reduced sulphur species.

4. Factors affecting effectiveness of SG inspection

4.1 Screening of array probe data

As the demands for reducing the time for steam generator inspection windows and to widen their scope increase, advanced eddy current array probes, such us the X-probe, are becoming more popular. They provide detection capabilities similar to those of industry standard rotating probes, yet they can scan tubes at speeds typical of bobbin probes. However, the large quantities of data generated by these probes make data analysis time consuming. The maximum benefit from steam generator inspections with the X-probe can only be realized if techniques are available to quickly analyze the large amounts of data.

AECL is studying the application of screening software to identify regions requiring the analyst's attention. It is expected that it will shorten analysis time and provide an additional safeguard against human error.

The effectiveness of this software to provide similar or better POD as manual analysis, while reducing the time and manpower needed for data analysis, will be studied. In particular, this could have a significant impact on large-scale X-probe inspections.

4.2 Effect of crack conductivity on detection

Low detectability of cracking has often been attributed to either the presence of ligaments along crack opening crack or to the possibility of having a family of short cracks. Understanding the correlation between flaw parameters such as crack depth, crack tightness, percent degraded area and the presence of crack ligaments to the NDE responses is paramount in predicting the reliability of SG inspections.

With funding from COG, AECL is currently using pulled tube specimens and a family of samples containing laboratory produced SCCs and EDM notches to measure electrical conductivity across the defects (cracks) in an attempt to correlate crack opening with eddy current probe responses.

The objective of the project is to establish correlations between these parameters and crack conductivity and to determine its effect in Probability of Detection and crack sizing, comparing results of the metallographic exam with the NDE results.

This study will lead to better interpretation of NDE signals and increase the understanding of some of the factors affecting detectability of cracking.

Research Topic

New nondestructive testing techniques for precise detection and evaluation of early stage material degradation and micro flaws (presented by Beok Hum Kim)

1. Background and technical issues

As operation time of nuclear power plants (NPPs) increases, possibility of generation of degradation and micro flaws in major components of nuclear power plants also increases significantly to have a crucial influence to integrity and economical efficiency of NPPs.

In the NPPs under current operation, growth rate of degradation and micro flaw accelerates since the NPPs' aging is continuously going on. Thus, it becomes one of major issues to have precise detection and evaluation of early stage material degradation and micro flaws that have been considered as no cause of serious problems such as stop operating NPPs.

However, using conventional nondestructive testing methods such as ultrasonic testing with bulk waves, eddy current testing, x-ray testing and etc, it is not possible to detect precisely and evaluate quantitatively the early stage material degradation and micro flaws, since these conventional testing methods have been developed primarily for detection and evaluation of flaws with relatively large size.

Therefore, new nondestructive testing techniques are necessary for detection and evaluation of early stage material degradation and micro flaws in NPPs.

Currently, for detection and evaluation of early stage material degradation and micro flaws there are three advanced methods including 1) high frequency ultrasonic surface wave technique, 2) high frequency focused ultrasound method and 3) phased array ultrasonic testing.

These advanced technologies, however, cannot show satisfactory performance if they applied without thorough understanding of underlined physics since they are knowledge-intensive. In fact, for proper use of these advanced methods for detection and evaluation of early stage material degradation and micro flaws, it is necessary to address followed key issues: 1) prediction of ultrasonic testing signals by quantitative description of underlying physics related to signal generation and acquisition process, 2) optimization of inspection conditions in order to maximize the probability of detection (POD), and 3) establishment of signal interpretation algorithms for quantitative evaluation of detected material degradation and micro flaws by an integration of signal processing steps and knowledge of interaction between acquired signals and early stage material degradation and micro flaws.

This task is amid at developing the new nondestructive testing techniques by addressing the key technical issues related to the advanced methods (using high frequency ultrasonic surface waves and/or high frequency focused ultrasound) for precise detection and evaluation of early stage material degradation and micro flaws.

2. Current Status

The current status of nondestructive testing techniques for detection and evaluation of early stage material degradation and micro flaws are as follows:

1) Possibility of detecting material degradation caused by corrosion-fatigue has been demonstrated using a computer controlled backscattered surface wave system.

2) Using an angular dependence of backscattered surface wave, evaluation of corrosion in a coated specimen has been attempted.

3) Theoretical interpretation of generation and propagation of surface waves at Rayleigh critical angle and its incoherent backscattered surface waves has been made.

4) Considerably high-frequency surface wave (in GHz range) has been used for detection of micro-scale stress corrosion cracks based on velocity variation.

5) Creep-fatigue damaged materials with different loading conditions have been evaluated by measuring attenuations and velocities using high-frequency focused ultrasound. It was reported that attenuation and velocity variations were due to grain size variation and present of micro voids in the grain boundaries.

6) Time reversal techniques for improving POD of small flaws such as hard alpha inclusions, stress corrosion cracks, circular cracks and etc have been adopted.

7) Possibility of detection and evaluation of material degradation and relatively small flaws using the advanced methods (High-frequency surface wave and focused ultrasound (up to 50 MHz), and phased array ultrasound) has been presented.

8) However, there is little research endeavor made currently for addressing key issues of the advanced methods for their application to precise detection and quantitative evaluation of the early stage of material degradation and micro flaws in the NPPs.

3. Objective

The objectives of the proposed work are as follows:

1. To provide the fundamental and key techniques of the advanced methods (high-frequency surface waves, focused ultrasonic methods and phased array ultrasound method) for precise detection and quantitative evaluation of the early stage of material degradation and micro flaws in the NPPs.

2. Based on fundamental and key techniques to be obtained, develop new nondestructive techniques for precise detection and evaluation of early stage material degradation and micro flaws.

4. New Researches to be conducted, scope, variables

1) Development of an ultrasonic testing system and a control program that can generate, acquire and save the high-frequency surface waves and ultrasound with enough accuracy.

2) Development and/or establishment of theoretical models for analysis of the propagation characteristics of high-frequency surface waves and their dependence on the angle of incidence in the early stage of material degradation or micro crack formation in the surface of material under investigation.

3) Characterization of the backscattering and absorption of high-frequency focused ultrasound in the early stage of material degradation or micro crack formation in the surface of material.

4) Development of the signal interpretation methods for high-frequency surface waves and high-frequency focused ultrasound.

5) Investigation of relationships of high-frequency surface waves and high-frequency focused ultrasound to the early stage material degradation or micro flaw formation.

6) Development of a technique for focusing and steering of phased array ultrasound.

7) Development of modeling approaches for description of micro flaws and their scattering of incoming waves.

8) Development of phased array ultrasonic testing models that can predict scattered signals from the micro flaws

9) Development of signal processing techniques to improve the S/N ratio and the probability of detection of micro flaws.

Topic Area #1 - Aging of Material Surfaces and Effects on Crack Initiation During Long-Term Exposures to LWR Environments

Task A: Surface Aging and Insights into SCC Crack Initiation for Alloy 600 and Alloy 182 in PWR Primary Water Environments

Scope

Surface and near-surface metallurgy changes in nickel-base alloys will be assessed in both service and laboratory samples after long-term exposures (10-30 yrs) to PWR primary-water environments. The need for proactive management of crack initiation drives this research as well as the lack of knowledge of surface aging processes. The focus of the examinations will be on nickel-base alloy 600 and alloy 182 weldments. Service samples will be prepared from various PWR upper head penetrations and steam generator tubing that have been removed over the last decade. In both cases, heats/conditions have been identified as being highly susceptible or more resistant to IGSCC in PWR primary water. Laboratory test materials will be also identified to obtain specific heats/conditions highly susceptible and resistant to SCC initiation after reasonable long-term exposures (months to years). Cross-sections will be fabricated at locations near crack-initiation sites (when present) enabling surface and near surface examinations by a combination of micro-to-nanometer resolution analytical techniques including analytical electron microscopy. Microstructural and microchemical characteristics of the multi-layer, surface corrosion-product films, metal/oxide interface regions and the altered metal zone beneath the surface film will be systematically documented for each material. Particular emphasis will be places on identifying changes that may have occurred at grain boundaries intersecting the surface. The goal of all characterizations is to establish environment-induced aging (changes to near surface metallurgy) and to link observations to SCC initiation and short-crack-growth processes.

Task B: Surface Aging and Insights into SCC Crack Initiation and Short-Crack Growth for 304SS and 316SS in BWR Environments

Scope

Similarly, surface and near-surface metallurgy changes stainless steels will be assessed in both service and laboratory samples after long-term exposures to BWR water environments. As for the nickel-base alloys, the need for proactive management of crack initiation drives this research. The focus of the examinations will be on 300-series stainless steels and may include heat-affected-zone regions. Service examples will include 304 and/or 316SS pipe samples where SCC has been promoted by surface grinding or damage. Laboratory test materials will be identified to obtain heats/conditions of highly susceptible and resistant heats to SCC initiation. Cross-sections will be fabricated at locations near crack-initiation sites (when present) enabling surface and near surface examinations by high-resolution analytical electron microscopy. Microstructural and microchemical characteristics of the multi-layer corrosion-product films and altered metal below will be documented and related to SCC initiation and short-crack-growth processes. Particular emphasis will be places on identifying deformation structures that may promote transgranular (TG) or intergranular (IG) crack initiation. The transition from TGSCC initiation to IGSCC short-crack growth will be evaluated at the corresponding near-surface depth.

Approach

The critical first step for elucidating initiation is to obtain service and laboratory samples with a well-documented pedigree of SCC behavior so that meaningful comparisons can be made. Some of these are available from recent or ongoing programs at laboratories and were examined as part of other projects. However, key partnerships will need to be established with utilities and vendors to gain access to additional materials, for example, Ni-base alloys from removed PWR upper-head penetrations (alloy 600 CRDM nozzles and alloy 182 adjacent welds) and BWR piping (304SS and 316SS base metal plus 316SS or 308SS weld metal). It will be essential to conduct a systematic characterization of material characteristics from macro (optical) to micro (SEM) to nano (TEM) dimensions clearly establishing details of the surface and subsurface. SEM approaches will include backscatter imaging for the alloy general grain size and structure, orientational imaging microscopy (OIM) for grain boundary character and strain distributions and energy dispersive x-ray spectroscopy (EDS) for compositional analyses at micrometer resolution for the surface film, crack corrosion products, possible bulk changes in the near-surface metal composition and large precipitates or inclusions in the metal. SEM-EDS compositional maps will also be used to document significant composition changes such as solidification segregation that is often seen in weld metals.

The total number of samples and near-surface regions that will be characterized by analytical TEM techniques will depend on the variability observed among different surface/near-surface structures, IG attack/oxidation, cracks and crack tips. Microstructures will be documented at several magnifications to illustrate corrosion-product films, sub-surface degradation and the near-surface alloy microstructure. A combination of techniques including high-resolution TEM imaging and nano-diffraction will be employed to characterize the multilayer films and altered base material that may be present near the surface. Nano-probe microchemical analysis will be performed using EDS (including compositional mapping) and possibly electron energy loss spectroscopy (EELS) techniques. Evidence for the local enrichment of alloying and impurity elements will again be assessed, with nanometer-scale resolution particularly at oxide/oxide and metal/oxide interfaces. Local compositions at grain boundaries will also be established as a function of distance below the surface and boundary regions leading intergranular attack or SCC will be evaluated if such degradation is observed. Detailed analysis of corrosion product phases in tight cracks will be performed by these various methods and the possibility of selective oxidation ahead of the crack tip will be assessed. The presence of solution impurities within existing cracks and in corrosion films will be ascertained. Composition profiles will be taken to indicate changes across films at the surface and at near-surface crack-tip regions.

The final step after establishing critical aspects of long-term, LWR service aging for both Ni- base and Fe-base stainless alloys should be to conduct SCC initiation tests in the laboratory. These tests should be designed to provide quantitative evaluations of the surface and near-surface metallurgy effects on cracking. As possible, actually LWR service materials should be used after detailed characterizations described above have been completed along with well-controlled laboratory samples.

Related Activities

The MEOG Materials Management Initiative is pursuing corrosion research projects in 2004 through 2006 directly related to the proposed research described above. One project is focused on developing specific understanding of SCC initiation and short-crack growth and the second project links localized deformation to environment-assisted cracking (EAC). Both projects will critically evaluate the current state of knowledge and identify key gaps for experimentation starting in later 2005 and continuing through 2007. Initial evaluations from the gap projects have identified the surface aging assessments as an important piece to the understanding of SCC crack initiation and short-crack growth. Therefore, the proposed PMDN activity should be coordinated with the corrosion research portfolio for the MEOG Materials Management Initiative.

It is critical to note that an extensive multi-component program has been underway for several years at TEPCO focused on SCC initiation and propagation of BWR materials. Research appears to include examinations of actual cracked stainless steel pipe and core shroud samples removed from service and laboratory tests on stainless steels in various conditions. Partnership and interactions with TEPCO should be established to coordinate key research activities as possible.

Topic Area #2: Thermodynamics and Kinetics of Corrosion-Product Films on Nickel- and Iron-Base Stainless Alloys in LWR Environments

Task A: Practical Assessment of Pourbaix Diagrams

<u>Scope</u>
An integrated series of experiments will be performed to effectively map important regions of the high-temperature-water, potential/pH diagrams for Ni- and Fe-base stainless alloys including alloy 600, alloy 690, alloy 800 and 300-series stainless steels. Reliable SCC susceptibility predictions are inhibited by the lack of understanding of oxide kinetics and stability. Contact electric resistance will be used to identify the metal to metal-oxide transition as a function of realistic changes in potential and pH expected at the surface and possible at crevices or crack tips. In order to better understand surface formation of thin films, laser Raman spectroscopy will conducted for selected materials and conditions. Oxide structures will be identified in-situ at several potential/pH/temperature combinations and Raman measurement will be repeated after the high-temperature-water environment is removed. Final detailed characterizations will then be conducted by high-resolution analytical transmission electron microscopy (ATEM) on cross-section samples to quantitatively determine the surface film structures and compositions. The combination of all three unique techniques on the same alloys during or after exposure to critical potential/ph/temperature conditions will provide key insights into the fundamental corrosion/oxidation processes controlling performance in LWR environments. In addition, comparisons will be made to high-resolution ATEM characterizations of crack-tip films in Task C.

Task B: Evaluating Material Composition and Solution Chemistry Effects on Corrosion-Product Film Formation

Scope

The integrated series of experiments proposed in Task A can also be effectively used to elucidate the influence of LWR solution additions/impurities and alloy composition differences. Knowledge of these influences enables predictive mitigation of alloy cracking. Potential changes in the thermodynamics and kinetics of surface film formation should be studied isolating the influence of independent additions of S, Pb and Zn. Only a few base LWR high-temperature-water environments can be used, but should be chosen to represent realistic crevice and crack-tip potential/ph conditions. Perhaps more important, material compositions should be modified to simulate segregated grain boundaries. This would include non-equilibrium thermal segregation in mill-annealed 316SSs where grain boundary Mo concentrations can reach ~10 at% and radiation-induced segregation in SSs where Ni and Si concentrations can exceed 30 at% and 15 at%. Such large non-equilibrium enrichments would be produced in a bulk alloy by high-rate sputter deposition, thereby producing a bulk material with the grain boundary composition. Surface film formation can then be dynamically measured in-situ by contact electric resistance and laser Raman, then quantitatively evaluated with cross-section ATEM. Key comparisons will be made to high-resolution ATEM characterizations of crack-tip films in Task C.

Task C: Film Formation in SCC Cracks and at Crack Tips for Insights into Environment-Assisted Crack-Growth Mechanisms

Scope

Stress-corrosion, crack-growth-rate (SCC-CGR) tests will be conducted on selected Ni- and Fe-base stainless alloys in LWR environments under well-controlled potential/ph/temperature conditions. For example, SCC-CGR tests will be performed spanning the Ni/NiO phase transition on alloy 600 using low-high hydrogen additions to move from an electrochemical condition where NiO is stable to one where Ni metal is stable. These specific conditions will be mapped in Task A following previous research performed at KAPL/Bettis. Samples will be removed under load and prepared for cross-section ATEM enabling quantitative characterization of crack and crack-tip corrosion films and local metallurgy changes. Fundamental alterations in the crack tips will be established by comparing each potential/pH/temperature condition and linking results to the surface work in Task A. Oxide film differences can be documented as a function of distance from the crack tip (very short exposure time) to the crack mouth (exposure times reaching several months). The kinetics of oxidation can be studied since crack-growth rates have been accurately established helping quantify exposure time along the length of the SCC cracks. It is also proposed that SCC-CGR tests and ATEM crack-tip examinations be conducted to investigate material composition and solution chemistry issues discussed in Task B. Key solution chemistry conditions will be selected where significant influence on the SCC-CGR is observed, i.e., where S and Pb enhances SCC propagation and where Zn decreases growth. Cross-section ATEM will then be employed to interrogate changes in the crack and crack-tip corrosion films and local metallurgy. In addition, the influence of Mo grain boundary segregation and high matrix Si concentration (as shown by Andresen) will be evaluated on SCC growth rates followed by detailed ATEM crack-tip characterizations. This final task integrates the in-situ and ex-situ surface-film examinations in Tasks A and B with processes that occur at the SCC crack tip during propagation.

Topic Area #3: Mechanistic Understanding of Radiation-Induced Materials Changes and Cracking of LWR Core Internals

Task A: Detrimental Material Changes and Embrittlement in Highly Irradiated Stainless Steels

Scope

Several evaluations have indicated that stainless-steel LWR core internals may become susceptible to intergranular embrittlement at high irradiation doses. Microstructure/property relationships at high LWR doses have not been sufficiently explored for proactive management of embrittlement. Recently, nanometer-scale cavities have been identified at grain boundaries during limited examinations on isolated samples by transmission electron microscopy (TEM) that may promote this low-toughness, intergranular fracture. Much more extensive research is needed on the microstructure, microchemistry, deformation and mechanical properties of highly irradiated stainless steels. It is proposed that primary work be centered on the dose-dependence material changes in BWR thimble tubes examining low-fluence (<0.1 dpa), moderate-fluence (20-40 dpa) and high-fluence (60-85 dpa) locations. Detailed microstructural and microchemical characterization will be performed including the presence of bubbles, voids, dislocation loops, cold work recovery and segregation in the matrix and at/near grain boundaries. Helium and hydrogen will be measured and related to the cavity observations. Where possible, these observations will be compared to existing tensile test data and to additional shear punch test assessing radiation hardening and ductility. Specially designed deformation tests will be conducted at ~300^{o}C on 3-mm disc samples documenting localized channeling behavior and grain boundary interactions to access precursors to intergranular cracking. Attempts should also be made to obtain high-dose PWR materials, such as baffle bolts, where comparative data could be generated to the BWR thimble tube response.

A second source of highly irradiated stainless steels is from the Bor60, fast-reactor irradiations performed as part of the Cooperative IASCC Research (CIR) project. Small test materials of commercial stainless steels and of high-purity stainless steels with single-element additions have been irradiated to doses of 5, 10, 20, 45 and 65 dpa. Once again important comparisons can elucidate the radiation-induced microstructure and microchemistry influences on mechanical behavior (deformation, strength and fracture). Differences in spectrum, dose rate and the environment (in gas versus water) will alter some aspects of microstructure/microchemistry development and helium and hydrogen levels in particular. High-purity alloys with and without Si will be evaluated in detail since strong radiation-induced segregation of this element occurs to grain boundaries and may impact the susceptibility to intergranular embrittlement.

Task B: Surface and Near-Surface Aging in Stainless Steel Core Internals and Influence on Irradiation-Assisted Stress Corrosion Cracking

<u>Scope</u>

Surface and near-surface metallurgy changes affecting initiation and short-crack growth will be assessed in a PWR baffle bolt and BWR top guide where IASCC has been discovered during service. These two materials have previously been examined in detail for bulk radiation damage structures and SCC crack tips by analytical transmission electron microscopy (ATEM). What has not been done to predict crack initiation is to examine changes in the near-surface that has been produced by the simultaneous irradiation and high-temperate water exposure for more than 20 years. Cross-sections will be fabricated at locations near crack-initiation sites enabling surface and near surface examinations by high-resolution analytical electron microscopy. Microstructural and microchemical characteristics will be documented and related to potential radiation- and environment-induced changes impacting SCC initiation. As for the nonirradiated case, the total number of samples and near-surface regions that will be characterized by ATEM techniques will depend on the variability observed among different surface/near-surface structures, cracks and crack tips. Microstructures will be documented at several magnifications to illustrate corrosion-product films, sub-surface degradation and the near-surface alloy microstructure. A combination of techniques including high-resolution TEM imaging and nano-diffraction will be employed to characterize the multilayer films and altered base material that may be present near the surface. Nano-probe microchemical analysis will be performed using EDS (including compositional mapping) and possibly electron energy loss spectroscopy (EELS) techniques. Evidence for the local enrichment of alloying and impurity elements will again be assessed, with nanometer-scale resolution particularly at oxide/oxide and metal/oxide interfaces. Local compositions at grain boundaries will also be established as a function of distance below the surface and boundary regions leading intergranular attack or SCC will be evaluated if such degradation is observed. Detailed analysis of corrosion product phases in tight cracks will be performed by these various methods and the possibility of selective oxidation ahead of the crack tip will be assessed. The presence of solution impurities within existing cracks and in corrosion films will be ascertained. Composition profiles will be taken to indicate changes across films at the surface and at near-surface crack-tip regions.

Task C: Isolating Matrix and Grain Boundary Deformation Mechanisms on Irradiation-Assisted Stress Corrosion Cracking

<u>Scope</u>

Recent studies have investigated matrix channeling and grain boundary sliding in charged-particle-irradiated stainless steels. Stacking fault energy has been implicated as an important parameter controlling localized deformation and potentially susceptibility to IASCC. The key missing assessments have been on neutron-irradiated stainless steels with direct links to SCC crack initiation. Proposed research focused on quantitative deformation studies on stainless steels where extensive IASCC testing has been performed. Disc-bulge tests will be conducted on polished sub-size samples at different levels of plastic strain and surface slip steps quantified by a combination of SEM and atomic-force microscopy (AFM) examinations. In addition, detailed characterizations of channel intersections with grain boundaries. Boundary distributions will be established by orientational imaging microscopy (OIM) to help quantify importance of boundary interactions. Direct comparisons will be made between surface slip steps and boundary interactions to previously measured IASCC response.

Topic Area #4: Metallurgy, Hot Cracking and Stress-Corrosion Cracking in Ni-Base Alloy Weldments

Task A: Improved Understanding of Microstructural/Microchemical Evolution and Hot Cracking in Nickel-Base Alloys Weld Metals

Scope

Characterizations will be performed at moderate-to-high resolutions of weldments removed from LWR service, mock-ups welds and various test welds made with alloy 182/82 and alloy 152/52. These studies are driven by the need to understand and mitigate known weld-metal cracking. Base weldment microstructural features will be documented including inclusions, precipitates, interdendritic boundaries and grain boundaries using scanning electron microscopy (SEM). Microchemical analysis will be performed using EDS and compositional mapping to document micrometer-scale segregation/precipitation in the SEM and nanometer-scale elemental distributions in the transmission electron microscope (TEM). The intent will be to greatly expand our understanding of weld metal structures in actual and simulated LWR service components with a focus on solidification segregation and second-phase precipitation particularly at interdendritic grain boundaries. Much of the initial work can be linked to the proposed surface examinations in alloy 182 weldments in Topic #1, Task A. The second key aspect will be relate these same microstructural and microchemical features to the susceptibility to hot cracking for both the low-Cr alloy 182/82 welds and the high-Cr, alloy 152/52 welds. The same SEM and TEM approaches will be employed to establish relationships between interdendritic segregation/precipitation and the cracking morphology at both micro-and nanometer resolutions. Crack and crack-tip cross-section samples will be prepared and investigated by analytical TEM approached described in the previous topic areas. Nanometer-scale segregation and precipitation will be documented both at interdendritic and grain boundaries with examinations focusing on boundaries where hot cracks have propagated. Although crack corrosion products will not be present, careful examinations and compositional mapping will be performed to determine if second-phase material is present in the cracks. Characterizations will attempt to establish crack-tip “signatures” for mechanical cracks produced during weld solidification.

Task B: Influence of Weld Metal Microstructure/Microchemistry and Pre-Existing Hot Cracks on Stress-Corrosion Cracking of Nickel-Base Alloys

Scope

An important disconnect between the technical community who believe cracking in Ni-base alloy weld metal (alloy 182 or 82) can occur solely due to SCC and utility perception that susceptibility primary results from pre-existing hot cracks due to poor manufacturing. Key tests are needed to critically assess the influence of not only pre-existing hot cracks, but solidification segregation or precipitation on SCC. An improved understanding of dendritic and grain boundary compositions in weld metals must be established and used to systematically create realistic material conditions for quantitative SCC crack-growth tests. Gleeble experiments should be conducted to document controlled heating and cooling on interfacial structure and composition. Finally, the influence of pre-existing hot cracks on SCC initiation and propagation must be explored. Initial experiments can be run on mock-up welds where hot cracking has been investigated.

Task C: Assessment of Stain and Stress States in Weld Metal and Heat-Affected-Zone Regions of LWR Weldments

<u>Scope</u>
Recent results have established the ability of modern OIM systems to measure residual plastic strains and stresses in stainless steel and Ni-base alloy welds. Without question, initial manufacturing and fabrication can produce conditions for future susceptibility or resistance to environment-induced cracking. An integrated experimental and modeling program is needed to create the quantitative capability to assess strains and stresses in realistic LWR weldments. Systematic studies using OIM on various stainless alloy weldment will be conducted both in the as-welded and repair-welded condition. Finite-element modeling will be employed to investigate welding parameters that modify the stress/strain profiles throughout the weld. Controlled experiments will be run to test model parameters and help validate predictions. The intent will be to tailor weld parameters to optimize material microstructure and final stress/strain condition.

Proposed topics for PMDM research, Roger W. Staehle, 06-03-05, (Six topics prepared in response to request from J. Muscara in 06-02-10 email)

Topic #1: Initiation and propagation of SCC in cold worked stainless steel and Alloys 600 and 690: Fundamental assessments of crack tips

1.0 Background, technical issues

Cold work accelerates both the initiation and propagation of SCC in stainless steels and high nickel alloys. Increasing cold work increases the intensity of both initiation and propagation. The observed rates of propagation in laboratory testing are sufficient to perforate thick piping in relatively short times, possibly several years. The initiation of SCC in cold worked surfaces can acquire sufficient depth to continue in less cold worked materials.

While the observed rates of propagation of SCC in laboratory tests are relatively rapid, such rates have not been observed in operating plants, and the explanation for such a divergence is not clear. Clearly, some explanations for this divergence might include retarded initiation, stress distributions in thick sections, stress relaxations and factors affecting the momentum of propagating SCC.

Cold work arises from three main sources of interest to LWRs. First, cold results from bending such as in forming elbows or U bends when the metal is cold. Second, cold work results from plastic deformation associated with the shrinkage in welding. Third, cold work results from abusive surface treatments.

Possibly rapid SCC associated with cold work that could increase its severity over long times is a particular concern since many of the locations where high cold work exists, e.g. elbows and surface abuse, are not usually inspected. In such locations SCC could be extensive before it is detected.

Of course, some cold work is mitigated by heat treatment and this reduces the locations of possible concern.

This task is aimed at understanding the processes whereby cold work affects the initiation and propagation of SCC via detailed characterizations of crack tips using analytical transmission electron microscopy (ATEM) and theoretical metallurgical and mechanics analysis of crack tips.

2.0 Current status

The current status of characterizing crack tips of initiating and propagating SCC is the following:

1. Tips of advancing SCC have been shown to be narrow and as wide as 1-2 nm as well as wider.

2. The extent of chemical reaction occurring at the tips of advancing cracks is small and less than the width of the overall crack tip.
3. The composition of metal ahead of advancing SCC for stainless steels has been shown to be significantly enriched in nickel. This enrichment appears to result from the presence of large vacancy concentrations that are associated with the crack tip strain field and possibly associated with the presence of grain boundaries. Such enrichments have been identified by at least two investigators.

4. While some work on the propagation of SCC in stainless steels has been conducted, little is available for initiation.

5. There is no definitive work on the state of strains adjacent to the tip of SCC and in the range where the enrichment of species is being observed.

3.0 Objectives

The objectives of the proposed work are the following:

1. Provide fundamental bases for predicting long term effects of cold work on the initiation and propagation of SCC in stainless steels and high nickel alloys of interest to LWRs.

2. Integrate the observations of ATEM work on both material head of SCC and following the head of SCC with fundamental studies of theoretical mechanics and solid state processes.

4.0 New research to be conducted, scope, variables

1. Characterize in detail the chemical composition ahead of propagating SCC.

2. Characterize the geometry of advancing SCC in during propagation and during early stages of initiation.

3. Characterize stainless steels and high nickel alloys in low potential and high potential ranges as are related to hydrogenated and non-hydrogenated environments.

4. Develop improved theoretical models for strain distributions immediately adjacent to very narrow tips of SCC.

5. Develop models for the creation of vacancies, their mobility, and the implications for diffusion of alloy species in the region of crack tips.

6. Develop models for the relaxation of strains at tips of advancing SCC.

Topic #2: Measurement of accumulation of Pb, as well as S^{y-} in line contact crevices of steam generators

1.0 Background, technical issues

Modern steam generators in PWRs now use line contract tube supports on the secondary side in place of the older drilled holes and associated flow holes. In the line contact crevices secondary coolant flows through the spaces in the line contact geometries and cools the outside surfaces of tubes more directly than in the drilled hole geometries.

While the initial assumption of the line contact geometries considered that there would be little accumulation of deposits on tube surfaces, in fact, the accumulation of deposits is significant; and it is likely that the superheat conditions produced by drilled holes may occur with the line contact geometries.

The detailed conditions on the OD surfaces of tubes associated with line contact crevices where significant superheats may develop are important in connection with the occurrence of SCC which can be produced by the presence of Pb and low valence sulfur, S^{y-}, that is produced by the reduction of higher valence sulfur due to the action of hydrazine.

These possible conditions of significant superheat together with the accumulation of Pb and S^{y-} as has been observed in the past in connection with drilled hole crevices is important since both Pb and S^{y-} produce aggressive SCC in Alloy 690TT.

However, the possibly deleterious effects of Pb and S^{y-} on Alloy 690TT are important only if these species can accumulate in the deposits associated with line contact crevices.

2.0 Current status

1. The aggressive effects of Pb and S^{y-} on Alloy 690TT have been identified. It has also been shown recently also that such aggressive behavior associated with Pb occurs in pH_T 7 solutions. Thus, there is little question that PbSCC can occur in SGs if the Pb accumulates and is soluble to some extent.

2. Extensive deposits have been observed in line contact geometries in the field. Further, preliminary experiments in the laboratory have shown that such deposits are substantial and not easily dispersed.

3. There is no information concerning the OD surface temperature associated with deposits in line contact crevices. Further, there is little information on the details of properties and compositions of deposits in line contact geometries as well as the distributions of species in these deposits.

4. There is no information concerning the possible immobilization of Pb, as this would change the chemical activity of the Pb.

3.0 Objectives

1. Measure the rate of accumulation and properties of deposits in line contact geometries.

2. Determine the effects of subsequent chemical cleaning on these deposits.

3. Determine the properties of these crevices relative to OD surface temperatures, distribution of surface temperatures, existence of two phase regions, associated electrochemical potentials and pH.

4. Determine the rate of accumulation of Pb and S^{y-} in deposits in line contact geometries, emphasizing the hottest surfaces on the inlet side.

5. Determine the existence and distribution of species that immobilize both Pb and S^{y-} species.

6. Determine the rate of accumulation of Pb and S^{y-} species as well as their speciation.

4.0 New research to be conducted, scope, variables

Topic

1. Obtain deposits from operating SGs with line contact geometries to assess general patterns of properties of deposits and chemical species and their distributions.

2. Develop a laboratory system, similar to that of Lumsden's, where flow and heat flux of operating SGs can be modeled, and where important quantities such as distributions of local temperatures, electrochemical potential, chemical species can be measured as functions of time. Possibly two such systems should be available for long and short term experiments.

3. Determine the rate of accumulation and subsequent distribution and speciation of Pb and S^{y-}.

4. Determine effects of possibly inhibitive species that would minimize the deleterious effects of Pb and S^{y-}.

Topic #3: Reduction of high valence sulfur species to lower valence aggressive species

1.0 Background, technical issue

The normal concentration of high valence sulfur, e.g. sulfates, species in feedwater for SGs is in the range of 10 ppb although sometimes transients due to the release of resin species raise this concentration.

In addition, hydrazine is intentionally added to the secondary side to minimize the concentration of oxygen and to maintain the electrochemical potential relatively low.

Owing to the thermodynamic properties of the high valence sulfur and the hydrazine, the high valence of sulfur species can be reduced to –2 or +2 valence species such as HS^- or H_2S and $S_2O_3^{2-}$ depending on the pH.

These low valence sulfur species have been show to accelerate corrosion of high nickel alloys, including Alloys 600MA, 600TT, and 690TT, as well as to accelerate SCC. These low valence sulfur species should be especially aggressive to the higher strength iron base alloys used in turbines.

So far, quantitative data for the rate, conditions, and speciation of reduction of high valence species of sulfur are lacking.

The presence of low valence sulfur is inimical to the high nickel alloys used in SGs; these low valence sulfur species would also produce SCC of turbine materials depending on the extent of carryover from the SG and the nature of any accumulation.

2.0 Current status

1. The fact that high valence sulfur species can be reduced in SG environments has been established.

2. The rates of reduction and resulting species of high valence sulfur species are minimally understood.

3. No data have been obtained for the transport of reduced sulfur species to turbines. No data have been obtained for any distribution of such species in turbines.

4. There are no direct data for the SCC of turbine alloys in the presence of reduced sulfur species although there are extensive data for the sulfide-related SCC of high strength alloys from the petrochemical industry. Such SCC for turbine alloys should be expected.

3.0 Objectives

1. Quantitatively characterize the rates and conditions for the reduction of high valence sulfur species to low valence sulfur species in the chemical and thermal conditions of SGs.

2. Characterize the distribution of reduced species of sulfur within SGs.

3. Characterize the carryover of reduced sulfur to turbines.

4. Characterize the distribution of reduced sulfur species in turbines.

4.0 New research to be conducted, scope, variables

1. Develop a model SG system in which the reduction of high valence sulfur species can be characterized under realistic conditions of steam generator operation.

2. Develop refined laboratory equipment where the reaction rates of high valence sulfur species with hydrazine can be characterized quantitatively.

3. Develop laboratory equipment where the carryover of sulfur species to turbines can be quantitatively characterized.

4. Conduct surveys of turbines in the shutdown condition for the presence and distribution of reduced sulfur species.

Topic #4: Long term LPSCC of Alloy 690TT

1.0 Background, technical issue

Alloy 690TT has performed well in PWR SGs since 1987. There is no evidence of LPSCC in any SG tube. Some Alloy 690TT thicker sections have been used without LPSCC being observed.

While Alloy 690TT has performed well both in service and in some laboratory testing, the alloy is quite prone to SCC in alkaline solutions and in Pb-containing solutions especially at mild to concentrated alkalinity. Further, Alloy 690 sustains significant SCC in mildly acidic solutions at somewhat elevated potentials in the higher part of the range expected on the secondary side of steam generators.

Studies of SCC propagation for Alloy 690TT have shown that it sustains SCC.

Further, studies of surfaces of Alloy 690TT in concentrated alkaline solutions show that chromium is preferentially depleted from the surface. Further, the transition from Cr^{+3} to Cr^{+6} exhibits a decreasing slope that is twice that of the H_2O/H_2 equilibrium; this means that the potential for the Cr^{+6}/Cr^{+3} transition is accessible to the potentials in the SG in the range of about pH_T 8.

Alloy 690TT is inherently reactive owing to the high concentration of chromium.

Finally, the observation in stainless steels that nickel is enriched at the tip of cracks in the metal ahead of the crack tip suggests that the metal ahead of crack tips for Alloy 690TT may also enrich in Ni and therefore become like Alloy 600 and therefore prone to LPSCC. The rate of growth of LPSCC then would be related to the rate of depletion of Cr from the material ahead of the crack.

2.0 Current status

1. Alloy 690TT has exhibited no failure in operating SGs since 1987.

2. There is abundant evidence that Alloy 690TT exhibits SCC in some environments and in some cases is more prone to SCC than Alloy 600MA as is the case for Pb contamination.

3. Propagation of SCC in Alloy 690TT has already been observed in primary water in laboratory tests.

4. SCC initiation and propagation in the LPSCC submode seem possible for Alloy 690TT but may require longer times.

3.0 Objectives

1, Determine the critical process, which affect the initiation and propagation of LPSCC for Alloy 690TT.

2. Determine the long term dependence for the initiation and propagation of SCC in Alloy 690TT as a function of PWR and BWR environments.

4.0 New research to be conducted, scope, variables

1. The first step in this study would involve the ATEM study of crack tips from Alloy 690TT that have been exposed over a range of conditions. These results would be compared with those from Alloy 600MA. Again, this work would concentrate on the material ahead of the crack tip with respect to structure and composition.

Topic #5: SCC and mitigation for Alloy 600TT and 690TT in Pb^- and S^{y-} contaminated solutions

1.0 Background, technical issue

The chronology of PbSCC and S^{y-}SCC has been reviewed in detail both at the PbS workshop and at the Environmental Degradation during 2005. Essentially, it appears that PbSCC could have been a contributor if not the major contributor to the past ODSCC of Alloy 600MA.

Further, Alloy 690TT is more prone to PbSCC than Alloy 600MA in alkaline solutions. Pb is readily enriched in superheated crevices starting with concentrations of Pb in the feedwater in the range of 10-100 ppt. Pb might be further enriched by possible electrodeposition on metallic surfaces.

While there have been significant experiments on the PbSCC of high nickel alloys, in fact, there is little coherent work that provides bases for prediction.

Also, there is little basis for explaining the transitions between TGSCC and IGSCC for PbSCC.

Finally, there are no bases yet for explaining the large variability of SCC of Alloy 600MA.

In view of the potential for future degradation of Alloy 690TT and he lack of a coherent basis for PbSCC, this submode of SCC needs a quantitative foundation.

2.0 Current status

1. PbSCC has been shown to be a potential cause of much of the past ODSCC of in drilled hole geometries where Alloy 600MA was used. While this hypothesis is controversial, it can neither be proved nor disproved. Based on the evidence, PbSCC as a cause of the ODSCC is more likely than not.

2. The past evidence was distorted by early misleading information published by the International Nickel Company. This early work argued that PbSCC was typically transgranular when internal work as well as later systematic work showed the opposite.

3. In view of the potential for extensive PbSCC of Alloy 690TT tubing in SGs a firmer basis for predicting the occurrence of PbSCC is required.

4. While there are limited experimental data for the S^{y-}SCC of high nickel alloys in alkaline solutions, there are negligible data at lower pH, especially in the neutral range. On the other hand examinations of crack tips and OTSG upper bundle tubing reveal that both S^{y-} and Pb are present with the S^{y-} sometimes being the dominant species.

3.0 Objectives

1. Develop multiple facilities for conducting controlled studies of both PbSCC and S^{y-}SCC over ranges of pH, potential, concentration, and temperature that are relevant to the secondary side. Owing to problems of contamination, facilities for the Pb and S^{y-} need to be separate. Further, it is unlikely that such facilities can be utilized for studying other chemistries owing to contamination from the Pb or S^{y-}.

2. Obtain specimens from operating SGs to calibrate the magnitudes of concentrations of Pb and S^{y-} as well as other species present that may contribute to immobilizing or activating the aggressiveness of the Pb and S^{y-}.

3. Concentrate mainly on initiation of SCC since the application is thin walled SG tubing.

4. Direct some experiment to rationalizing the IG or TG morphology manly of PbSCC.

5. Develop approaches to mitigating Pb and S^{y-}.

4.0 New research to be conducted, scope, variables

1. Determine the dependencies of PbSCC and S^{y-}SCC on pH, potential, concentration, and temperature in ranges that are relevant to the deposits on free surfaces, TTS crevices, and line contact crevices.

2. Assess the action of possible inhibitors for PbSCC and S^{y-}SCC.

3. Assess the possible acceleration of PbSCC and S^{y-}SCC when normal impurities, e.g. Si, Al, are depleted from crevices, with respect the possibility that such impurities are providing inhibition.

Topic #6: Scaling of Alloy 690TT in Pb-containing environments

1.0 Background, technical issue

In the development of the Alloy 690TT chemistry, in addition to assessing the occurrence of SCC in Pb solutions as a function of compositions of Ni, Cr, and Fe, the rate of scaling was also determined as a function of the same alloy variables. While the occurrence of SCC decreased in Pb-containing solutions of otherwise pure water with increasing Cr and Fe, scaling in the same solutions increased with increasing Cr but decreased with increasing Fe. Scaling on high nickel alloys has been observed on Alloy 690TT and Alloy 800 but not on Alloy 600MA in accordance with the early comprehensive studies of alloy dependencies.

The scaling process becomes important both from denting types of processes in tube supports and TTS geometries and in the acceleration of crack growth via the wedging action inside growing scales. The magnitudes of scaling for the various higher Cr alloys are such as to justify these concerns.

This scaling process in Pb-contaminated solutions depends first on the accumulation of Pb under heat transfer deposits. If no Pb accumulates, then the scaling does not seem to occur.

2.0 Current status

1. Scaling of higher Cr alloys such as Alloy 690TT and Alloy 800 occurs at rates of at least 25 μm or greater and sometimes in the range of 250 μm or greater.

2. There are no data that characterize the rates of growth of scales in Pb-containing solutions as a function of the variables on secondary sides of PWR SGs.

3. The growth of scales should be considered for possibly producing high local stresses due to denting or wedging conditions at long times.

3.0 Objectives

1. Determine the rate of growth and properties of scales on Alloys 690TT and 800 as a function of potential, pH, concentration of Pb, and temperature.

2. Develop rate laws that permit extrapolating data to long times.

3. Determine the magnitude of forces that can be produced in tight geometries.

4.0 New research to be conducted, scope, variables

1. Measure rates of growth of scales on Alloys 690TT and 800 compared with Alloy 600MA in Pb-contaminated water as a function of chemistries expected to occur in deposits in line contact TSP geometries and in TTS crevices as well as on free span surfaces such as in OTSG upper bundles. Include variables of electrochemical potential, pH and temperature.

2. Measure forces that can be exerted by such scales.

NRI & PMDM

ANNA BROŽOVÁ
Division of Integrity and Technical Engineering

Charleston, 11 – 13 May 2006

INTEGRITY AND TECHNICAL ENGINEERING DIVISION

- STRESS ANALYSIS,
  - PSR
  - PLIM, LONG TERM OPERATION PROGRAMS
- CORROSION AND MATERIAL STRUCTURE
  - Autoclaves and loops, also in hot cells
  - Model of SG – stend
  - Microscopy
- MECHANICAL TESTING
  - STANDARD AND LARGE SCALE
  - HOT AND SEMI-HOT CELLS incl. RECONSTITUTION
- NDE
  - DEVELOPMENT, QUALIFICATION, ISI
  - SG AND PRESSURIZER – ISI AND REPAIR

POTENTIAL PARTICIPATION

- **REACTOR PRESSURE VESSELS**
  - **EAC initiation in cladding**
  - **BORIC ACID CORROSION**
- **REACTOR INTERNALS**
  - **EAC AND IASCC (IN-PILE, EX-PILE) initiation**
- **STEAM GENERATORS**
  - **EAC initiation in TUBES**
  - **CREVICE CORROSION**
- **PIPINGS**
  - **EAC**

PROPOSED NRI PARTICIPATION

- **EAC initiation and growth**
- **WWER COMPONENTS AND MATERIALS**
- **WWER environment**
- **Share techniques and methods**

EAC and PWSCC/IASCC

- **cold worked or heat sensitised austenite steels 08Ch18N10T/08Ch18N12T is considered the potential threat for the reactor pressure boundary in WWER's.**
  - **Reactor vessel internals: core shroud, core barrel and baffle to former bolts**
  - **CRDM Vessel Head Penetrations.**
  - **Dissimilar welds in nozzles (RPV, Pressurizer and Steam Generators)**
  - **Primary Piping**
  - **Steam Generator Tubes and Collectors**

EAC and PWSCC/IASCC

- **Even primary water conditions are controlled under the threshold value for EAC occurrence of the non-irradiated austenite stainless steels there is unknown long-term behaviour of the in-service irradiated materials and cold worked surface layers. The presence of short cracks in RVI cannot be avoid in the long-term aspect.**

Pacific Northwest National Laboratory
CELEBRATING 40 Years OF SCIENCE & DISCOVERY 1965-2005

Potential Research Areas and Ideas for Discussion

Steve Bruemmer
Pacific Northwest National Laboratory

Third Planning Meeting for the International Cooperative Group on Proactive Materials Degradation Management

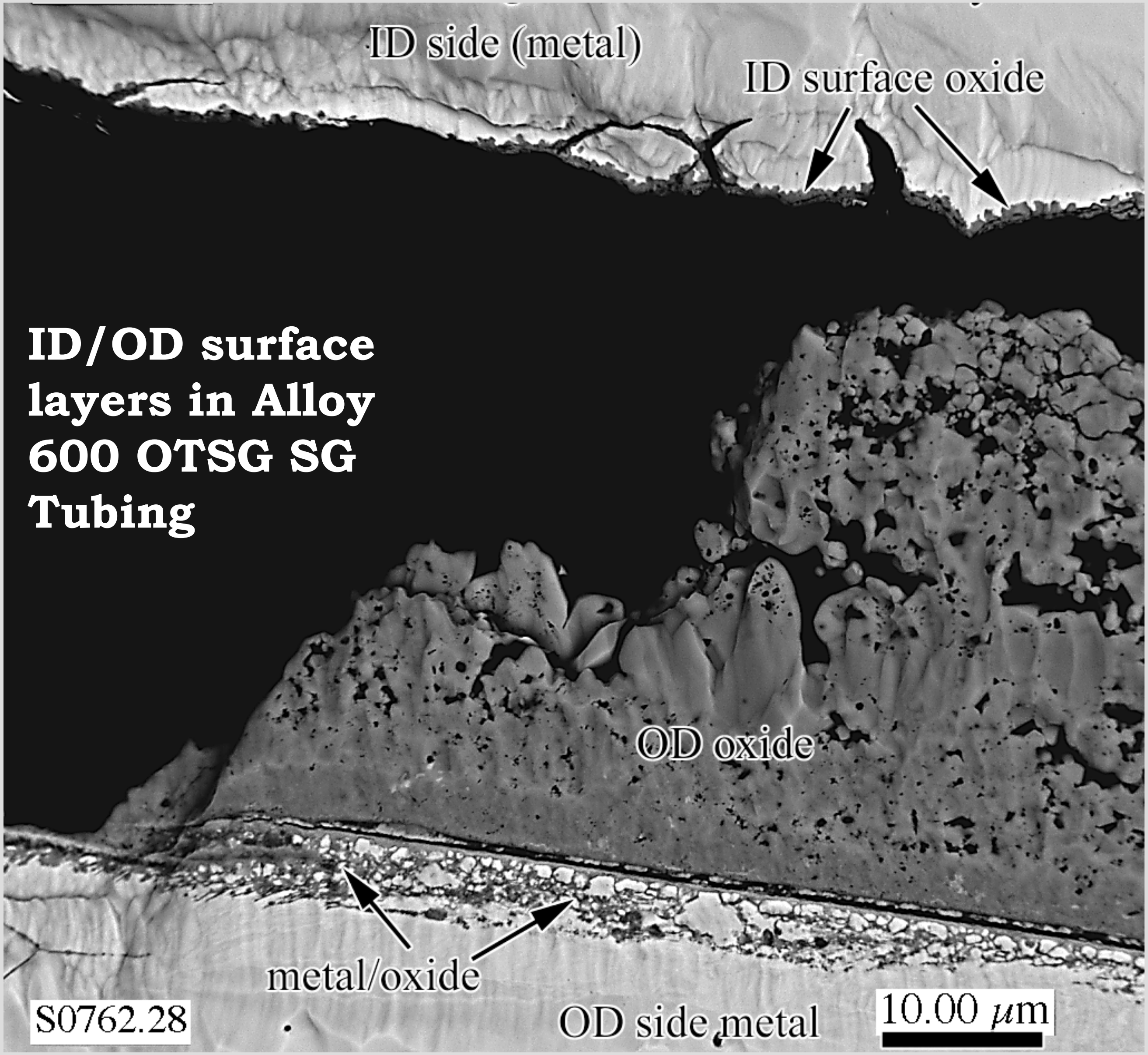
May 11-13, 2006
Charleston, South Carolina USA

Topic Area #1

Aging of Material Surfaces and Effects on Crack Initiation During Long-Term Exposures to LWR Environments

Task A: Surface Aging and Insights into SCC Crack Initiation for Alloy 600 and Alloy 182 in PWR Primary Water Environments

Task B: Surface Aging and Insights into SCC Crack Initiation and Short-Crack Growth for 304SS and 316SS in BWR Environments



ID Surface Degradation

OD Surface Degradation

Topic Area #2

Thermodynamics and Kinetics of Corrosion-Product Films on Nickel- and Iron-Base Stainless Alloys in LWR Environments

Task A: Practical Assessment of Pourbaix Diagrams for Improved Understanding of SCC Behavior

Task B: Evaluating Material Composition and Solution Chemistry Effects on Corrosion Film Formation

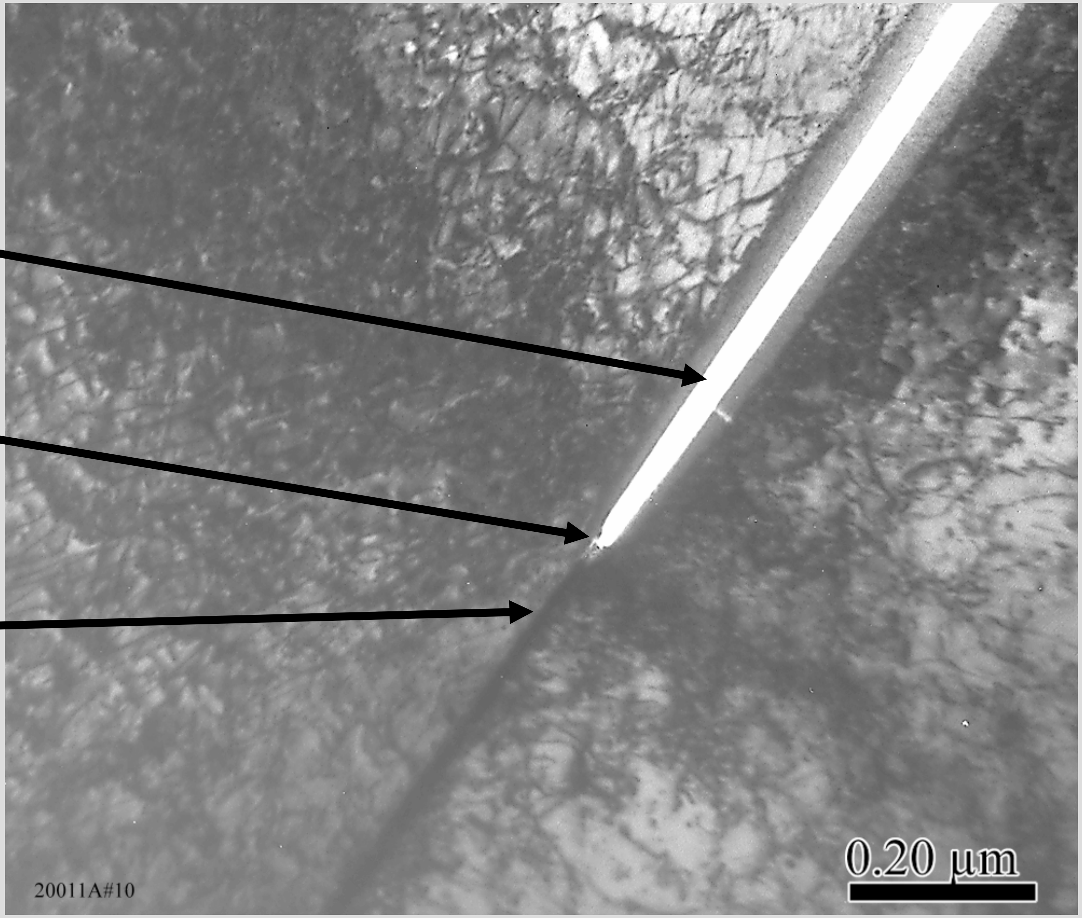
Task C: Film Formation in SCC Cracks and at Crack Tips for Insights into Crack-Growth Mechanisms

SCC Crack-Tip Modeling

Transport to crack tip quantified

Oxide phase prediction

Alloy composition change calculated



Crack tips are influenced by kinetic and thermodynamic conditions that can be modeled and measured

Topic Area #3

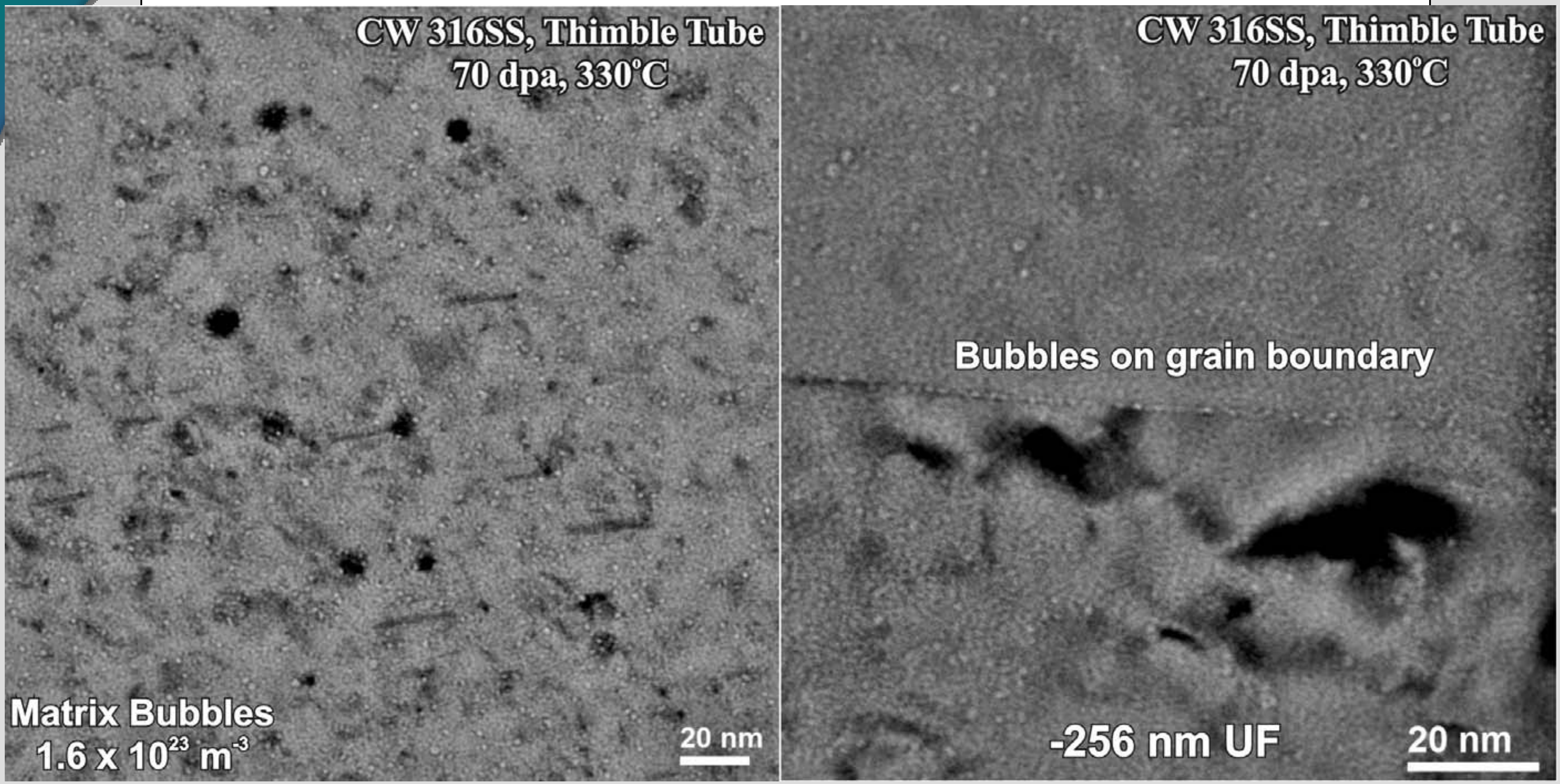
Mechanistic Understanding of Radiation-Induced Materials Changes and Cracking of LWR Core Internals

Task A: Detrimental Material Changes and Embrittlement in Highly Irradiated Stainless Steels

Task B: Surface and Near-Surface Aging in Stainless Steel Core Internals and Influence on Irradiation-Assisted Stress Corrosion Cracking

Task C: Isolating Matrix and Grain Boundary Deformation Mechanisms on IASCC

Cavities in BWR Flux Thimble Tube



- High density of He bubbles present at 33 and 70 dpa conditions
- Formation of grain boundary bubbles may promote IG cracking
- Additional characterizations needed at intermediate to high doses

Topic Area #4

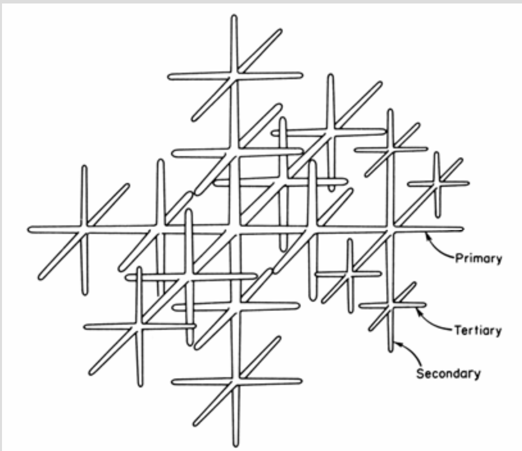
Metallurgy, Hot Cracking and SCC in Ni-Base Alloy Weldments

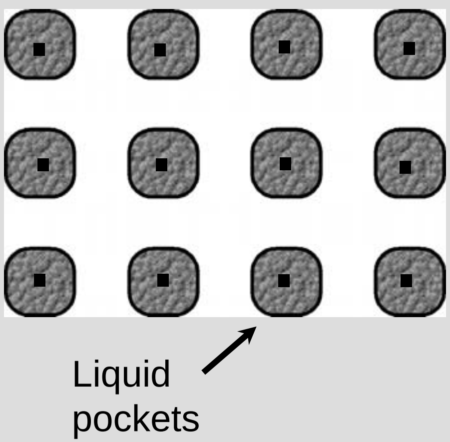
Task A: Improved Understanding of Microstructural-Microchemical Evolution and Hot Cracking in Nickel-Base Alloys Weld Metals

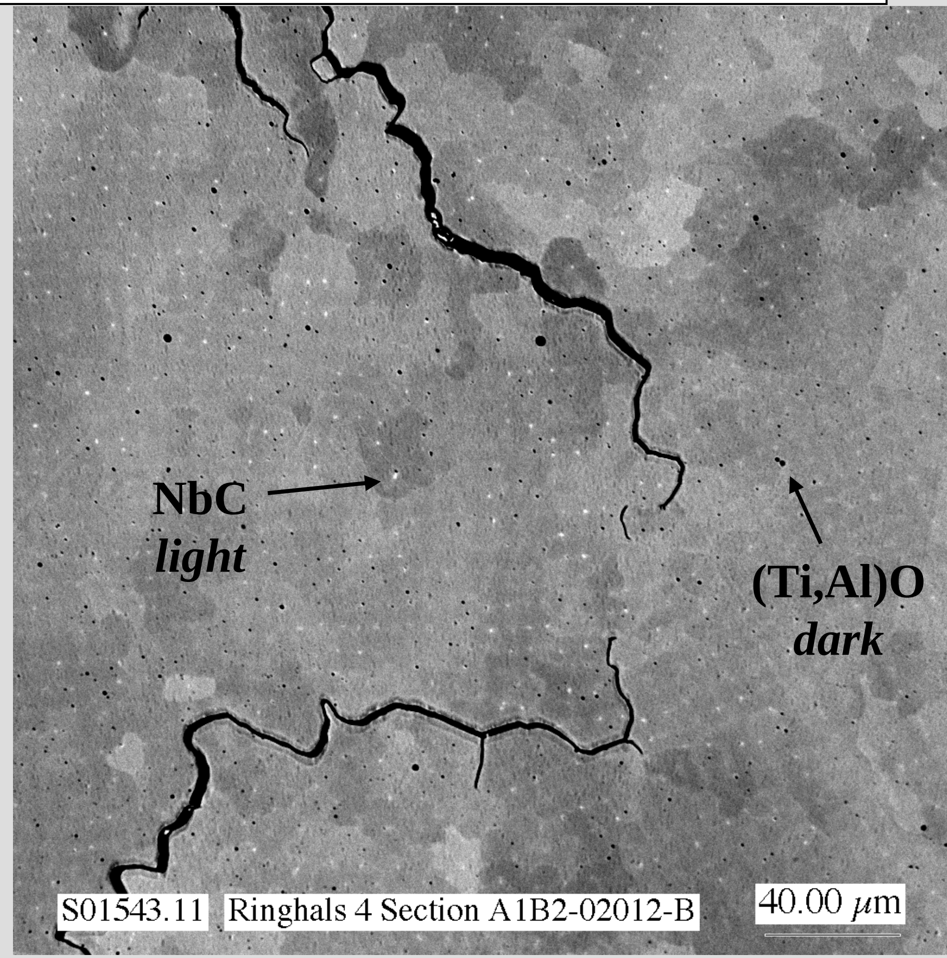
Task B: Influence of Weld Metal Microstructure-Microchemistry and Pre-Existing Hot Cracks on Stress-Corrosion Cracking of Nickel-Base Alloys

Task C: Assessment of Stain and Stress States in Weld Metal and Heat-Affected-Zone Regions of LWR Weldments

Dendrite Solidification and Coring







Dendrite arms in three dimensions grow towards each other and trap "enriched" liquid (e.g., Mn, Nb) in the interstices along with melt oxides; regular "matrix" of particles identified.

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Numerical simulations of environment

S. Van Dyck, S. Gavrilov

SCK•CEN

Third Planning Meeting for the International Cooperative Group and Research Program for Proactive Materials Degradation Management

May 11 – 13, 2006, Charleston, South Carolina, USA

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SCK•CEN reactor materials research for plant life management

- Pressure vessel steels:
  - "Classic" surveillance programs for monitoring embrittlement of RPVs.
  - Enhanced surveillance – Master Curve approach for fracture toughness prediction.
  - Multi-scale modelling – experimental validation for prediction beyond surveillance data.
- Reactor internals:
  - Irradiation induced mechanical property changes: Embrittlement of stainless steel for internals and RPV cladding.
  - Irradiation Assisted stress corrosion cracking.
  - Microstructure characterisation & swelling.
- Nickel base alloys:
  - Stress corrosion cracking in primary & secondary environment.

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Tools

- Hot & cold laboratories
  - Mechanical testing
  - Corrosion test loops
  - Microstructure investigation
- Irradiation facilities
  - BR2 Materials Test Reactor, BR1 reactor, gamma irradiation facility
- Material simulation tools
  - Multiscale modelling of (mechanical) material behaviour
  - Electrochemical simulations

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Electrochemical simulation for SCC studies

- Scope & objectives
  - Research tool for unravelling complex interactions in (stress) corrosion problems in reactor environment.
  - Predictive tool for stress corrosion crack propagation in reactor materials.
  - Evaluation tool for mitigating actions
- Approach
  - FEM based Numerical simulation tool to describe (electro)chemical interaction between material and environment.
  - Coupling between electrochemistry and mechanics for SCC simulation.
  - Detailed description of interactions in complex geometry.
  - Experimental input of electrochemical kinetics and mechanical material behaviour

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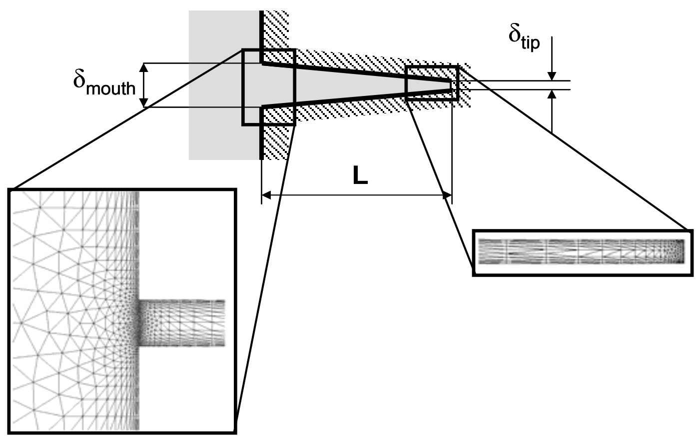
Principles of electrochemical simulations

Input

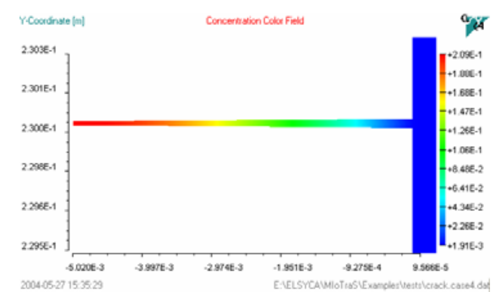
- Geometry
- Solution chemical composition at the inlet
- Chemical reaction kinetics
- Electrochemical reaction kinetics

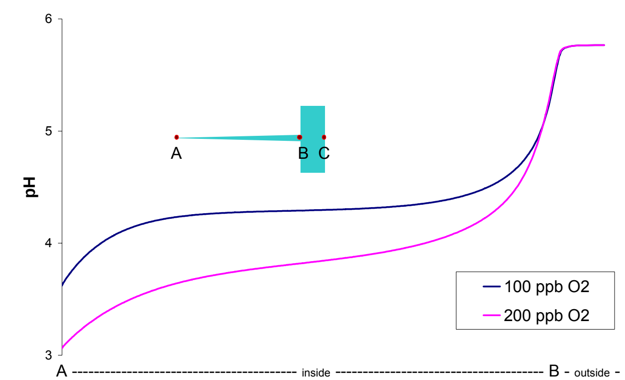
FE simulations



Results

- Concentration
- Potential
- Currents





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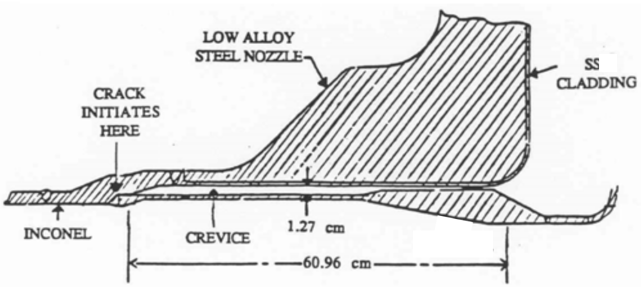
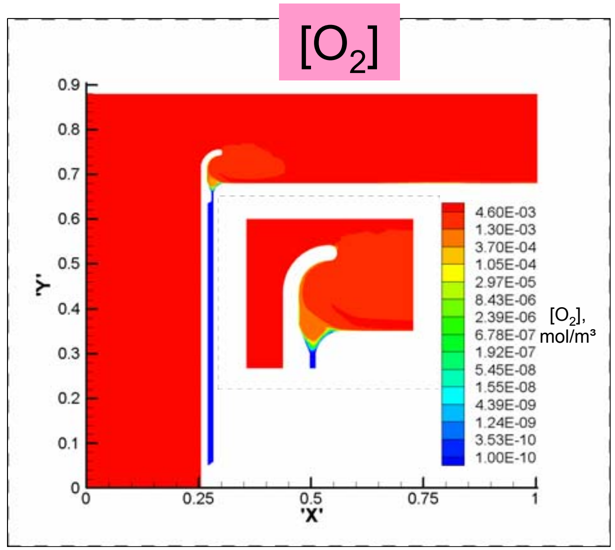
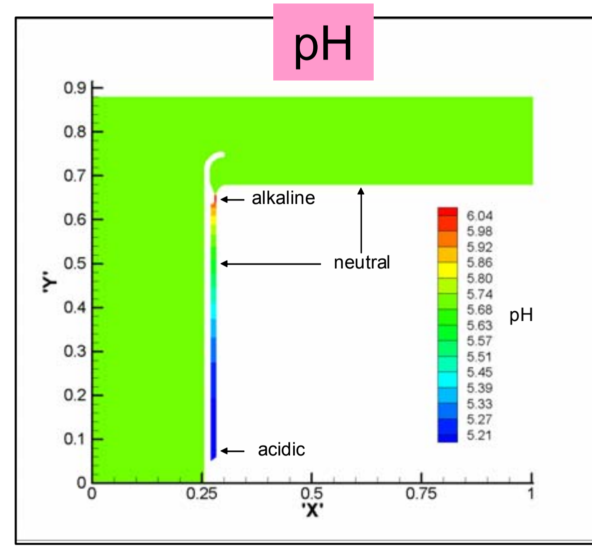
Case study: safe end

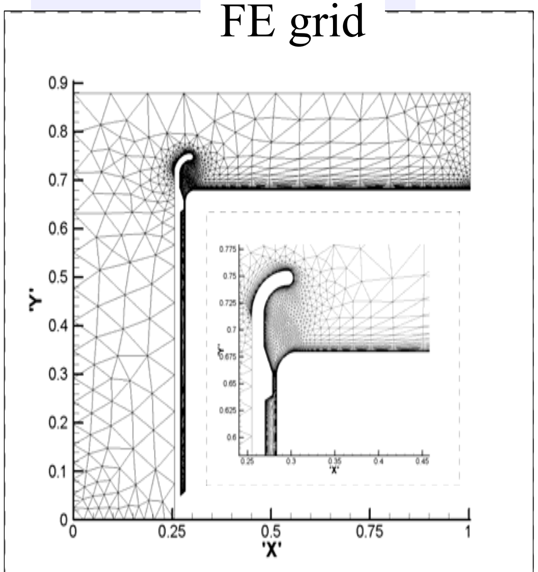
Axi-symmetrical cross-section



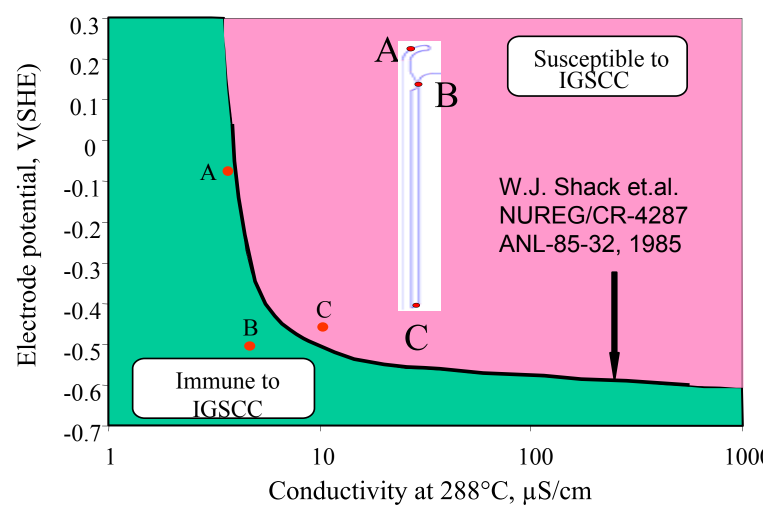




FE grid



288 °C
200 ppb O_2



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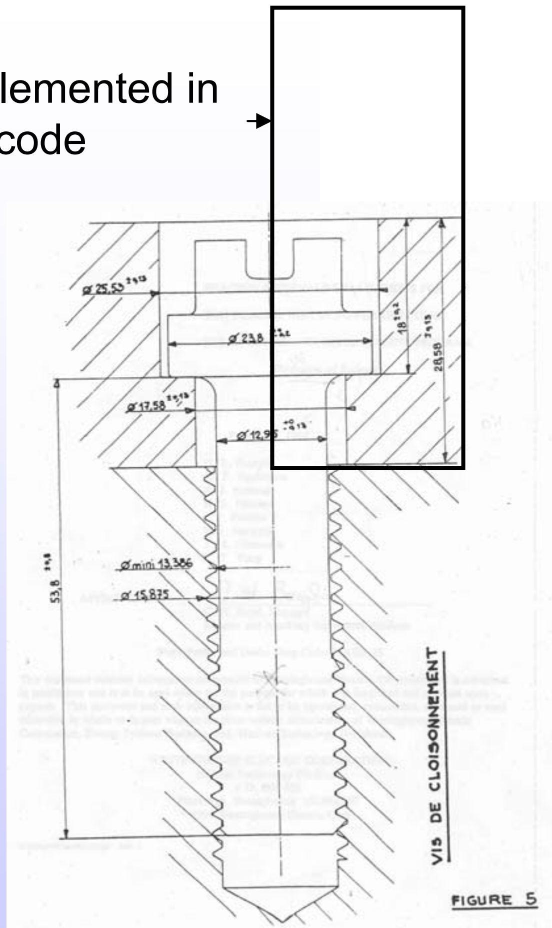
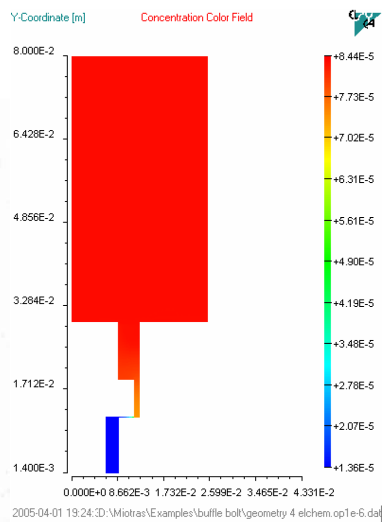
Case study: baffle bolt crevice

Implemented in FE code

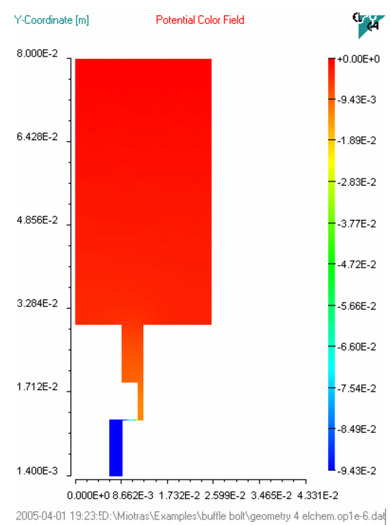




[H$^+$]↓

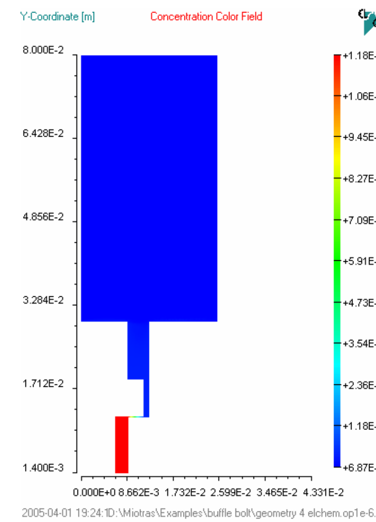
1000 ppm B
2 ppm Li
300 °C
Deaerated water

Assuming oxygen reaction for anodic current



Potential

E↑



[O_2]↑

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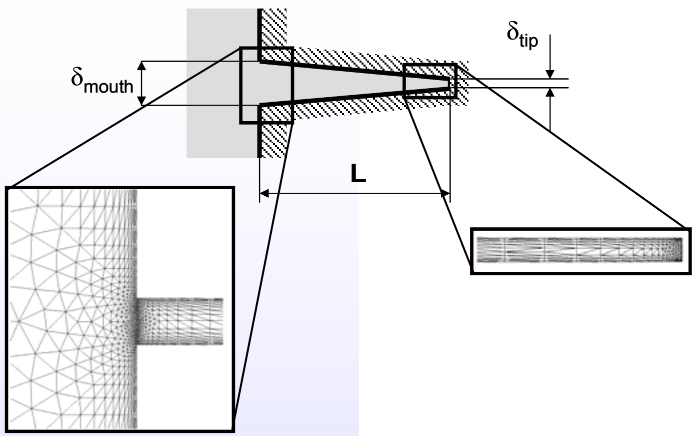
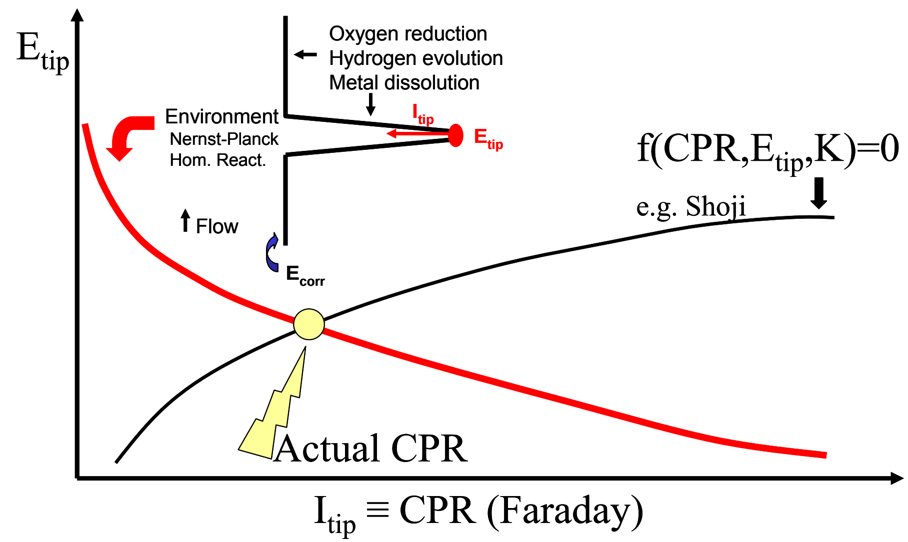
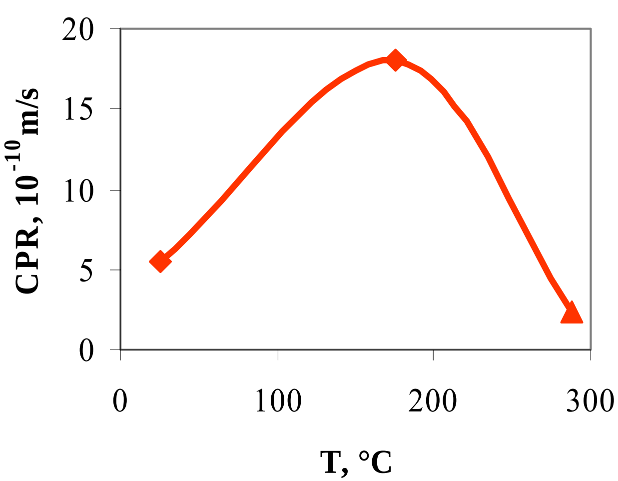
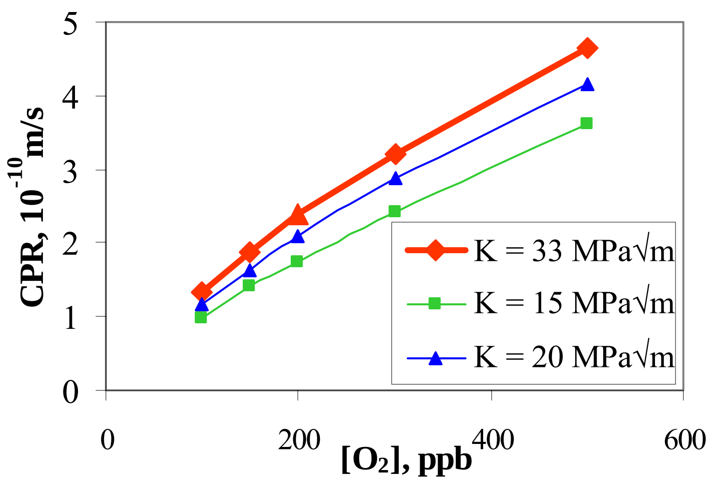
Case study: CGR simulations









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Possible contribution to PMDM program (Y1)

- 1 year evaluation (1p.y.) of application of electrochemical simulation in “pure” water or primary PWR water.
- Application of computational electrochemistry for assessment of local conditions in selected components:
  - Lithium hydroxide accumulation in crevices upon boric acid transients.
  - Assessment of electrochemical/chemical conditions in occluded regions with limited refreshment.
- Tasks include:
  - Construction of FEM model of selected component – lab set-up.
  - Experimental determination of appropriate electrode kinetics.
  - Calculation of (electro)chemistry as function of bulk chemistry applied.
  - Verification against experimental data from PMDM partners.

Predicting Failures Which Have Not Yet Been Observed in LWR Applications--

The Microprocess Sequence Approach (MPSA) Modified for PDMA

Roger W. Staehle
Consultant,
North Oaks, Minnesota

Presented PDMA
Tokyo, Japan
05-11-08

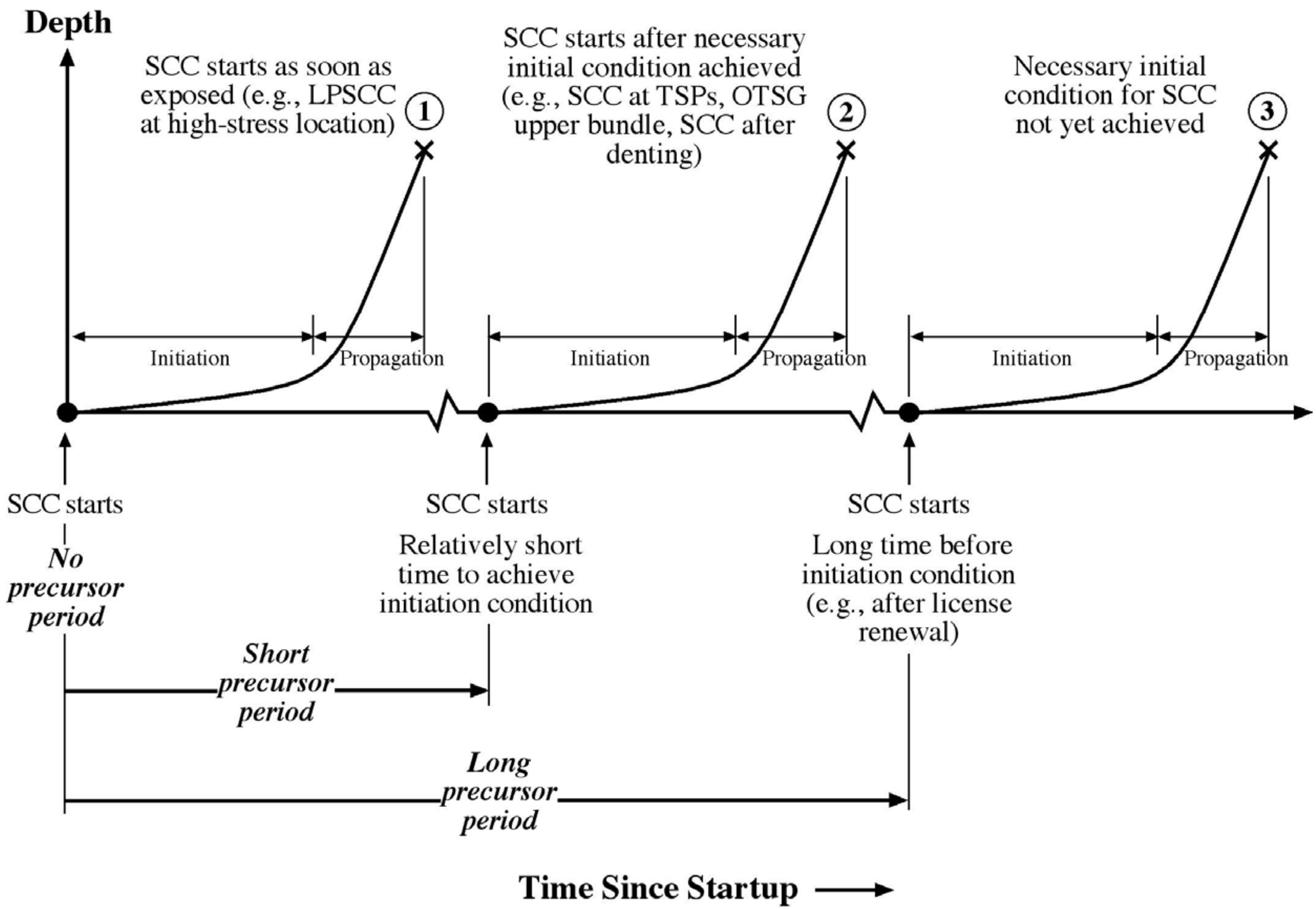
All materials are chemicals--
the surprise is
not that they fail.

The surprise is
that they work!

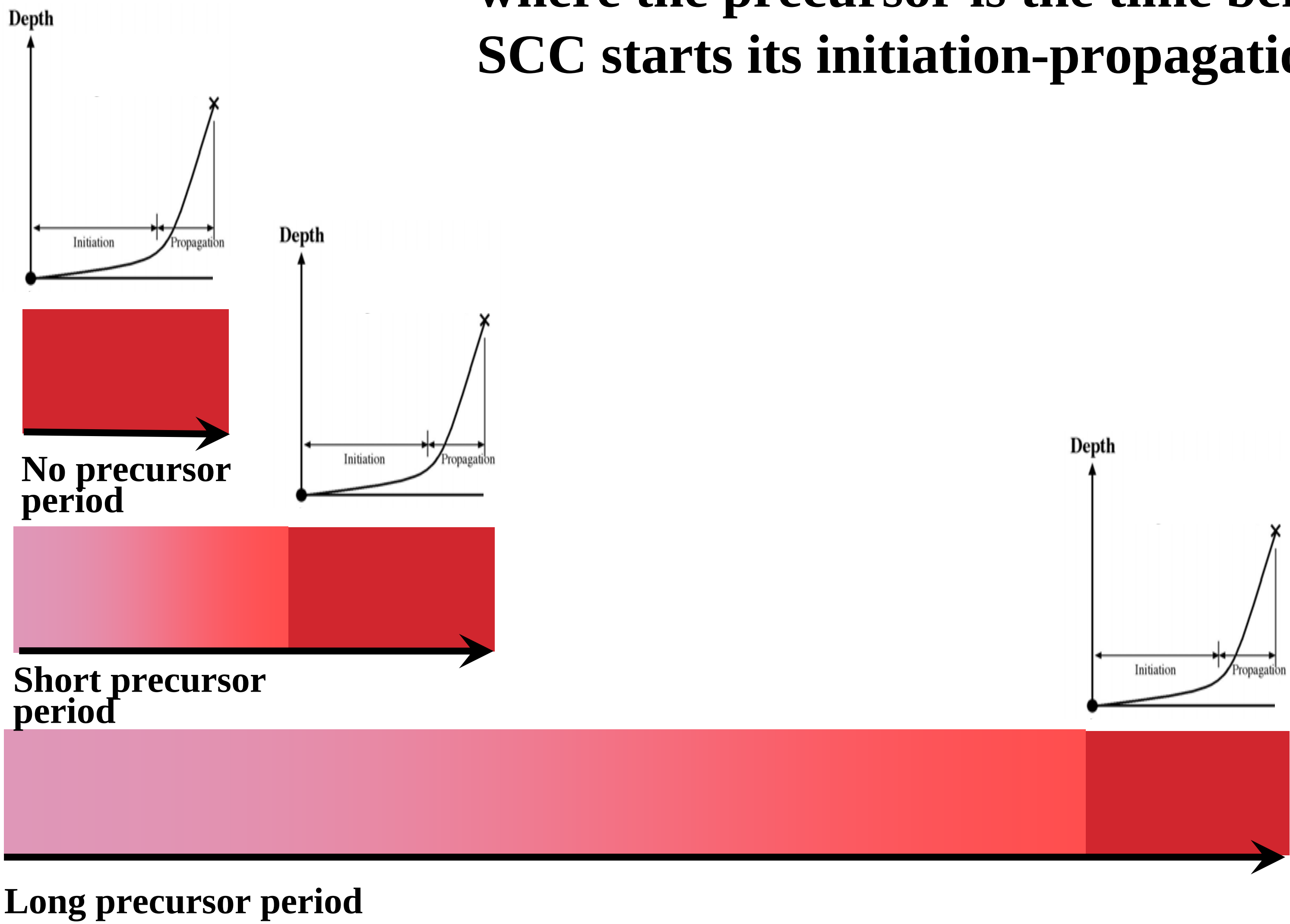
Eternal vigilance
is not only the
price of liberty--
it is the price of
reliability

Introduction to MPSA

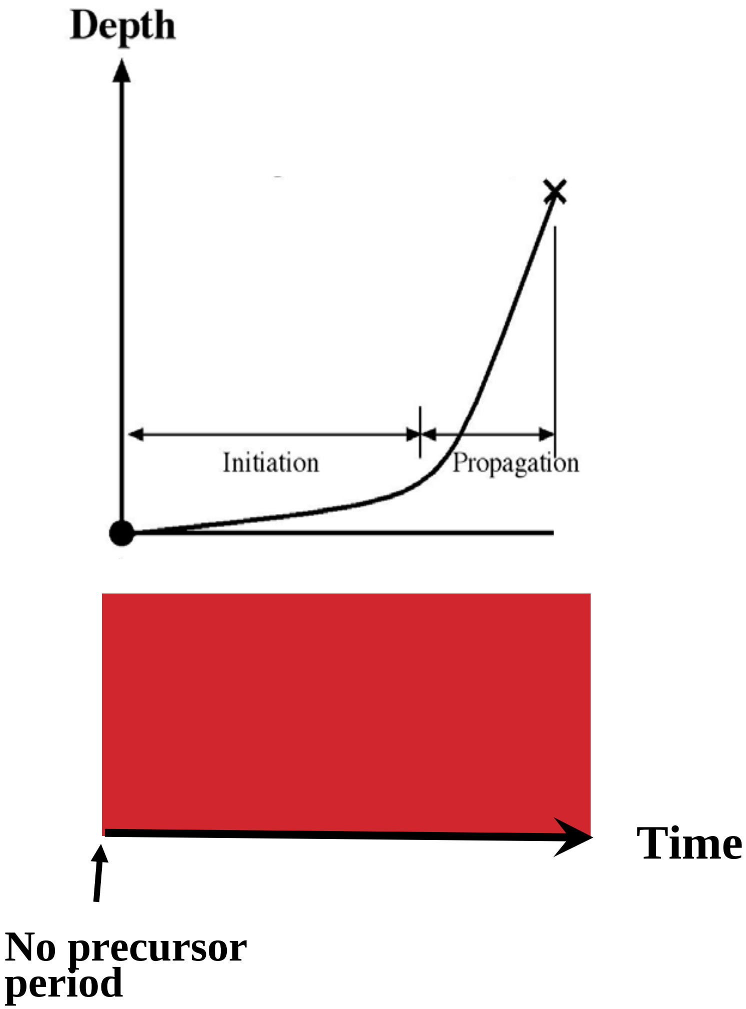
Three cases for prediction of SCC



Predicting corrosion (e.g. SCC failure) at long times is progressively more a problem of predicting the "precursor" where the precursor is the time before SCC starts its initiation-propagation process



No precursor period



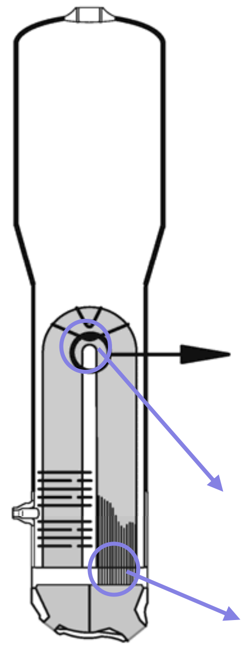
Examples

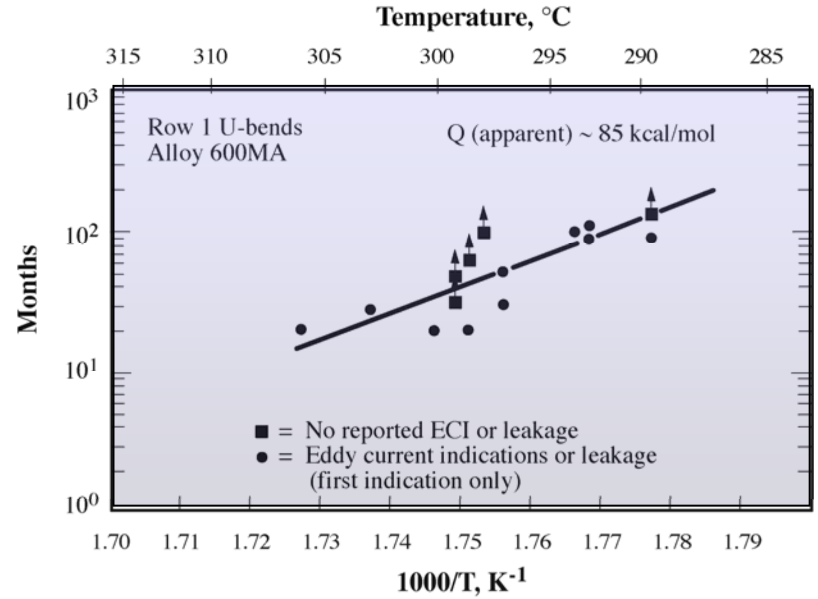
- IDSCC in SG tubing (LPSCC)
- ODSCC at scratches in cold leg of SG tubing
- FAC, e.g. Mihama 3, secondary system
- BWR sensitized piping and non-sensitized core structurals

No precursor

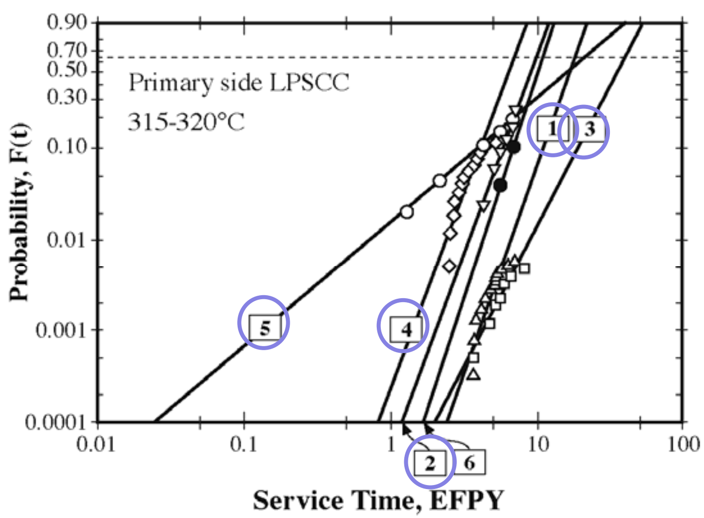
LPSCC on primary side of SG tubes

(a)





(b)



1. French plants, LTMA tubing
θ = 18.7 EFPY
β = 4.48
r^2 = 0.82

2. Part depth roll
θ = 10.0 EFPY
β = 4.29
r^2 = 0.95

3. U.S.-made row 2 U-bends, French plants
θ = 41.1 EFPY
β = 3.07
r^2 = 0.95

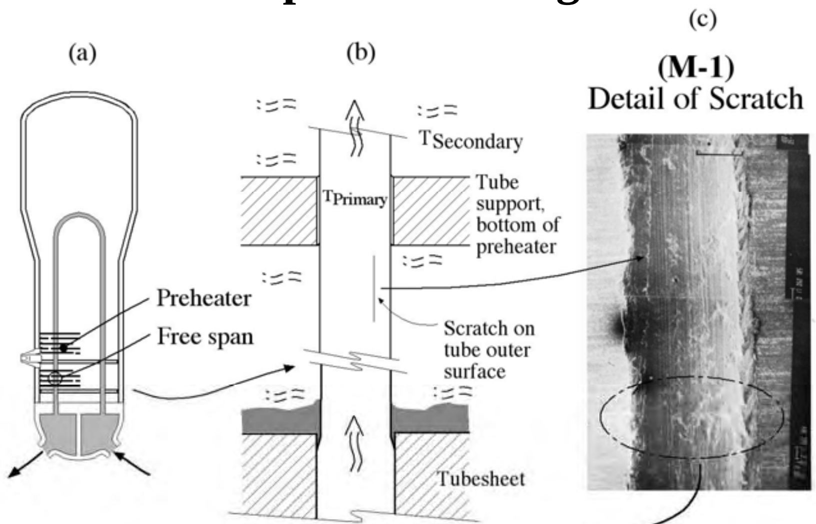
4. U.S.-made row 1 U-bends, French plants
θ = 7.13 EFPY
β = 4.29
r^2 = 0.77

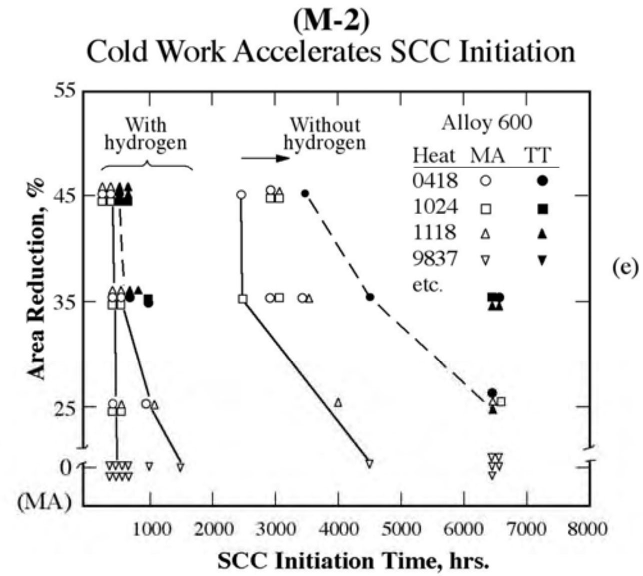
5. Roll transitions for kiss rolls
θ = 22.23 EFPY
β = 1.36
r^2 = 0.98

6. Primary side denting
θ = 10.95 EFPY
β = 4.93
r^2 = 1.0

No precursor

SCC on secondary side at scratches in free span of cold leg

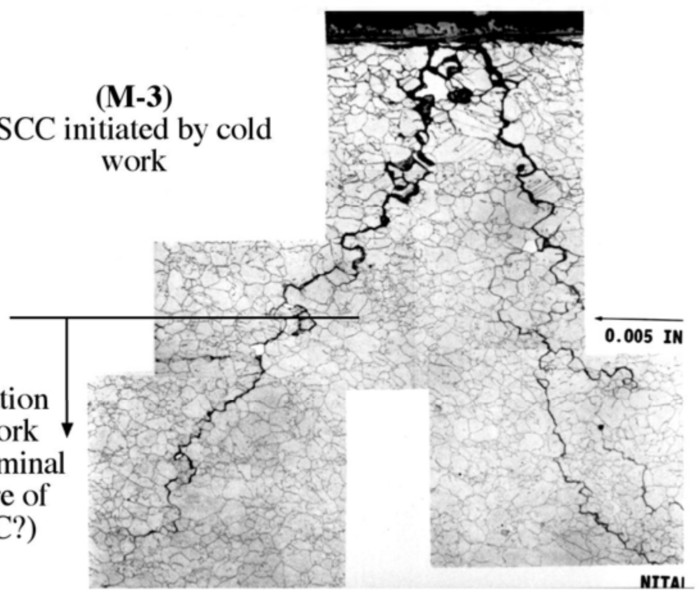


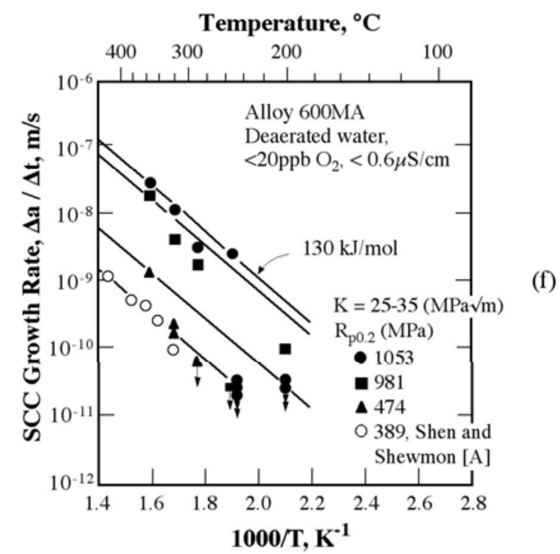


(M-3)
SCC initiated by cold work

(d)

(M-4)
SCC propagation from cold work initiation in nominal microstructure of tube (LPSCC?)





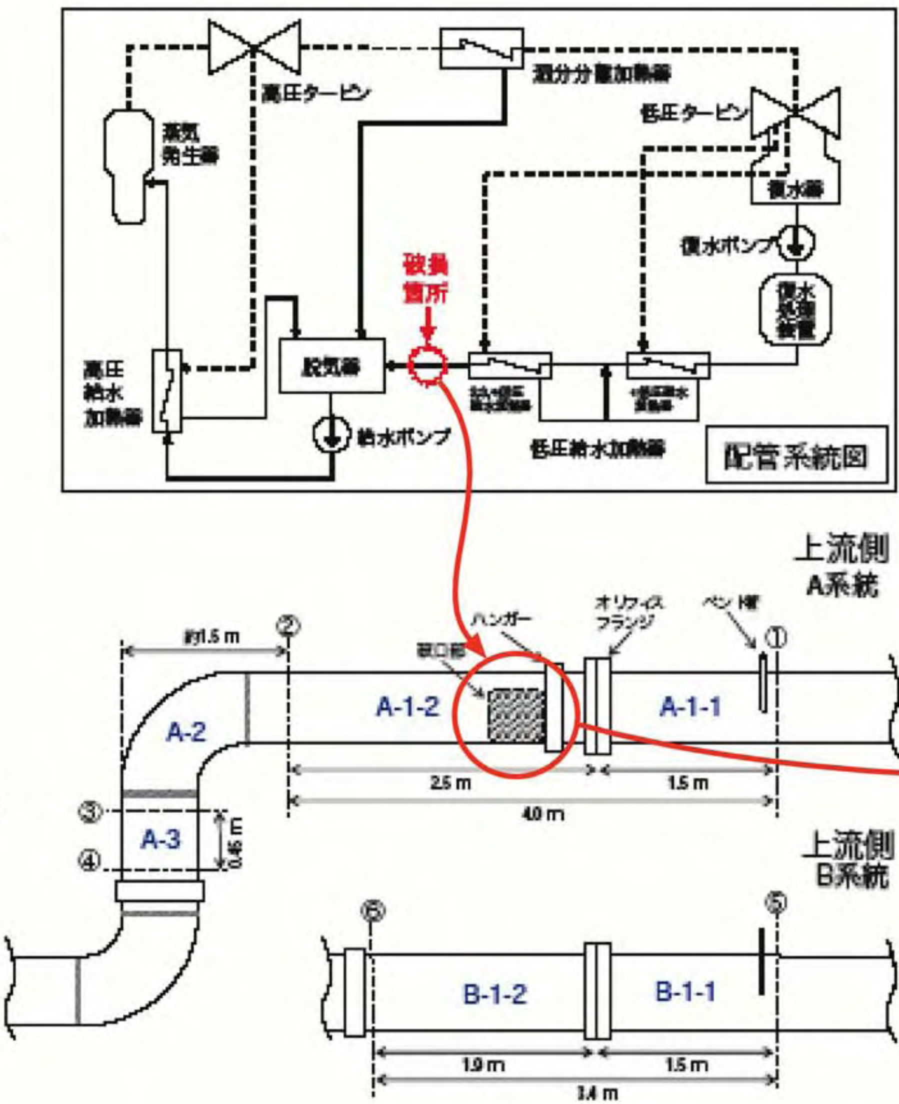
No precursor

FAC on secondary side

- 560mm diam, 10mm wall
- 22 m/s, 0.93MPa, 142°C, 8.6-9.3pH
- 185,700hr operation

(a)

(b)

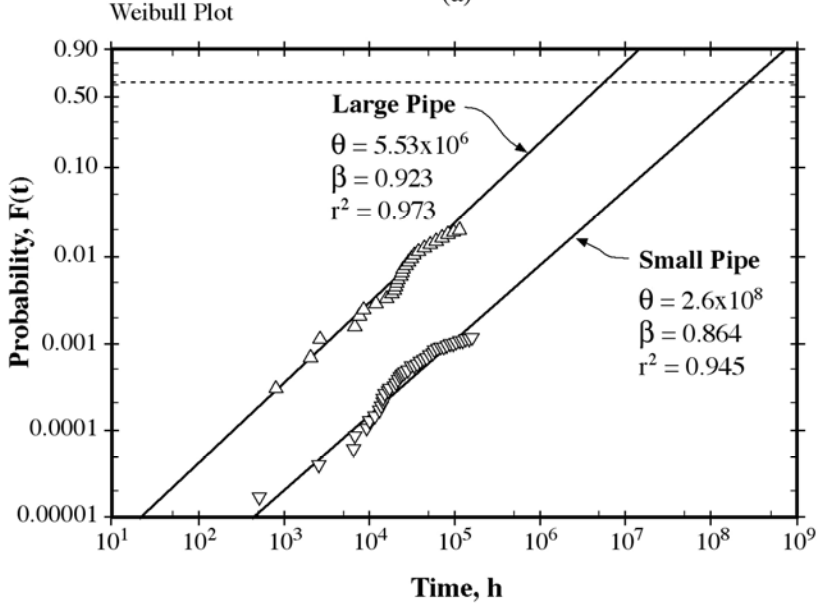


(c)

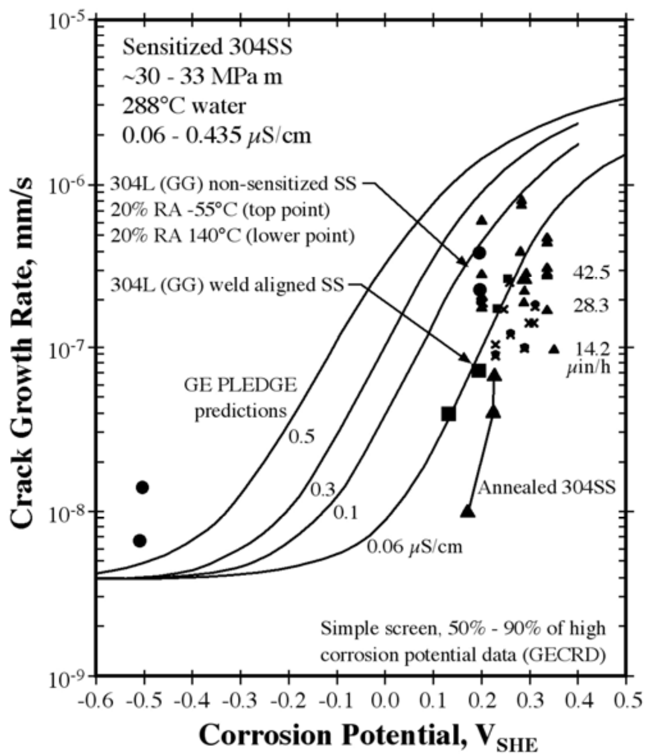
No precursor

SCC of stainless steel in BWR normal water chemistry, sensitized and non sensitized

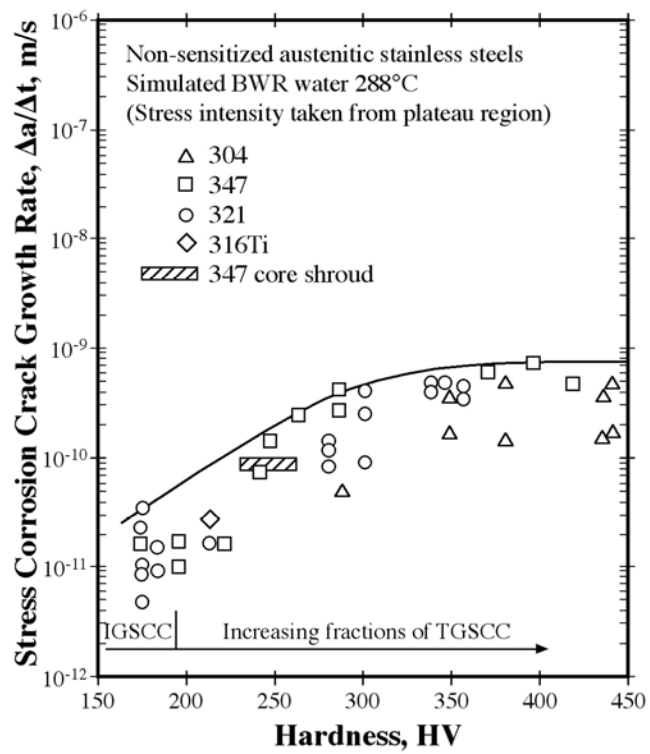
(a)



(b)



(c)



Short precursor period

Examples

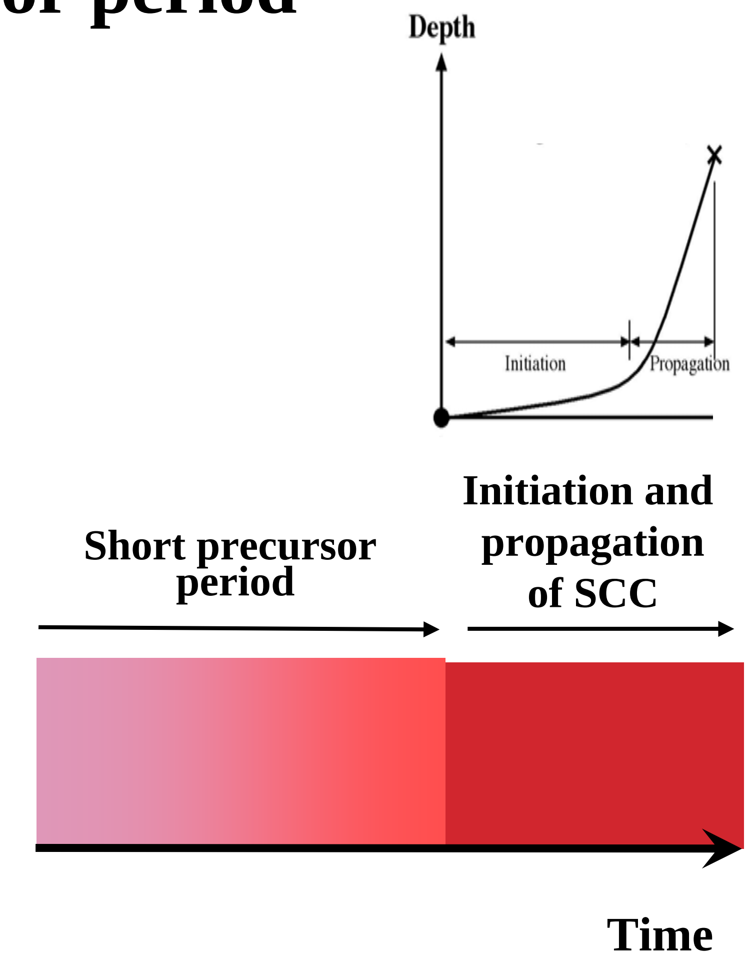
- Accumulation of aggressive chemicals on heat transfer surfaces

- “Denting” resulting from the expansion of growing corrosion products in tube supports and TTS

- Accumulation of chemicals on superheated surfaces of upper bundle of OTSG

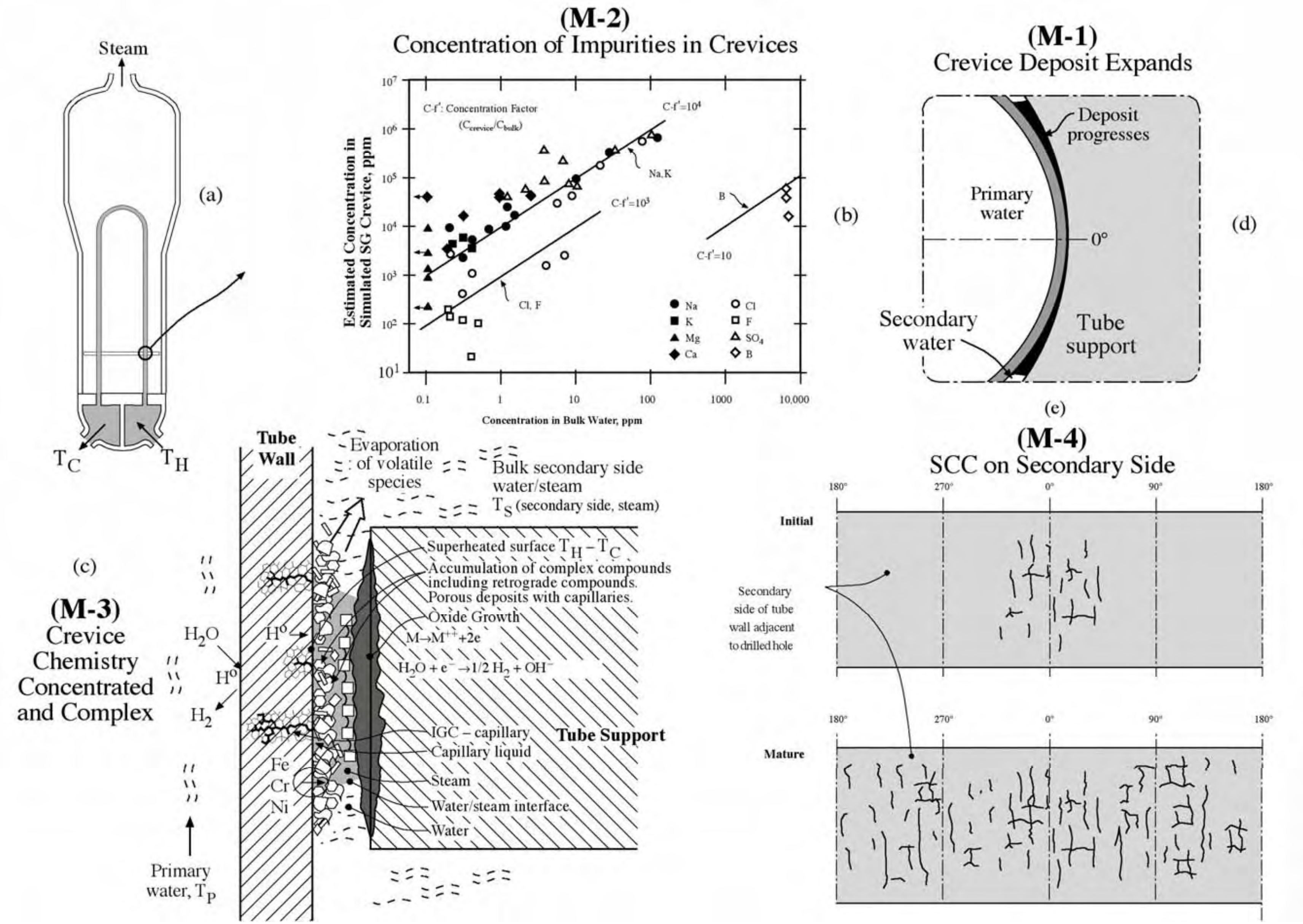
- Accumulation of deposits and corrosion products leading to increased thermal resistance and then to perforation of fuel cladding (not SCC but rapid perforation).

- Vessel head perforation at Davis Bessie



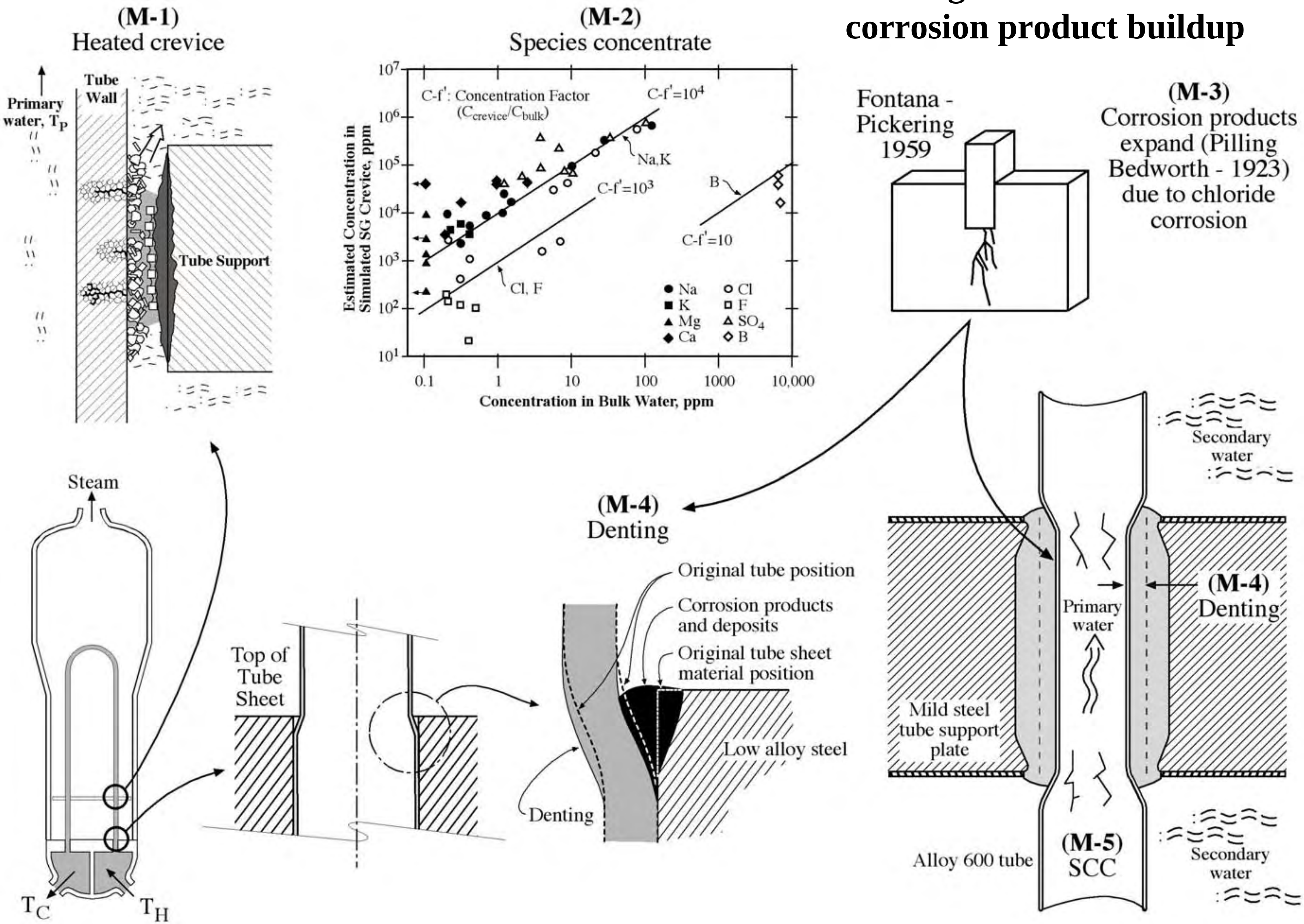
Short precursor period

Buildup of concentrated chemistry in heat transfer crevices



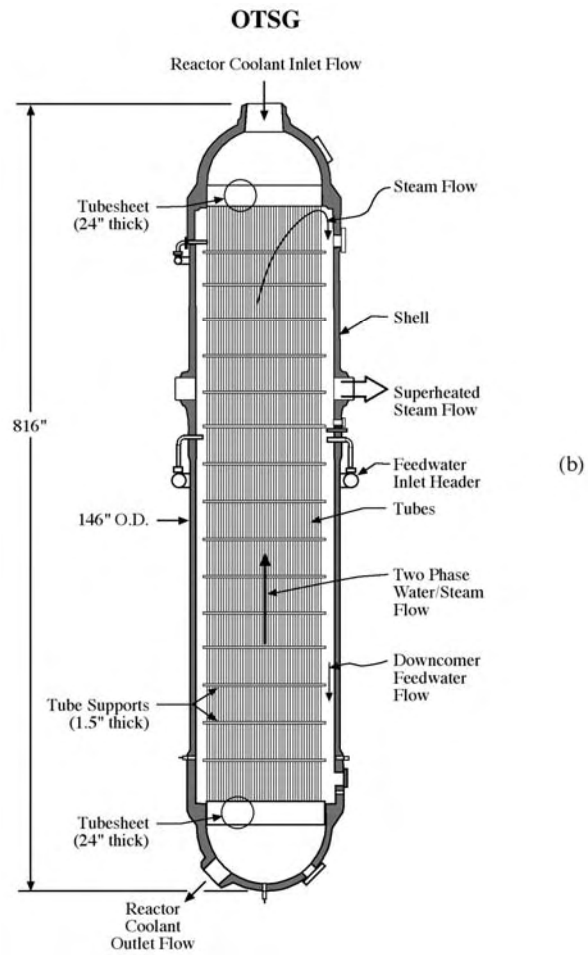
Short precursor period

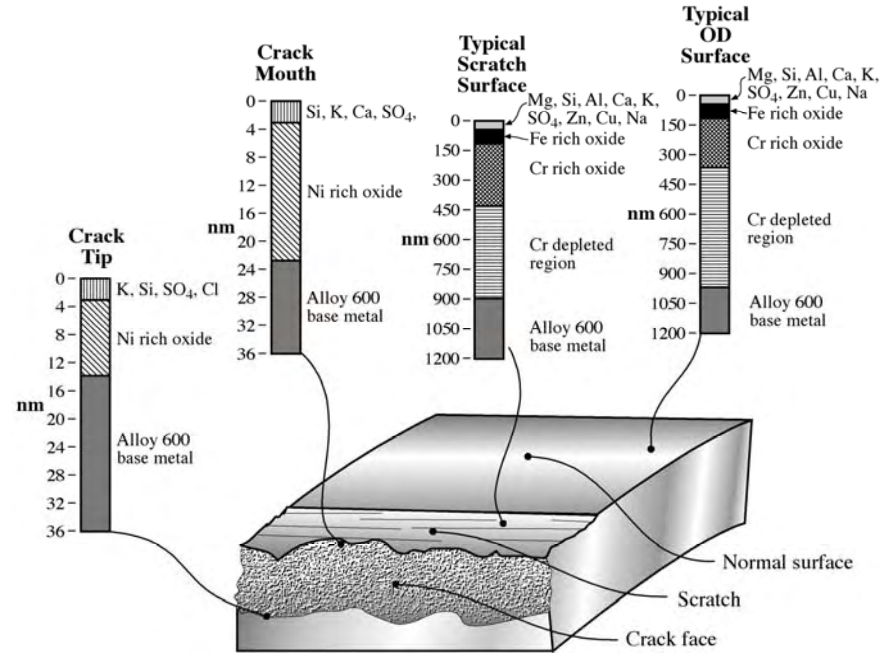
Denting due to stresses from corrosion product buildup

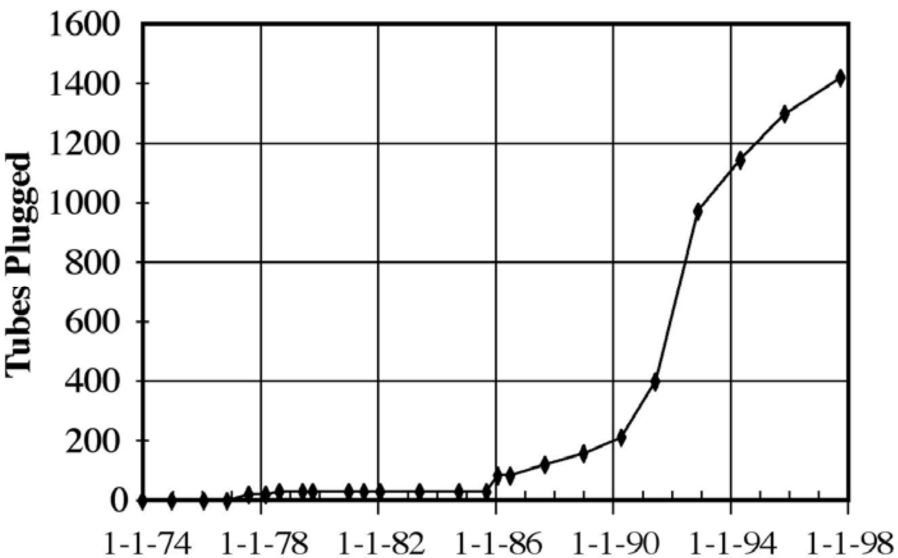


Short precursor period

Accumulation of chemicals in upper bundle of OTSG

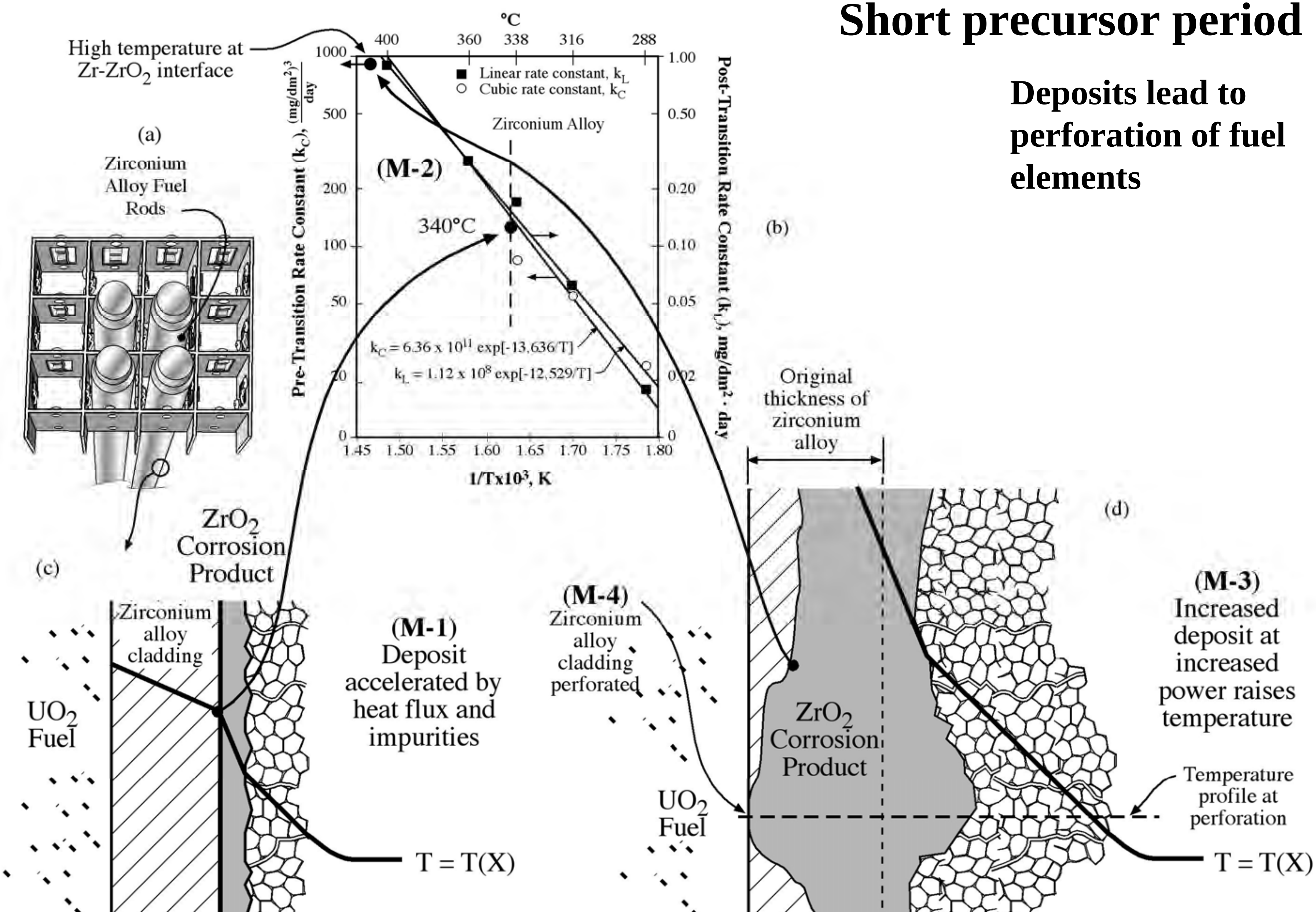






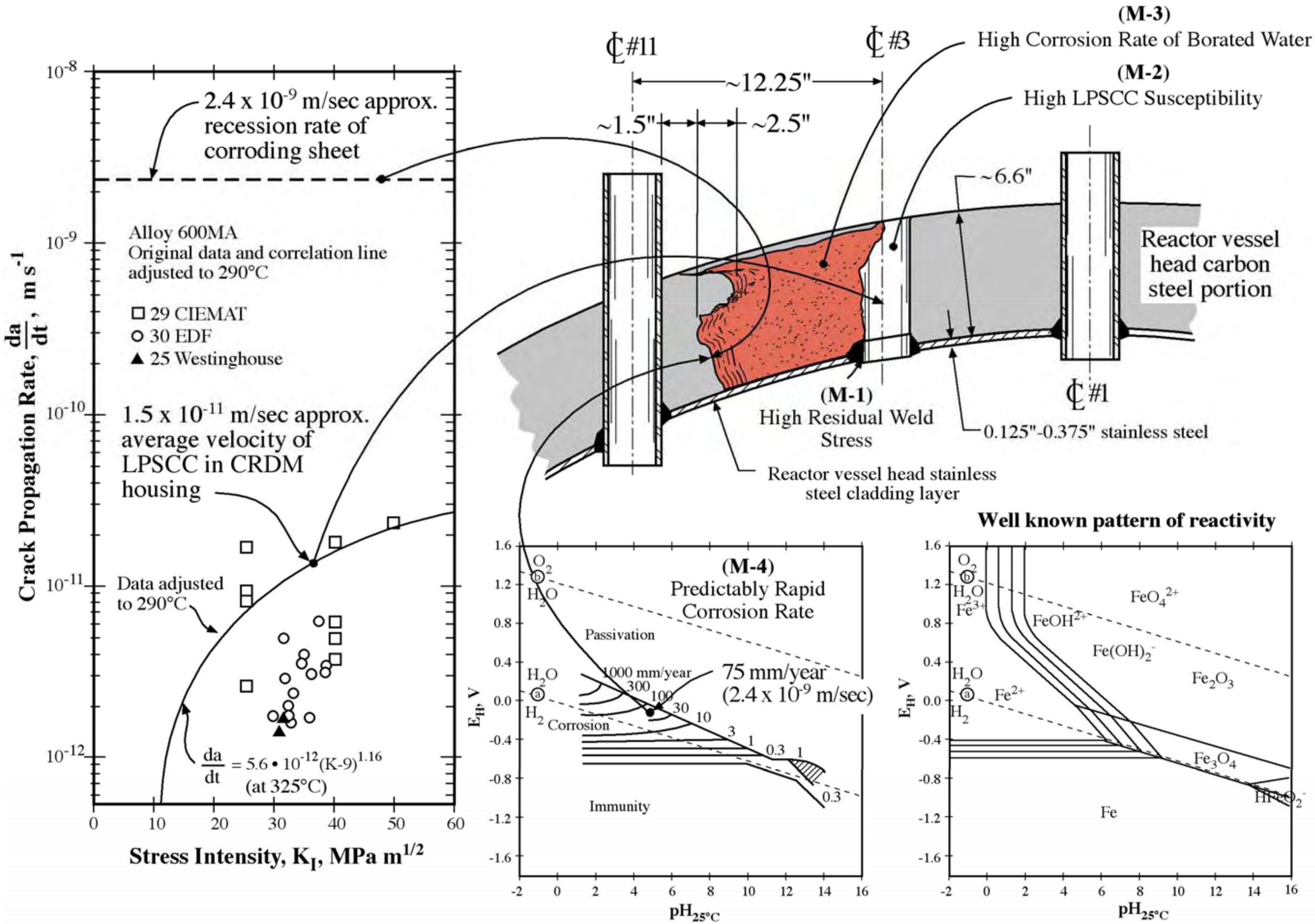
Short precursor period

Deposits lead to perforation of fuel elements

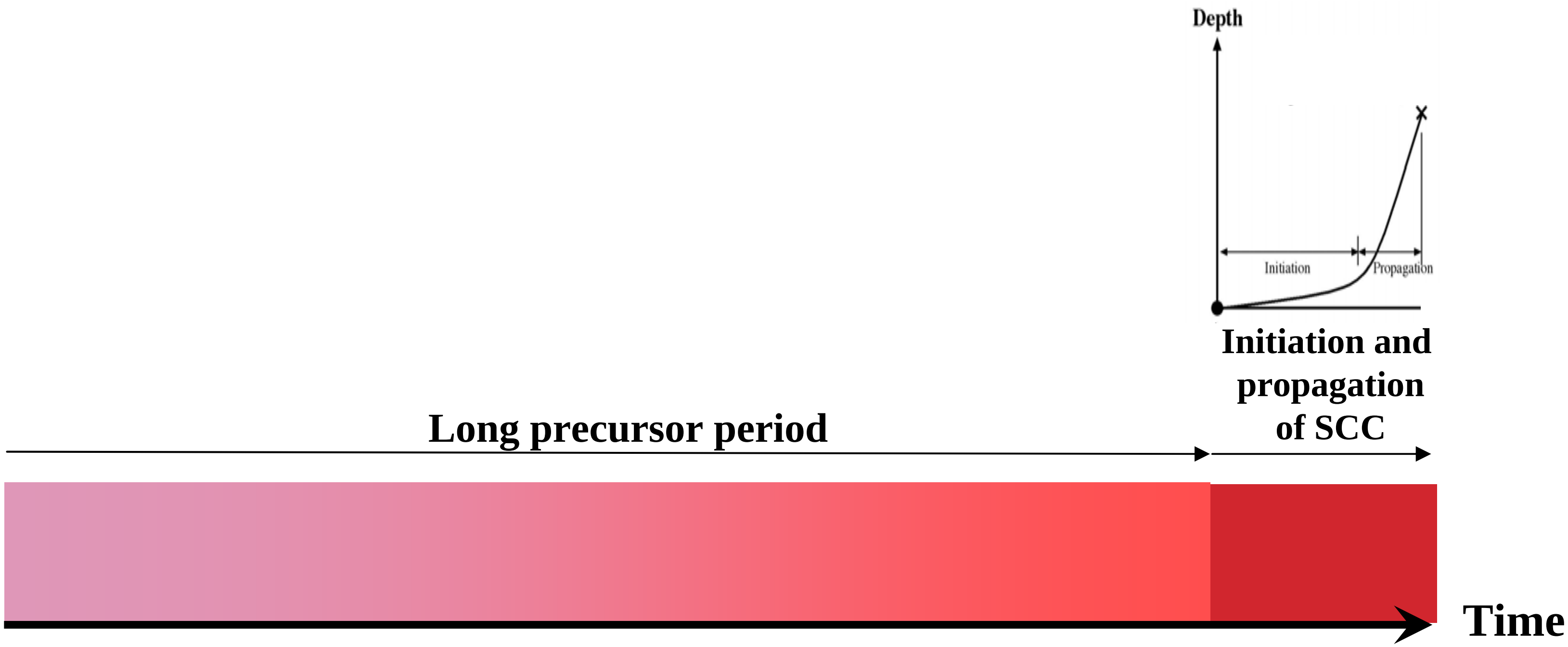


Short precursor period

SCC of Alloy 600 leads to release of steam and boric acid to corrode vessel head



Predicting failures associated with a long precursor period – Failures that have not occurred in the past

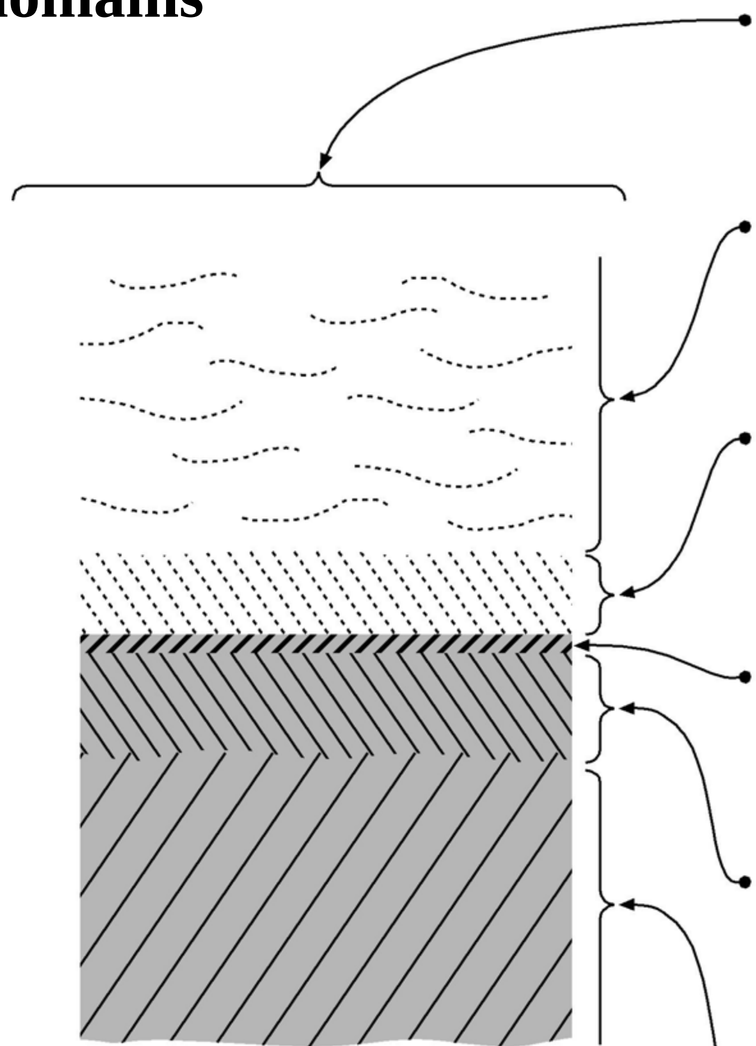


The approach →

- **Develop long precursor period on physical bases using the six domains from bulk environment to bulk metal**
- **Elaborate on domains with "microprocesses"**
- **Develop a scenario period based on a sequence of microprocesses within each domain**
- **Identify "targets" for the critical conditions of SCC to be approached by the scenarios.**

Approach to predicting long precursor periods

First step in MPSA: Identify "domains"



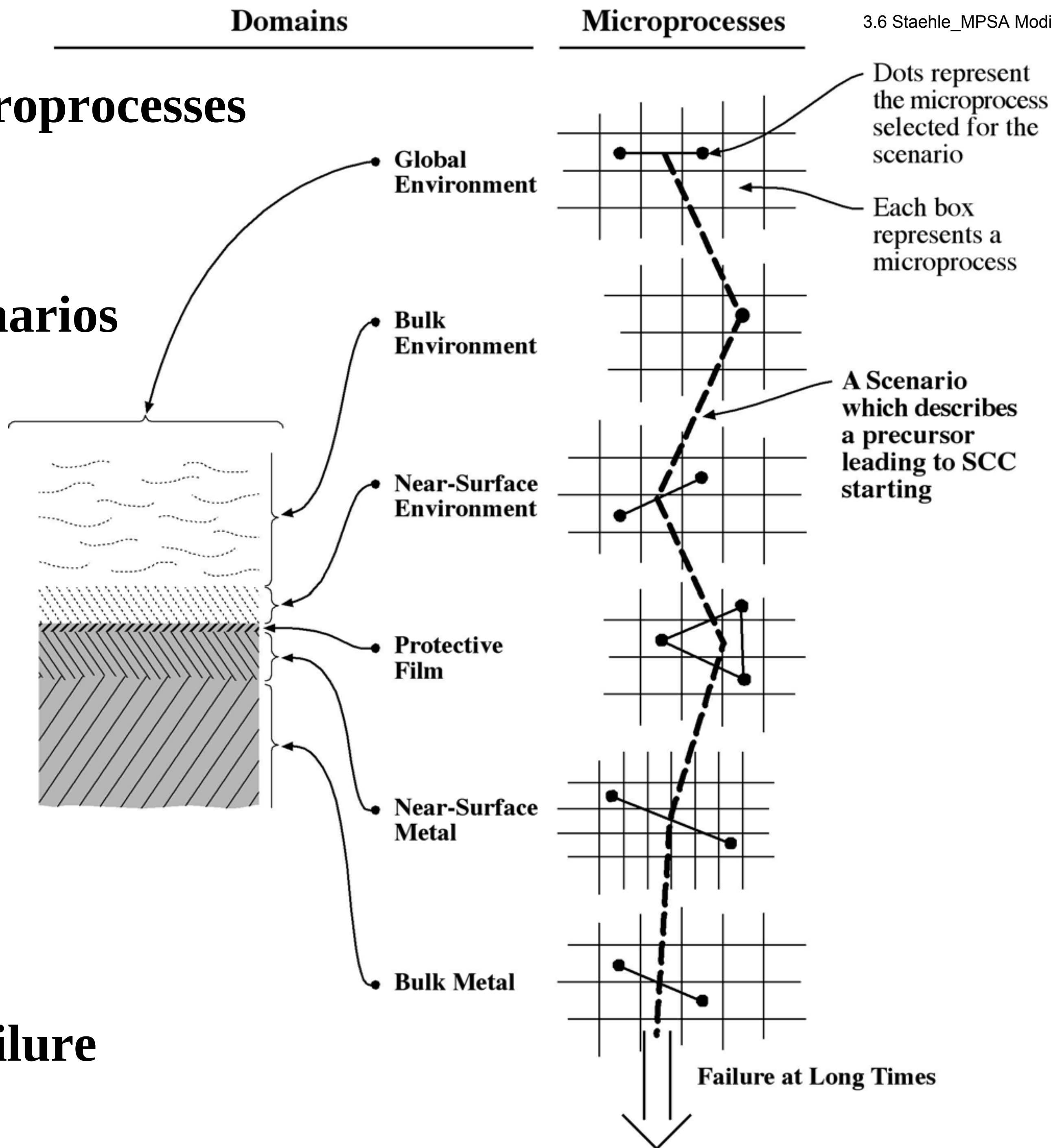
Domains
(Examples of microprocesses)

- **Global Environment**
  - ΔG
  - Temperature
  - Nuclear radiation
  - . . .
  - . . .
- **Bulk Environment**
  - H_2 concentration
  - N_2H_4 concentration
  - O_2 concentration
  - . . .
  - . . .
- **Near-Surface Environment**
  - Deposits
  - Electrochemical cells
  - Heat transfer
  - Concentration
  - . . .
  - . . .
- **Protective Film**
  - Thickness
  - Epitaxial
  - Surface slip interaction
  - . . .
  - . . .
- **Near-Surface Metal**
  - Depletion of alloy
  - Tunnel formation
  - Hydrogen entry
  - . . .
  - . . .
- **Bulk Metal**
  - Grain boundary composition
  - Grain boundary sliding
  - Grain matrix precipitation
  - . . .
  - . . .

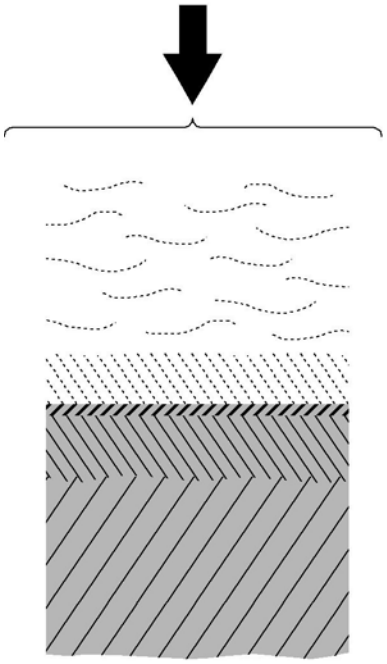
Second step:
Identify microprocesses

Third step:
Develop scenarios

Fourth step:
Predict failure



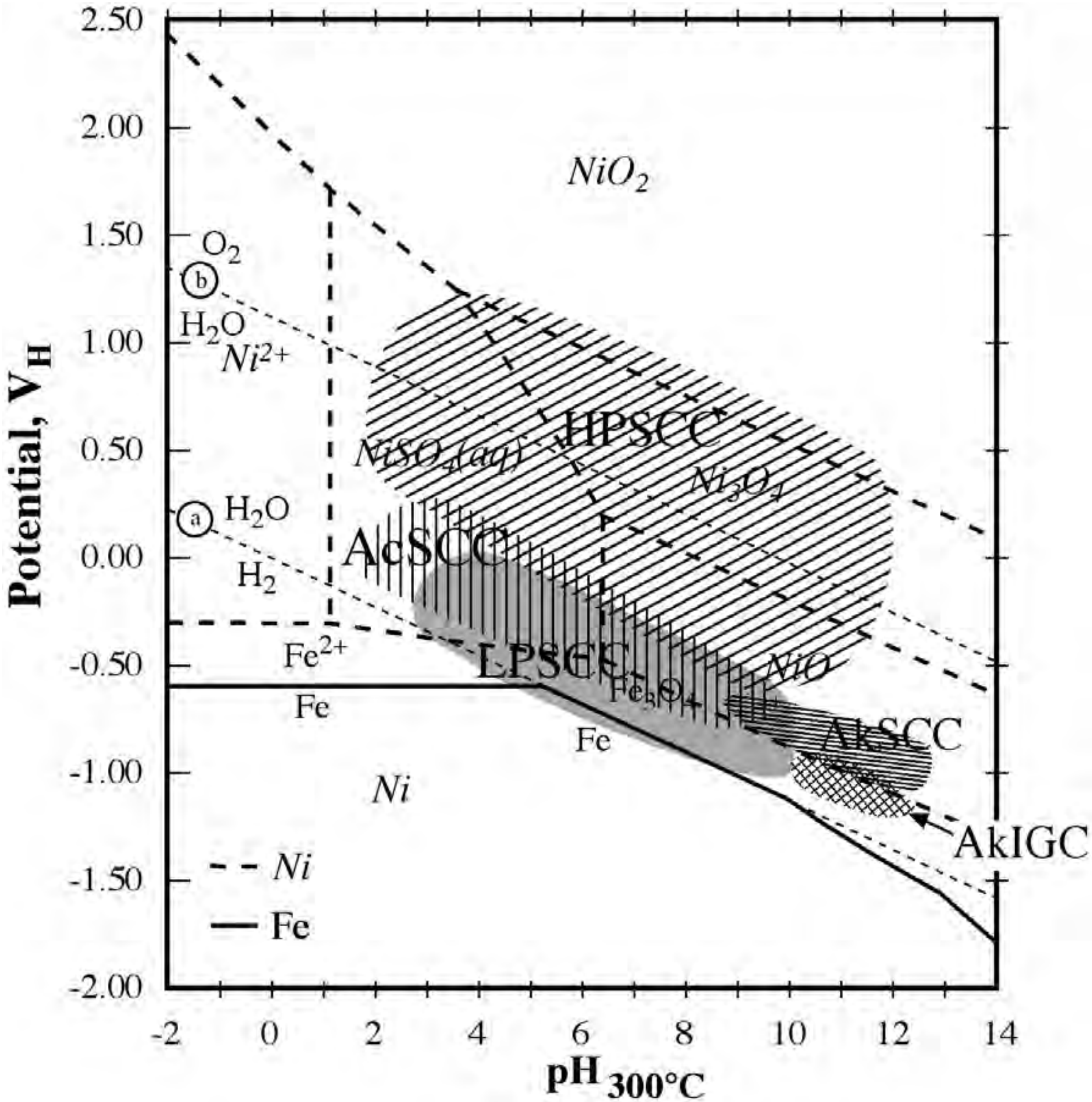
Examples of microprocesses and effects in global domain



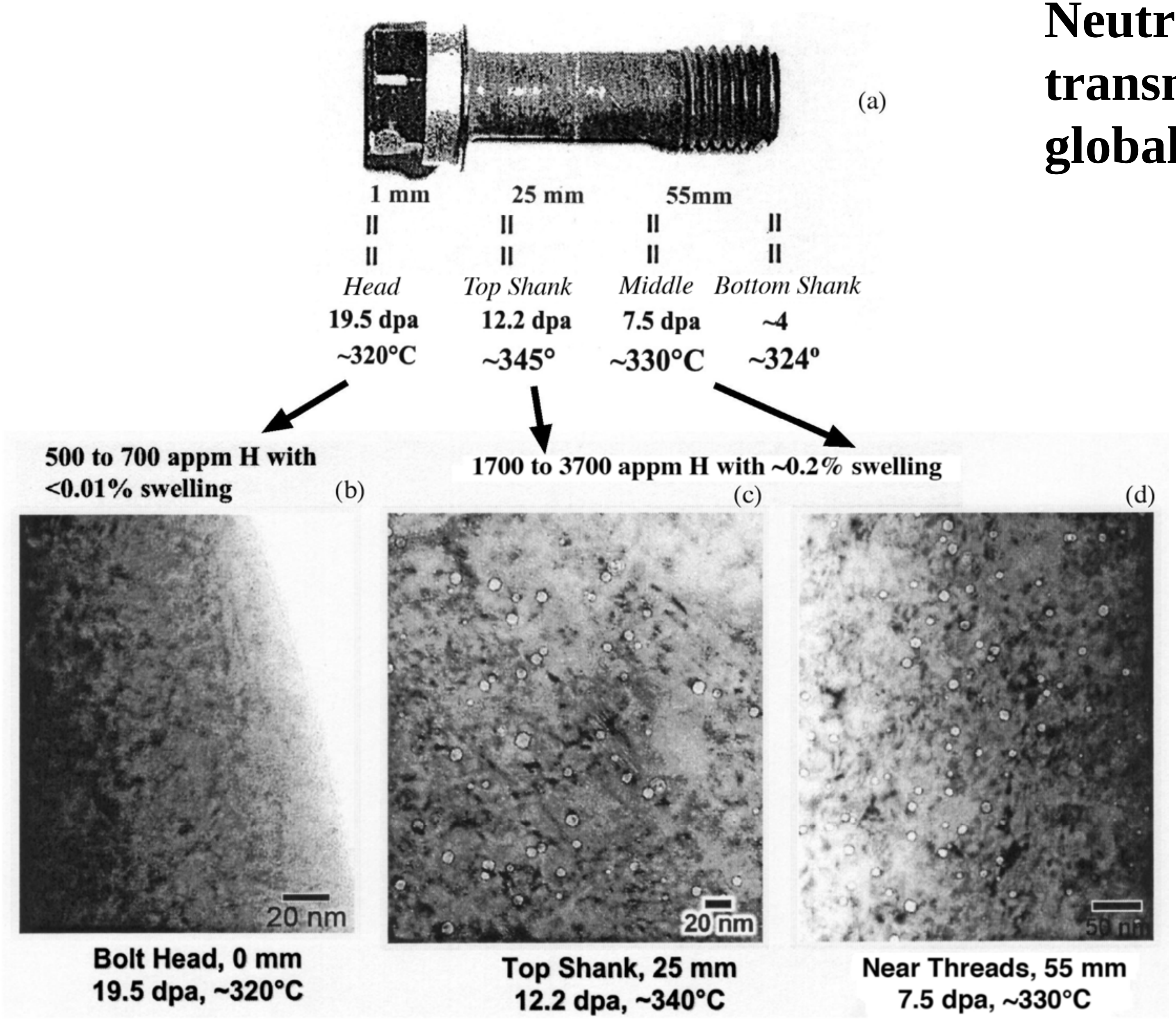
Global Domain

Microprocesses (Time Related)	Effects
1. Component in system	• Produce products that damage other components • Products from other components damage subject components
2. ΔG - Overall free energy change: environmental chemistry (pH, H_2O, O_2, H_2, N_2H_4) to material (Fe, Ni, Cr, Cu, Ti, . . .)	• Driving force for chemical reactions • Boundaries for SCC modes
3. Ambient temperature	• Reaction rates • Thermal stresses
4. Heat Flux	• Surface deposits • Surface temperatures
5. Cyclic stresses (Cyclic Frequency)	• Fatigue, corrosion fatigue
6. Crevices	• Accumulation of chemicals • Stress intensity
7. Irradiation	• Local differences • Voids • Radiolysis

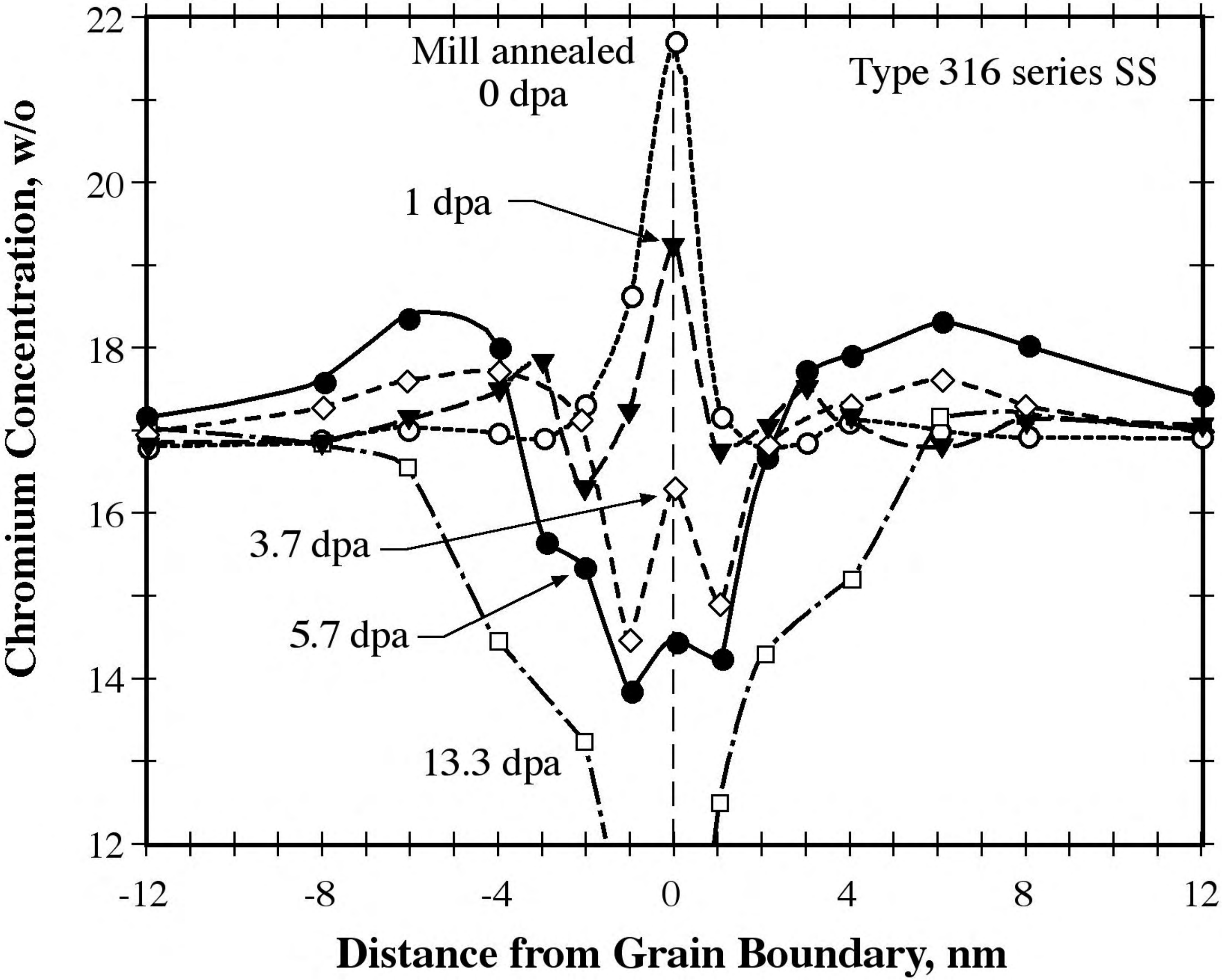
Thermodynamic driving force in global domain



Neutron flux and transmutation in global domain

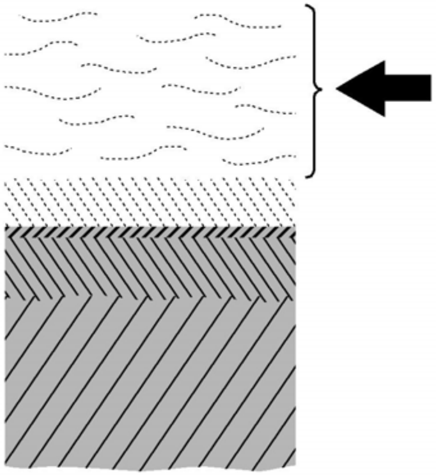


Neutron flux producing displacements in global domain



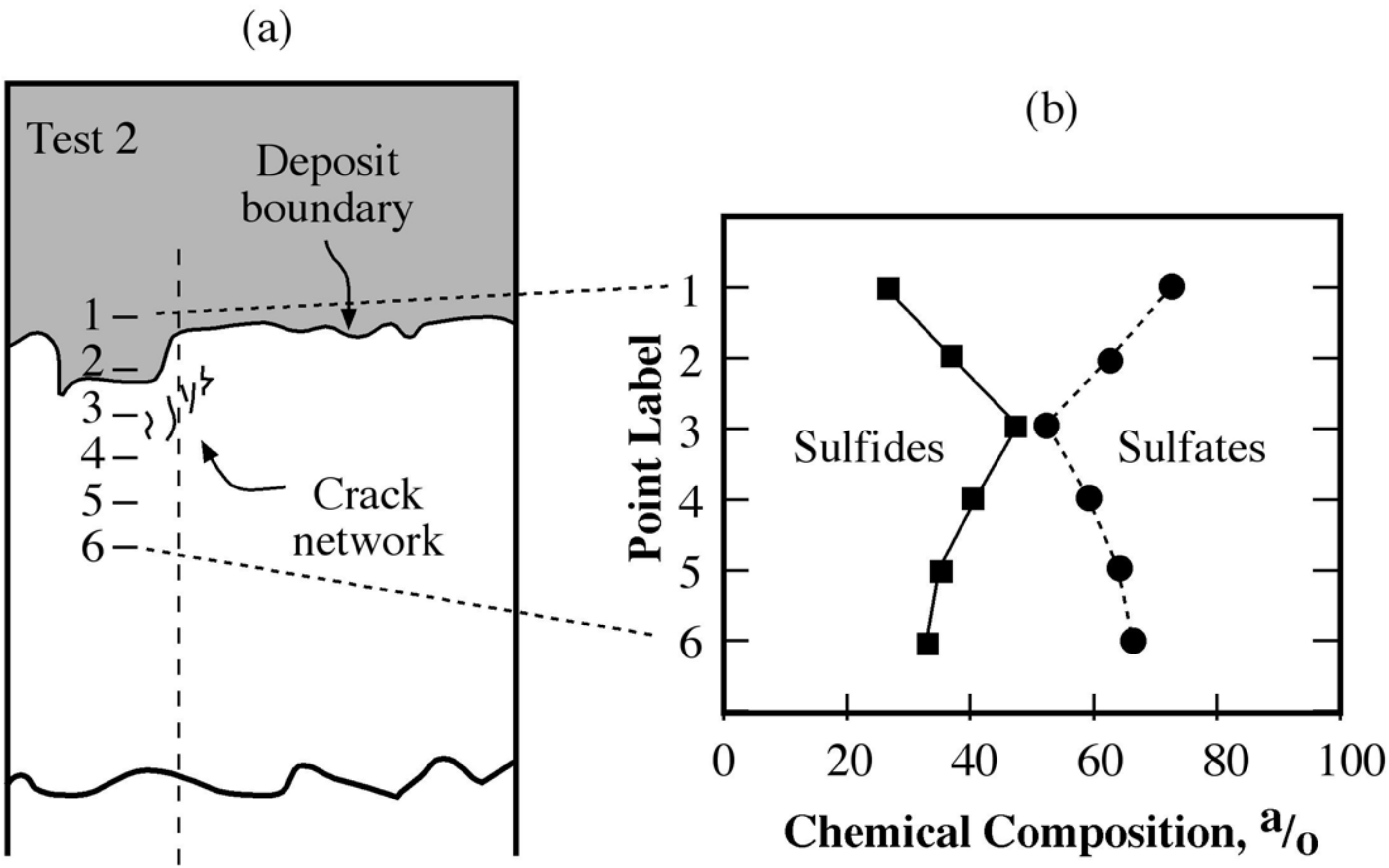
Examples of Microprocesses and effects in bulk environment domain

Bulk Environment Domain



Microprocesses (Time Related)	Effects
1. Flow	• Transports chemical and suspended solids • Influence rates of surface reactions • Low flow / high flow deposits solids • FAC
2. Boiling	• Deposit solids
3. Transport to or from other components	• Cu^{2+}, HS^-
4. Chemical composition • O_2, H_2, N_2H_4 impurities (Pb, Cl^-, SO_4), pH inhibitors, suspended solids	• Electrochemical state • Corrosion reactions • Raise E with low H_2
5. Homogenous chemical reactions	• Reduce $SO_4^{=} \rightarrow HS^-$ with N_2H_4
6. Radiolysis and radiolytic synthesis	• $H_2O \rightarrow O_2 + H_2$ • $N_2 + H_2O \rightarrow HNO_3$ • $O_2 + N_2H_4 \rightarrow H_2O$
7. Multiple oxygen incidents	• Corrosion • SCC

Chemical transformation in bulk environment domain



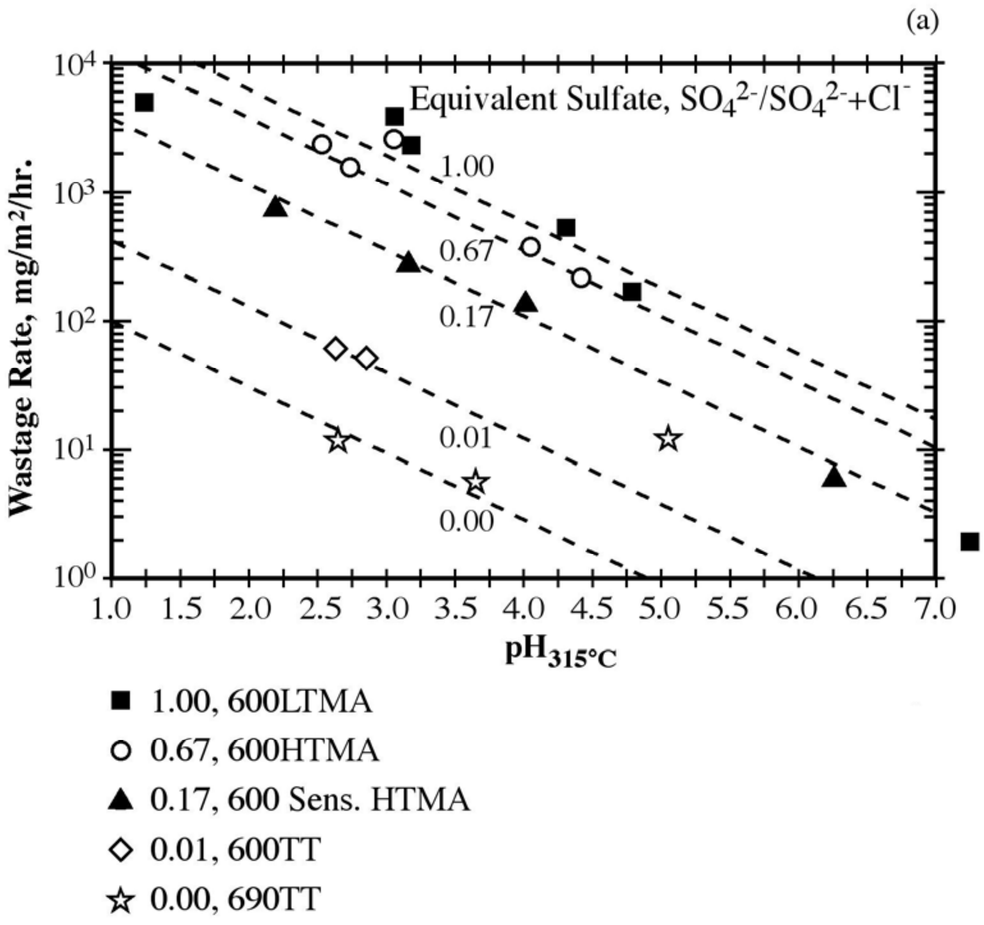
Sulfate is reduced to S^{2-} by hydrazine

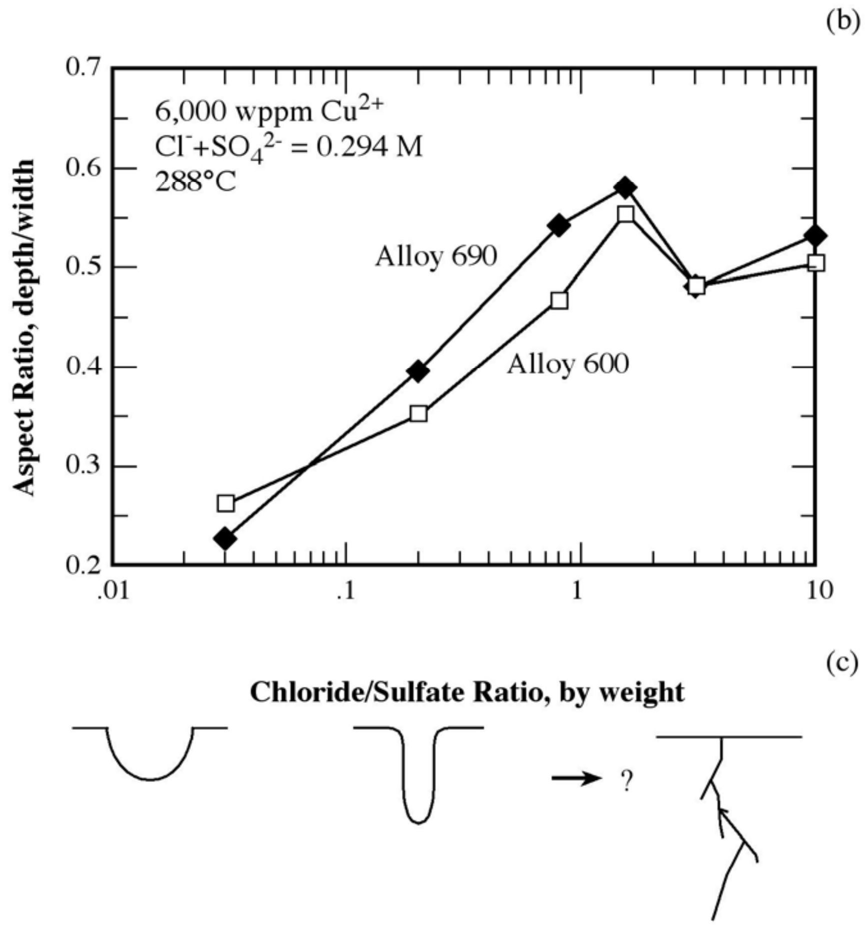
$$2SO_4^{2-} + 18H^+ + 12e^- \longrightarrow 2HS^- + 8H_2O$$

Hydrazine is oxidized

$$3N_2H_4^+ + 12OH^- \longrightarrow 3N_2 + 12H_2O + 12e^-$$

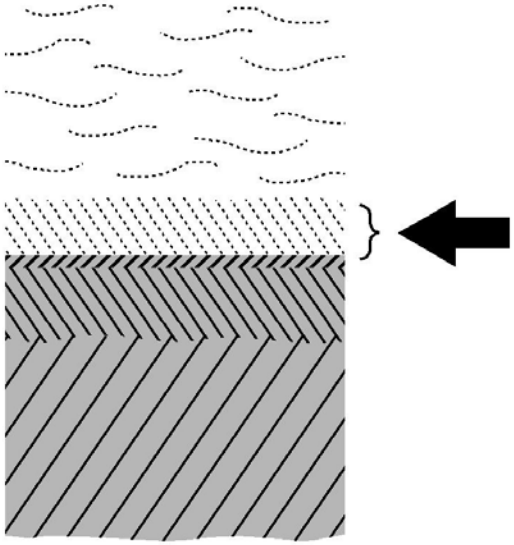
Relative inhibitive effects in bulk environment domain





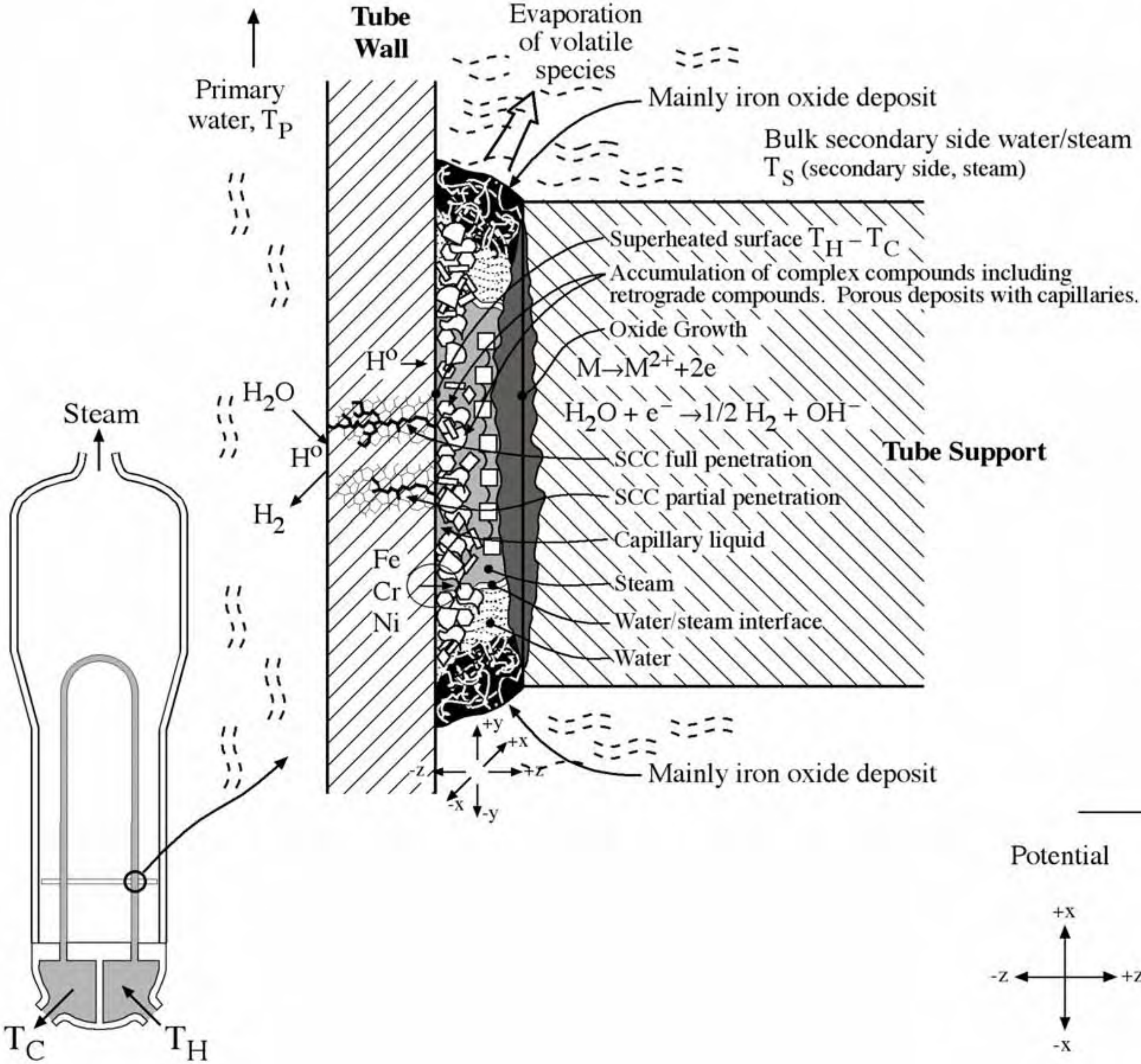
Microprocesses and effects in near-surface domain (environment side)

Near-Surface Domain (Environment Side)



Microprocesses (Time Related)	Effects
1. Deposits	• Corrosion cells • Heat transfer resistance • Galvanic processes
2. Heat flux	• Concentrate chemicals • Raise surface temperatures
3. Sequestering, crevices	• Concentrate chemicals
4. FAC	• Remove material • Produce hydrogen • Inhibit initiation of SCC
5. MIC	• Act at temperatures below 100°C • Acidic and other corrosive environments

Concentration on heat transfer surfaces in near surface domain

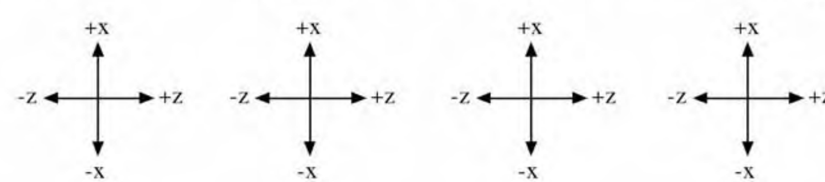


Typical species and reactions found in the sequestered geometry

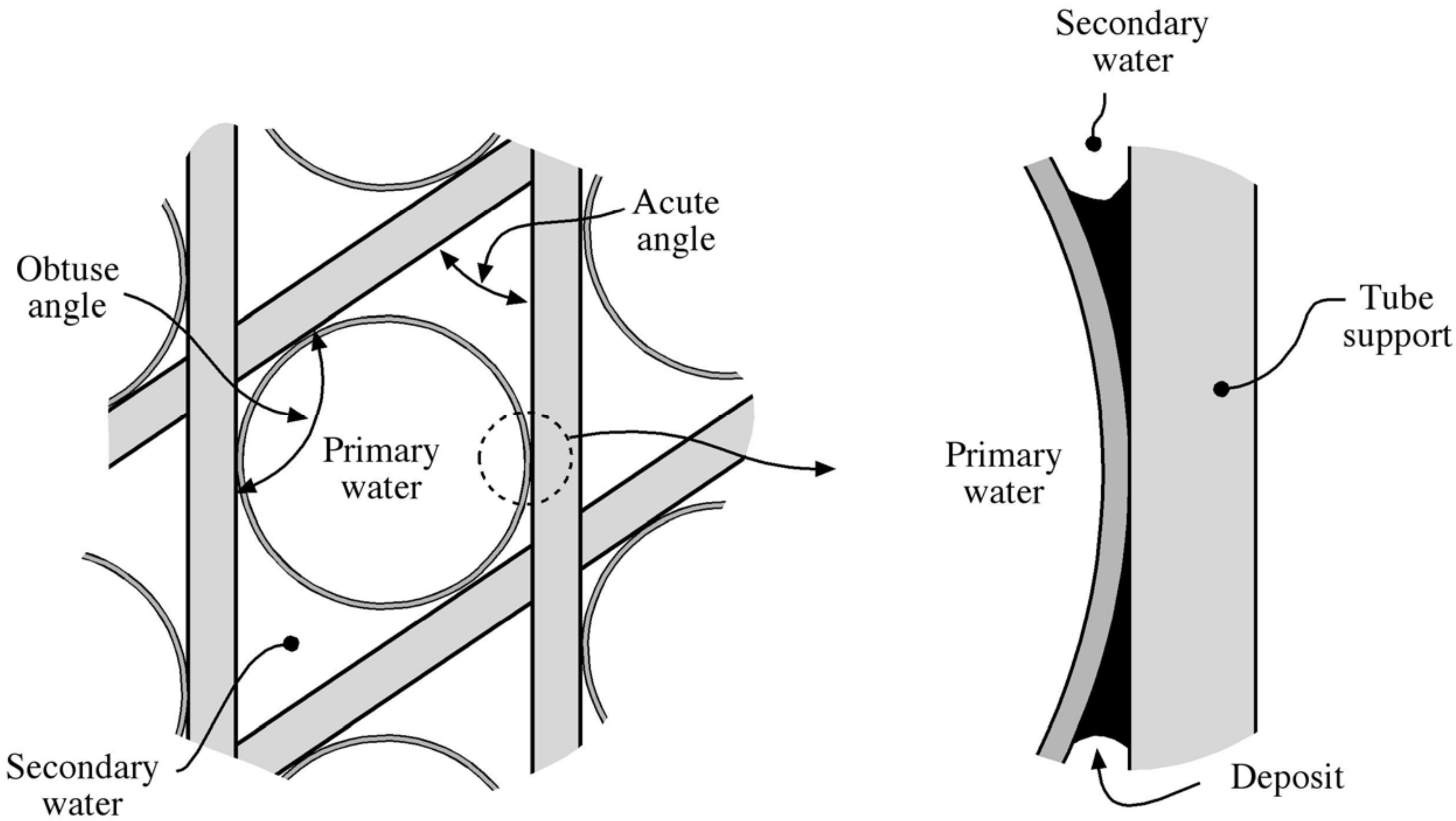
Cl	(Cl^-, HCl)
SO_x	($S^{+6} \rightarrow S^{+4} \rightarrow S^{+2} \rightarrow S^o \rightarrow S^=$)
SiO_x	(SiO_2, complex compounds)
AlO_x	(AL_2O_3, complex compounds)
Cu	(Cu^o, Cu^{++}, CuO)
Pb	(Pb^o, PbO_x)
Na, Ca, Mg	(complex compounds)
Na_2HPO_4	(retrograde compounds plus H_3PO_4)
B, Ti, Zn	(inhibitors)
O_2	(H_2O, compounds)
H_2	(H^+)
N_2H_4	(NH_3, N_2)
C	($CO_3^=$, organic)
N	(NO_x, organic)
Fe, Cr, Ni	(Fe^{+2}, Cr^{+3}, Ni^{+2}, complex compounds)
Organics	Acetate, Formate, Glycolate, others

Gradients

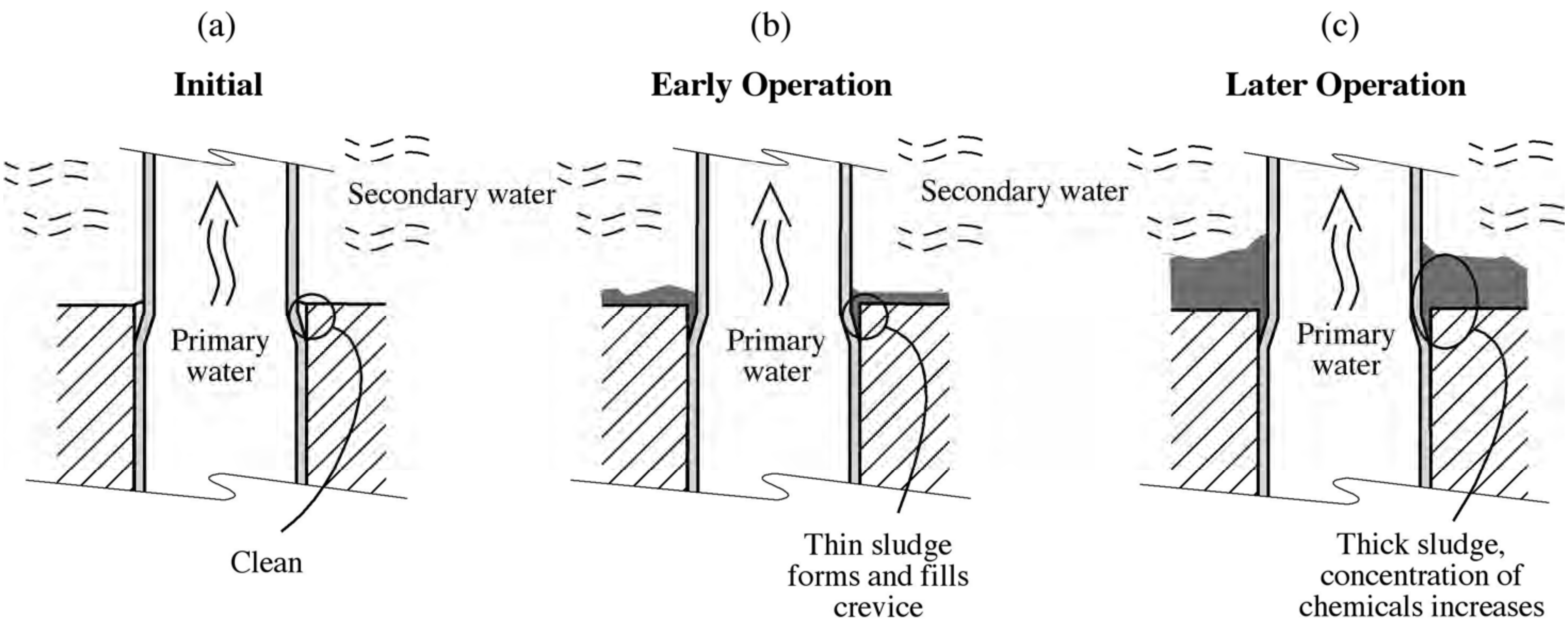
Potential   Temperature   Concentration   Fluid Density



Concentration of deposits in near surface domain

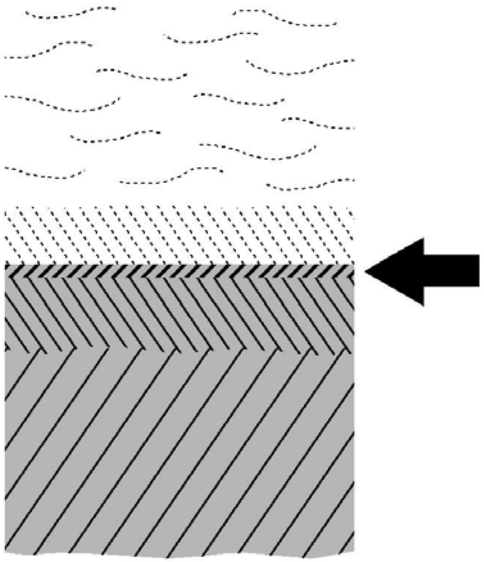


Build up of deposits due to gravity in near surface domain



Examples of Microprocesses and effects on protective film domain

Protective Film Domain

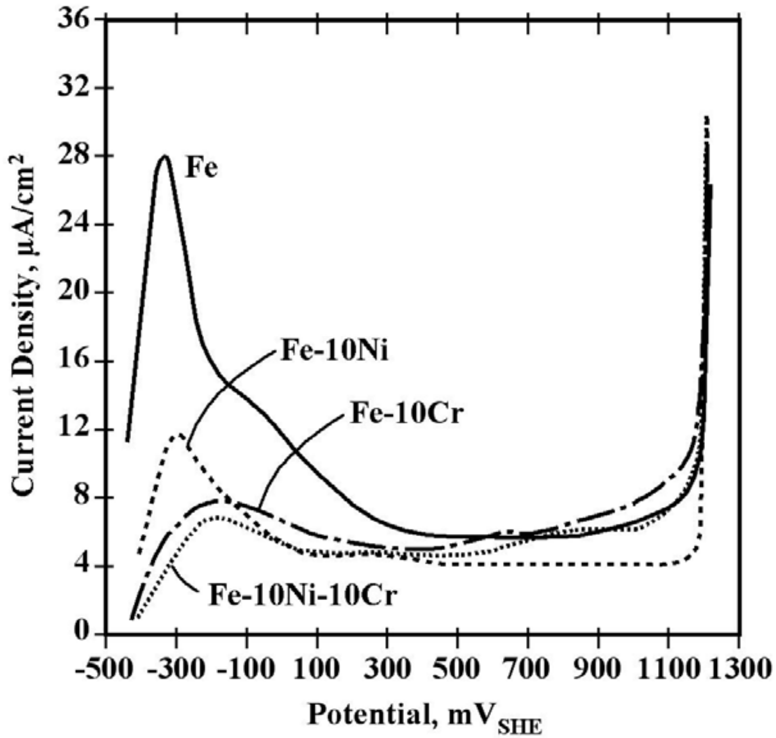


Microprocesses (Time Related)	Effects
1. Thickness	• Surface stress • Heat transfer
2. Composition (environment contribution, alloy contribution, defect structure, xtal/amorphous)	• Conductivity • Pit nucleation • SCC initiation
3.Stresses (average, metal interface)	• Film degradation
4. Kinetics (repassivation, dissolution, growth)	• Local penetration • Slip dissolution
5. Slip interactions	• Slip height • Step distribution • Dislocation nucleation

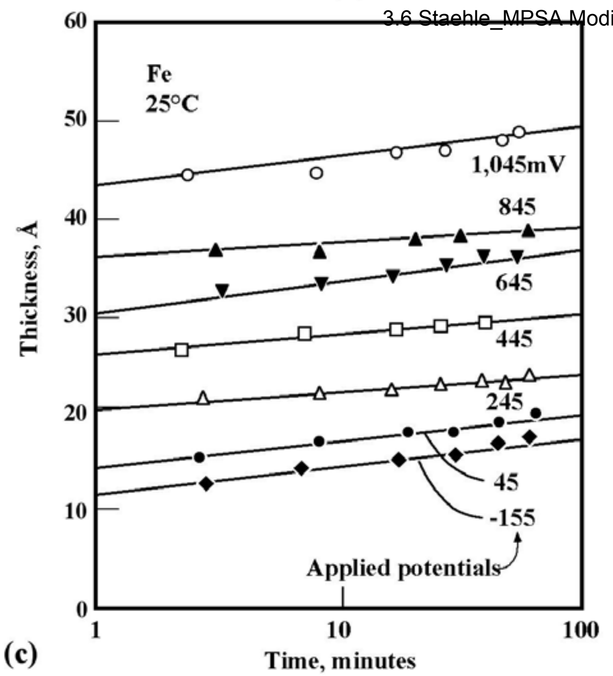
Passive films on iron-base alloys in borate solutions

(Ellipsometric and electrochemical study)

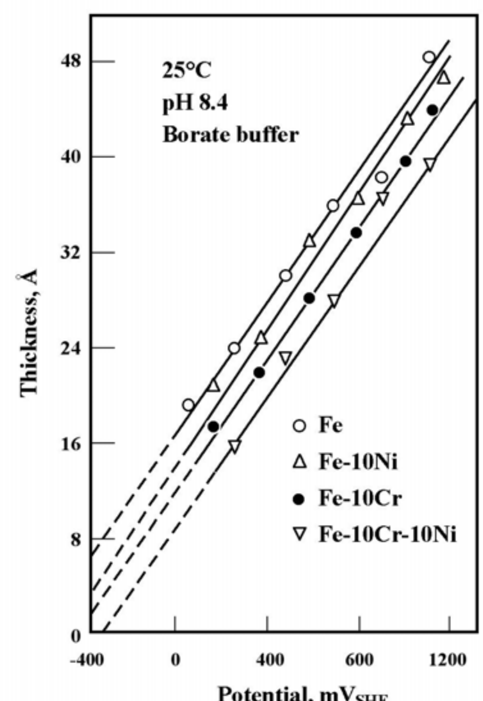
(a)



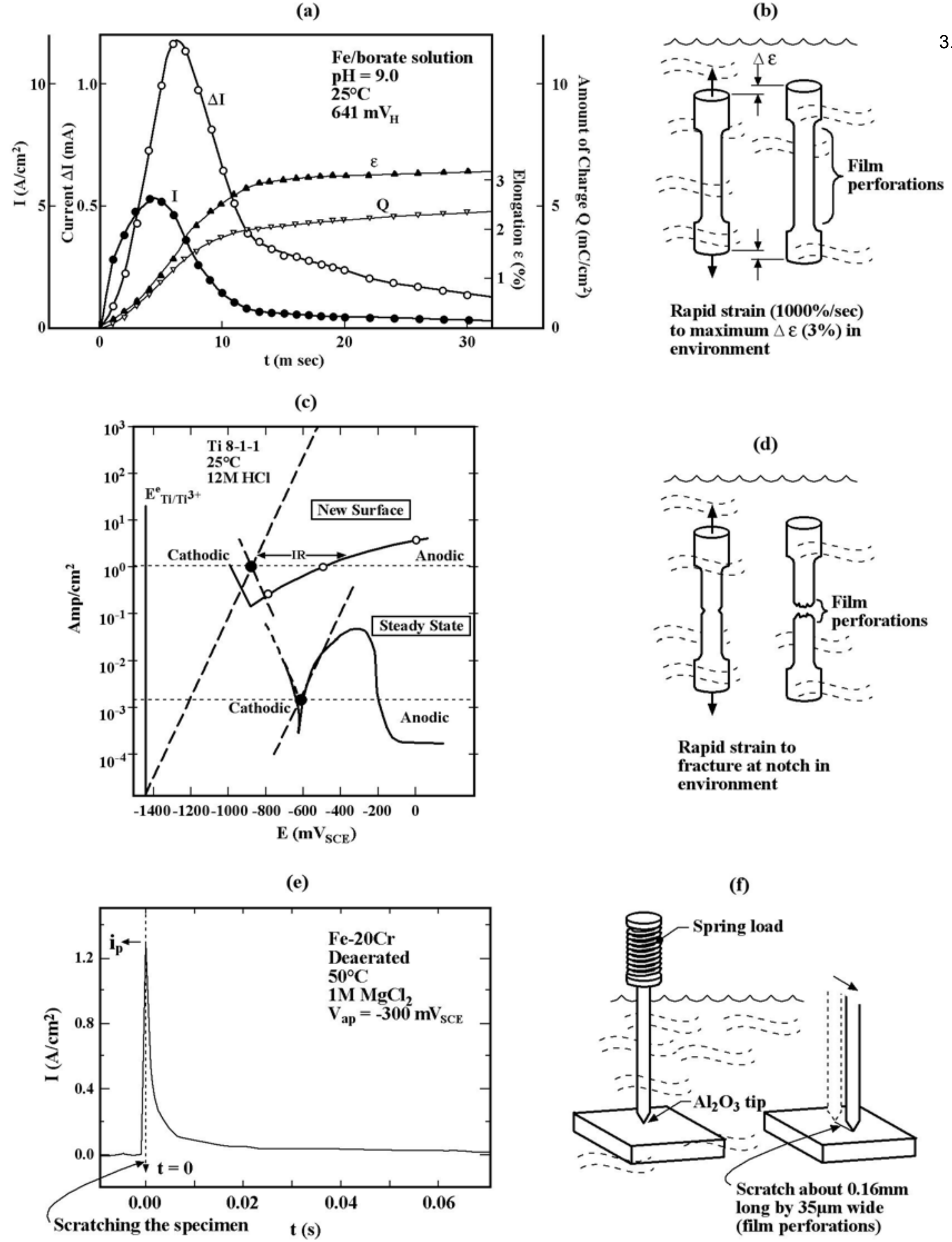
(b)

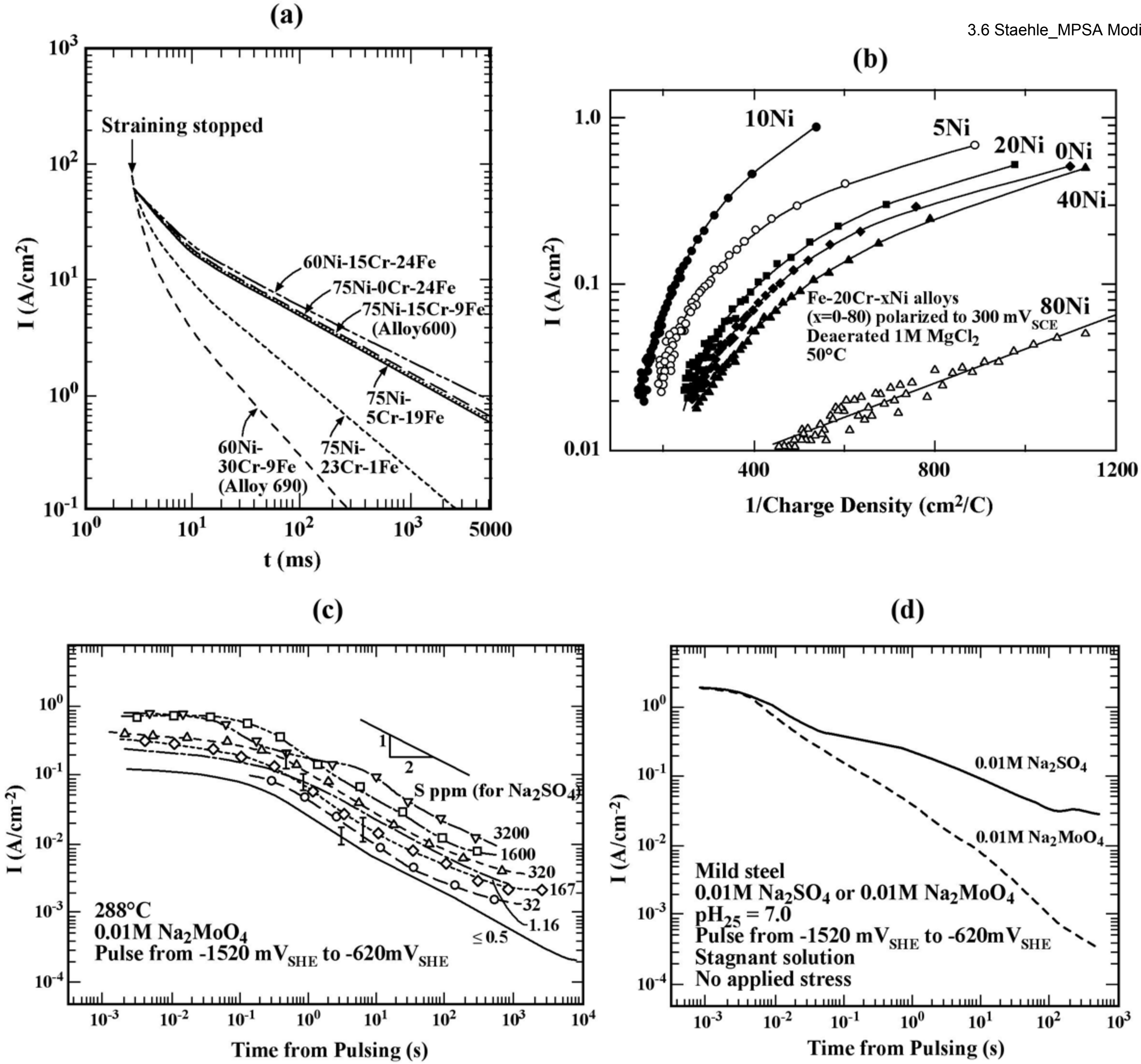


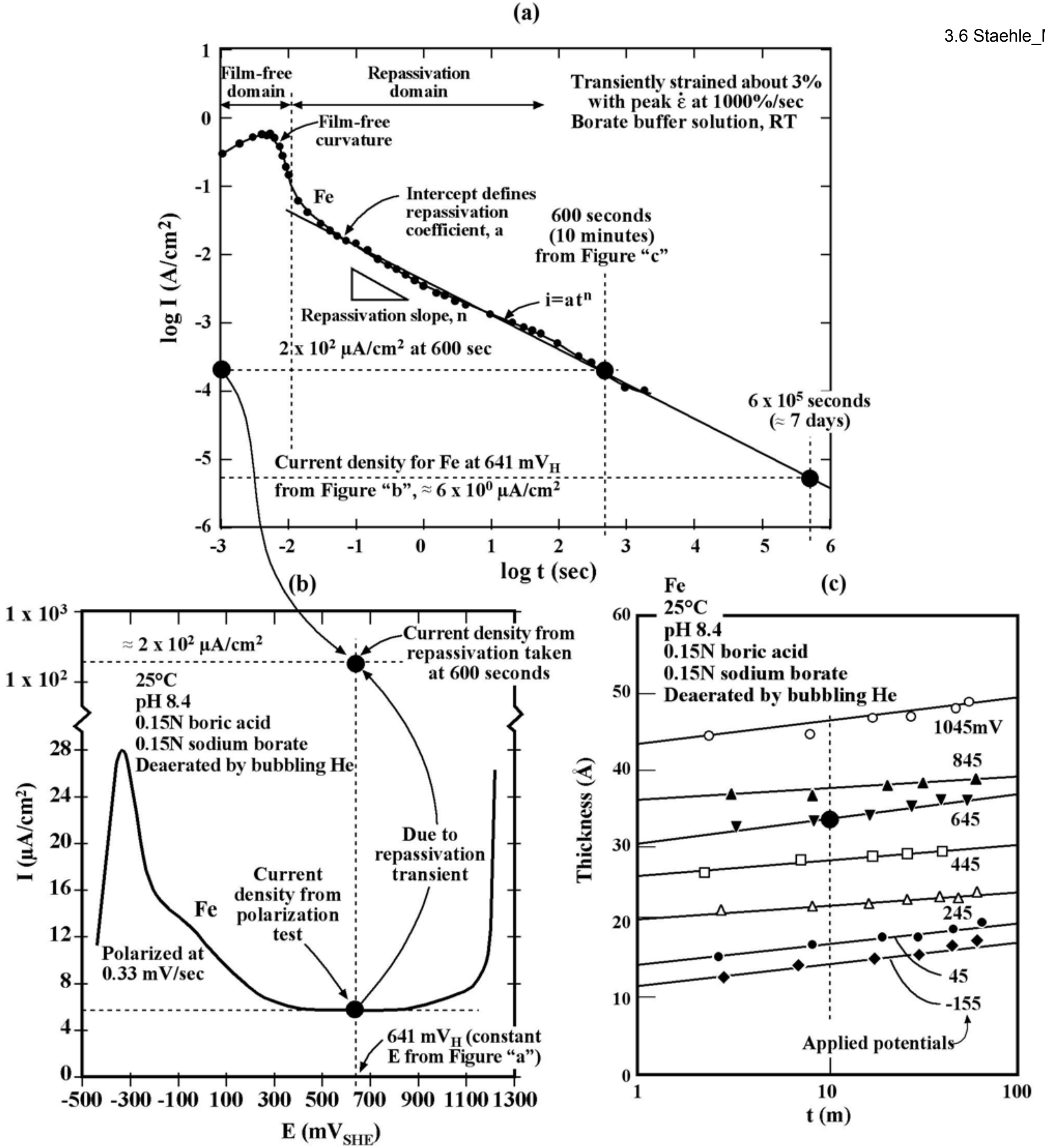
(c)



From Goswami and Staehle

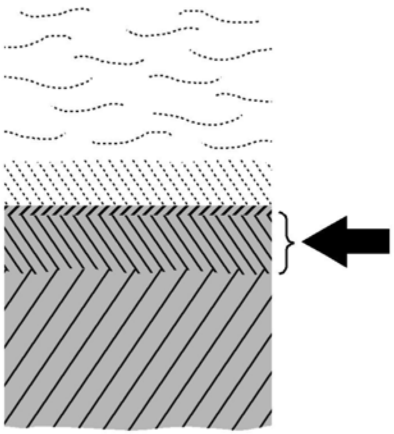

(a)
Fe/borate solution
pH = 9.0
25°C
641 mV_H
ΔI
I
ε
Q
I (A/cm²)
Current ΔI (mA)
Elongation ε (%)
Amount of Charge Q (mC/cm²)
t (m sec)
(b)
Δε
Film perforations
Rapid strain (1000%/sec) to maximum Δε (3%) in environment
(c)
Ti 8-1-1
25°C
12M HCl
E^e Ti/Ti^3+
New Surface
Cathodic
IR
Anodic
Steady State
Cathodic
Anodic
Amp/cm²
E (mV_SCE)
(d)
Film perforations
Rapid strain to fracture at notch in environment
(e)
i_p
Fe-20Cr
Deaerated
50°C
1M MgCl₂
V_ap = -300 mV_SCE
I (A/cm²)
t = 0
Scratching the specimen
t (s)
(f)
Spring load
Al₂O₃ tip
Scratch about 0.16mm long by 35µm wide (film perforations)


(a)
Straining stopped
60Ni-15Cr-24Fe
75Ni-0Cr-24Fe
75Ni-15Cr-9Fe
(Alloy600)
75Ni-
5Cr-19Fe
60Ni-
30Cr-9Fe
(Alloy 690)
75Ni-
23Cr-1Fe
I (A/cm^2)
t (ms)
(b)
10Ni
5Ni
20Ni
0Ni
40Ni
80Ni
Fe-20Cr-xNi alloys
(x=0-80) polarized to 300 mV$_{SCE}$
Deaerated 1M $MgCl_2$
50°C
I (A/cm^2)
1/Charge Density (cm^2/C)
(c)
S ppm (for Na_2SO_4)
3200
1600
320
167
32
1.16
≤ 0.5
288°C
0.01M Na_2MoO_4
Pulse from -1520 mV$_{SHE}$ to -620mV$_{SHE}$
I (A/cm^{-2})
Time from Pulsing (s)
(d)
0.01M Na_2SO_4
0.01M Na_2MoO_4
Mild steel
0.01M Na_2SO_4 or 0.01M Na_2MoO_4
pH$_{25}$ = 7.0
Pulse from -1520 mV$_{SHE}$ to -620mV$_{SHE}$
Stagnant solution
No applied stress
I (A/cm^{-2})
Time from Pulsing (s)


(a)
Film-free domain
Repassivation domain
Transiently strained about 3% with peak ε̇ at 1000%/sec
Borate buffer solution, RT
Film-free curvature
Fe
Intercept defines repassivation coefficient, a
600 seconds (10 minutes) from Figure "c"
Repassivation slope, n
i=at^n
2 x 10^2 μA/cm^2 at 600 sec
6 x 10^5 seconds (≈ 7 days)
Current density for Fe at 641 mV_H from Figure "b", ≈ 6 x 10^0 μA/cm^2
log I (A/cm^2)
log t (sec)
(b)
≈ 2 x 10^2 μA/cm^2
Current density from repassivation taken at 600 seconds
25°C
pH 8.4
0.15N boric acid
0.15N sodium borate
Deaerated by bubbling He
Fe
Current density from polarization test
Due to repassivation transient
Polarized at 0.33 mV/sec
641 mV_H (constant E from Figure "a")
I (μA/cm^2)
E (mV_SHE)
(c)
Fe
25°C
pH 8.4
0.15N boric acid
0.15N sodium borate
Deaerated by bubbling He
1045mV
845
645
445
245
45
-155
Applied potentials
Thickness (Å)
t (m)

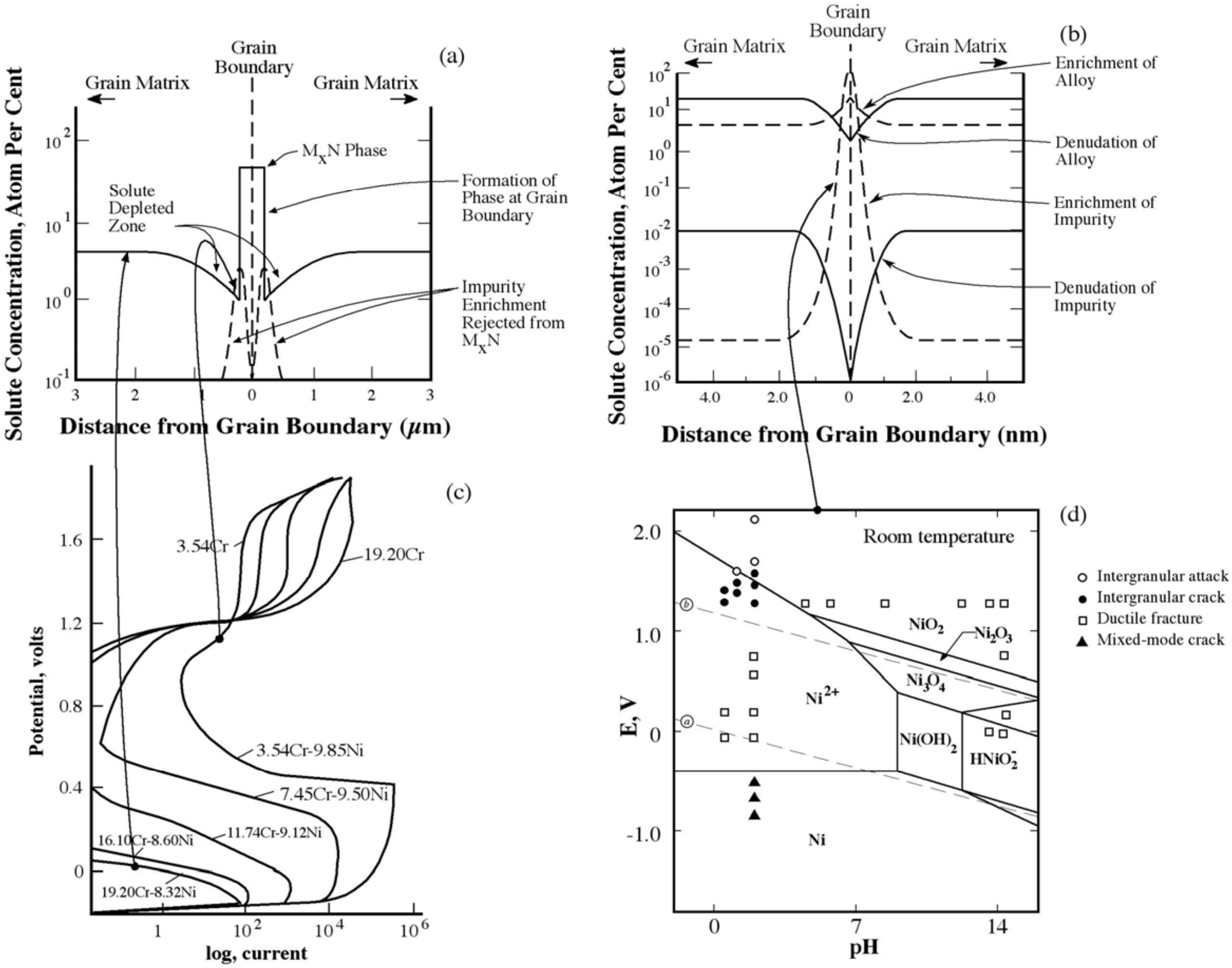
Examples of microprocesses and effects in near surface domain of metal side

Near Surface Domain (Metal Side)

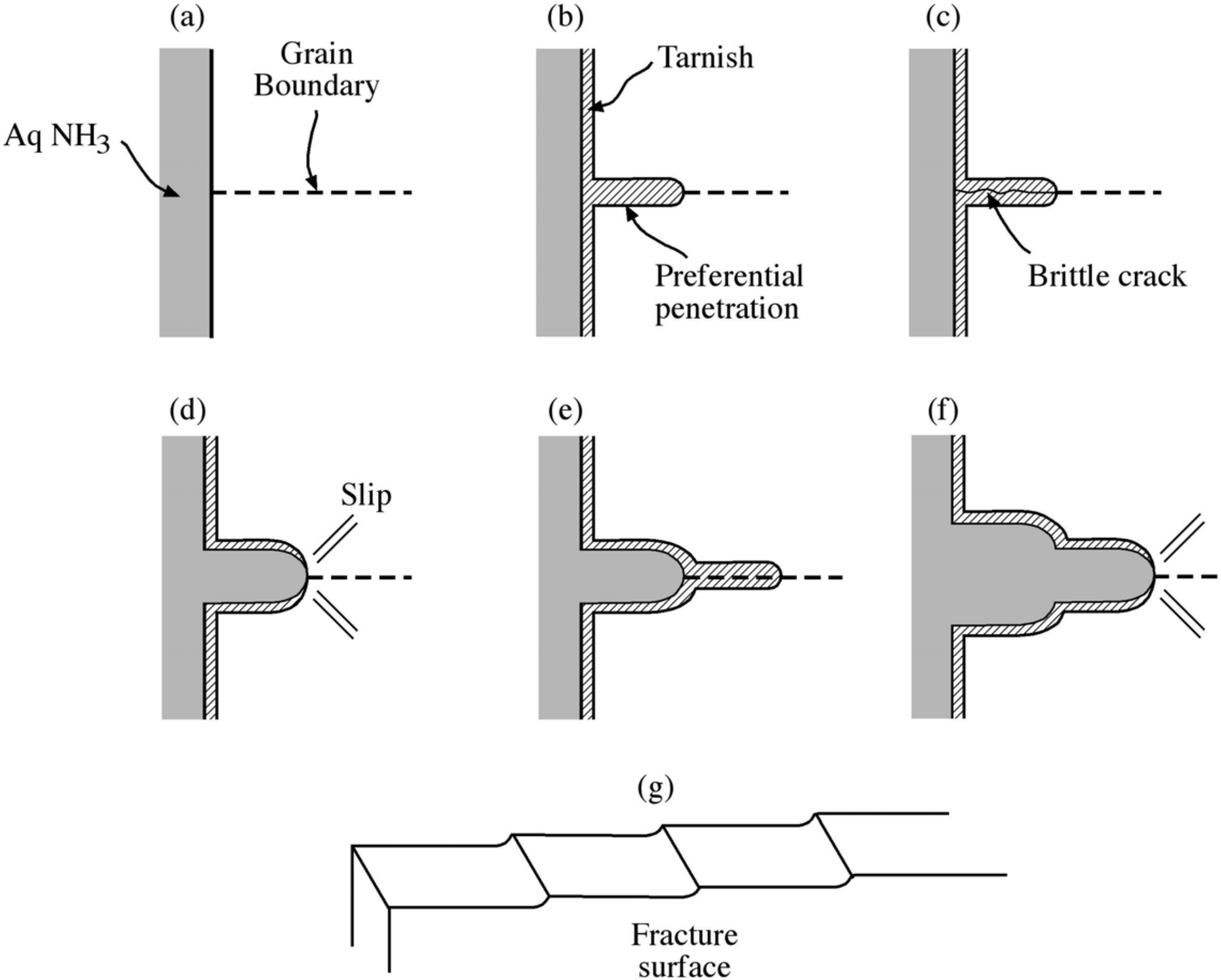


Microprocesses (Time Related)	Effects
1. Enrichment/depletion	• Brittle layer • Catalysis • Change chemistry into SCC mode • Galvanic • Voids
2. Hydrogen entry	• SCC
3. Surface slip	• SCC initiation
4. Grain boundary (composition, diffusion)	• IGC • G.B. diffusion
5. Irradiation-induced voids	• Stresses, distortion
6. Slip dissolution	• SCC initiation
7. Tunnels	• SCC initiation
8. General dissolution	• Surface recession
9. Pits, IG corrosion, electrochemical cells	• Penetration • CF initiation
10. SCC initiation	• Accelerate
11. FAC	• Recession • Remove SCC initiation • Hydrogen production
12. Abuse (dings, dents, machining, grinding)	• SCC initiation

Grain boundary chemistry affects chemical reactivity in bulk metal domain

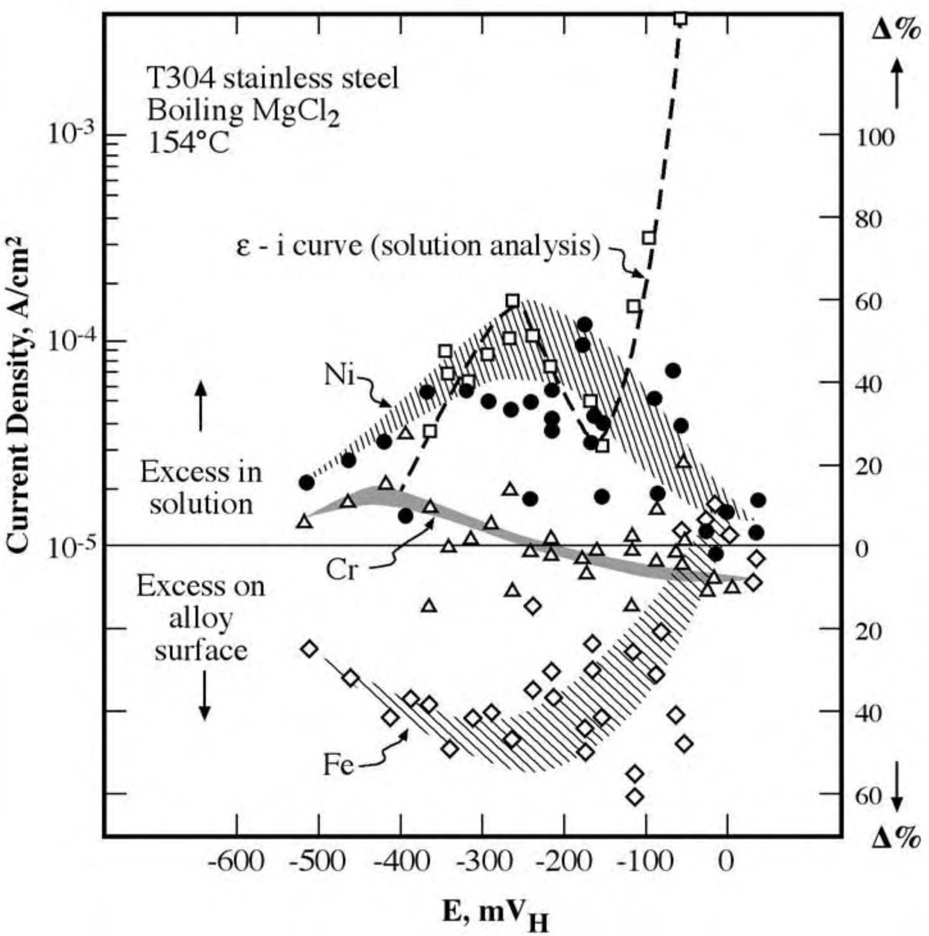


Brittle film rupture in near surface domain metal side

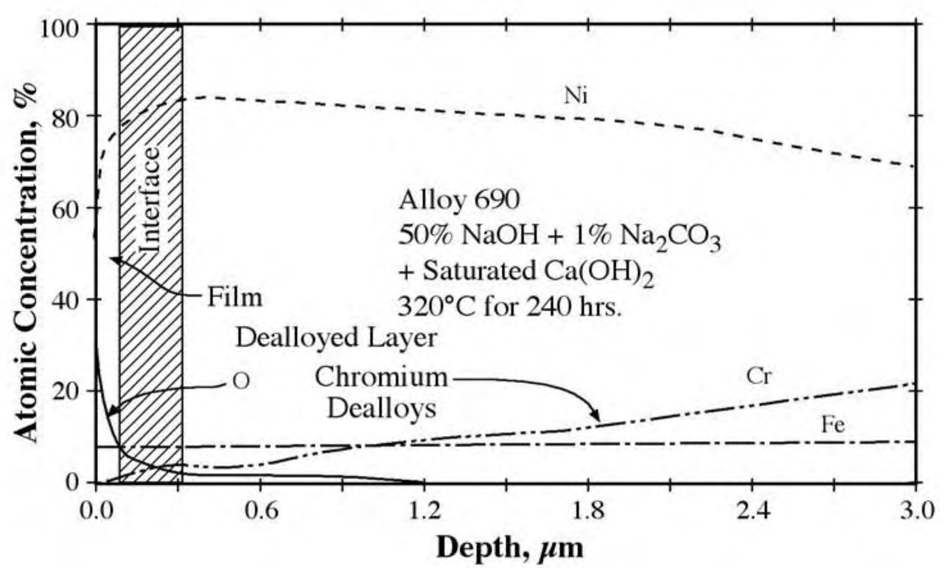


Enrichment of alloying elements in near surface metal domain

(a)



(b)



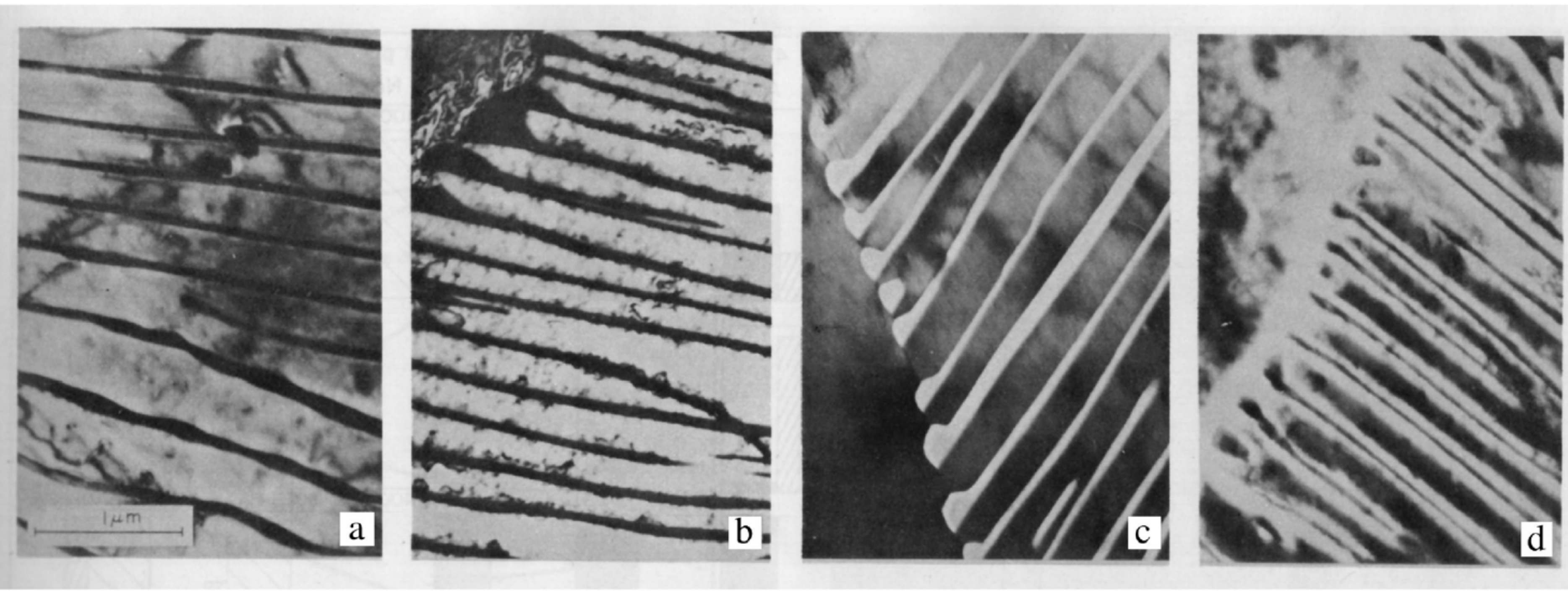
Preferential dissolution of metallurgical phases in near surface metal domain

α_{Fe}

α_{Fe} preferential dissolution

Fe_3C preferential dissolution

Preferential dissolution at interface between α_{Fe} and Fe_3C



Fe-0.45 $^{w}/_{o}$ C as forged pearlitic structure

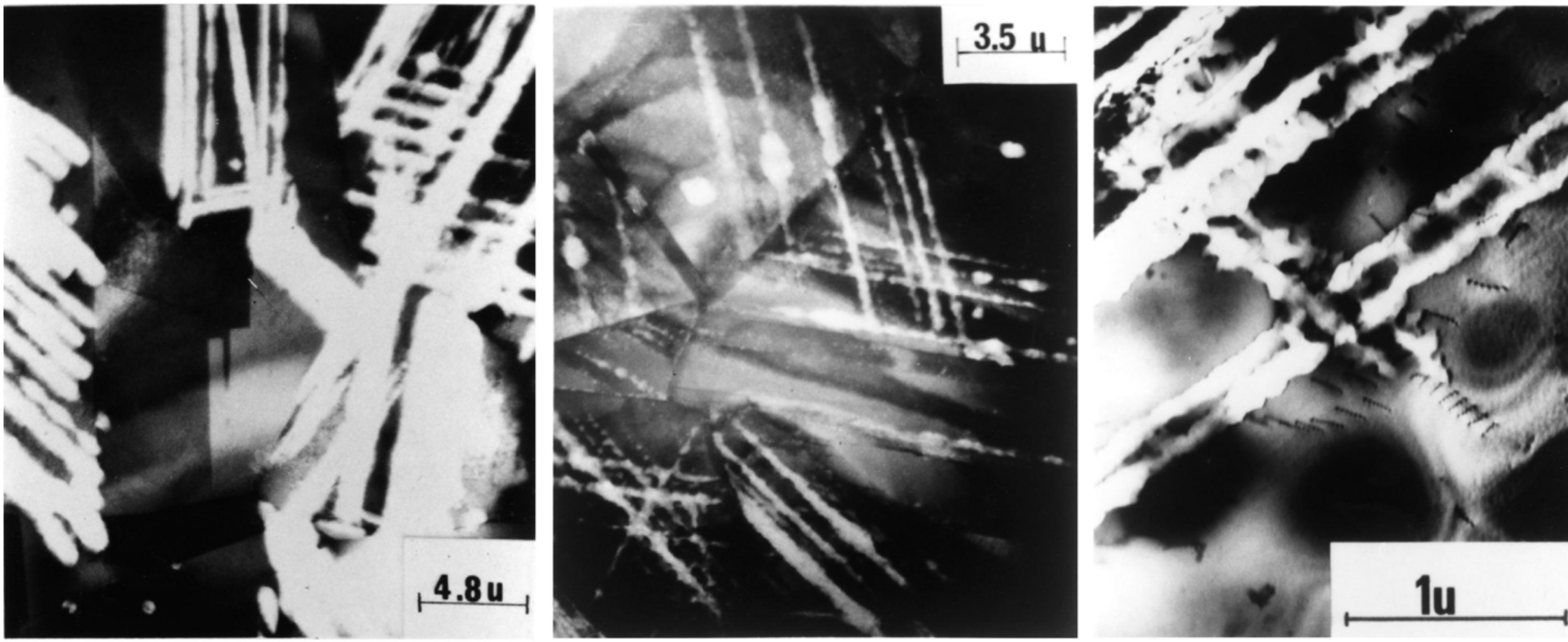
pH4 at -290 mV_H
10 min.
0.1N NaOH +
0.1M $KHC_8H_4O_4$

pH4 at +10 mV_H
60 min.
HCl

pH4 at -250 mV_H
10 min.
Acetic acid

Stressed foils of stainless steel type base with additions of Si or Be

(a) (b) (c)



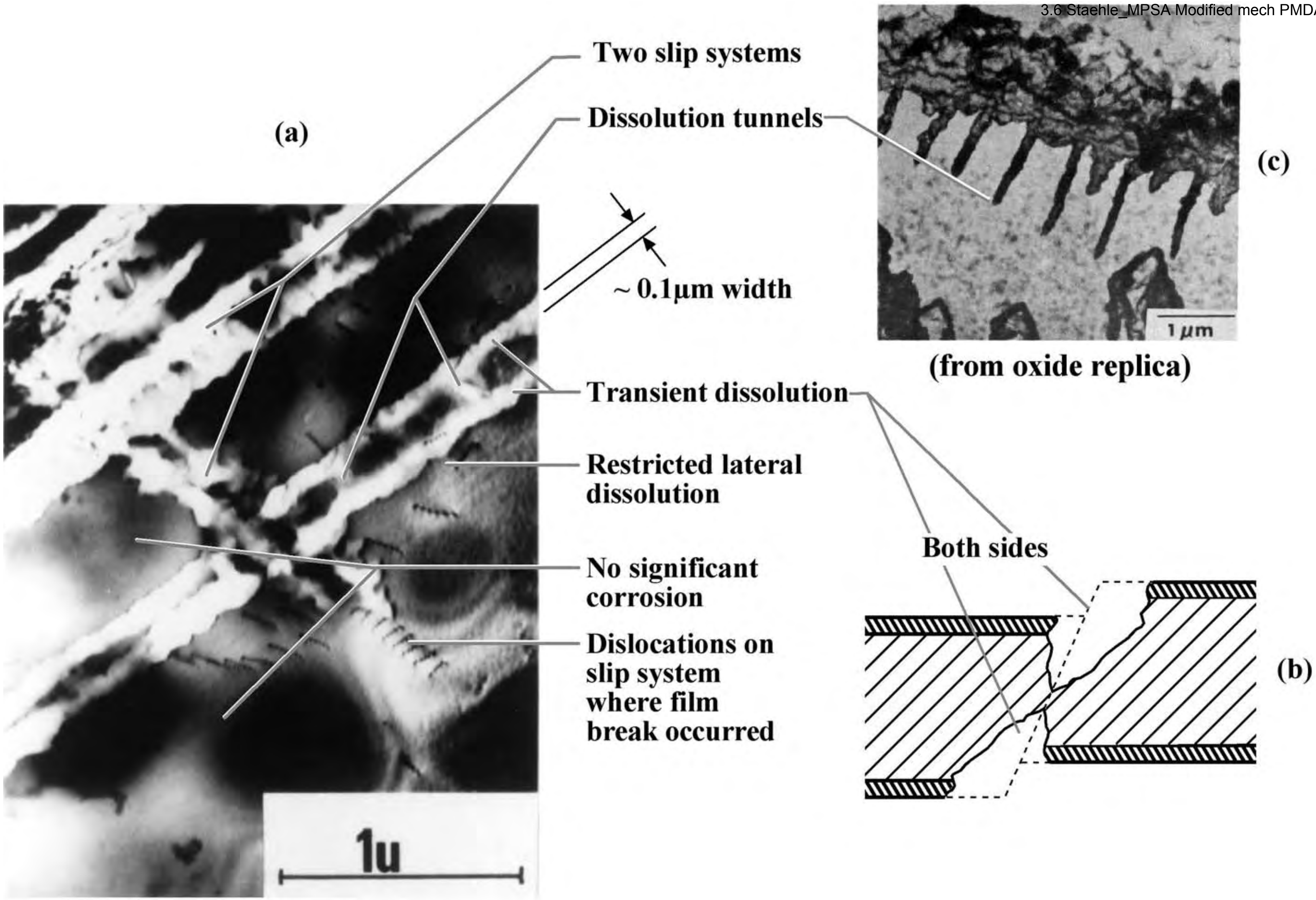
(a) 10 minutes
69.85Fe-19.95Cr-14.20Ni

(b) 15 minutes
64.46Fe-19.20Cr-14.9Ni-1.44Si

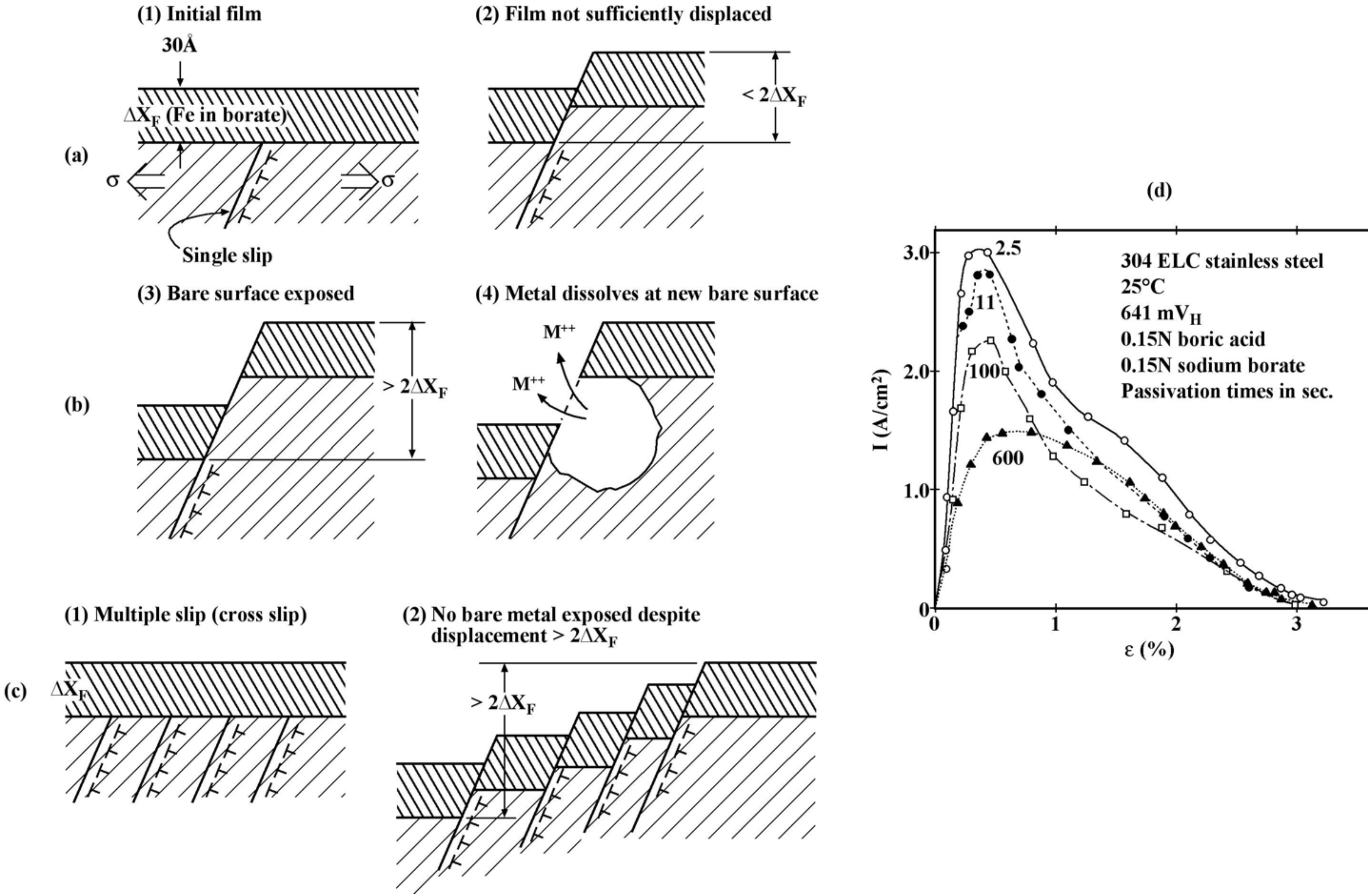
(c) 10 minutes
64.5Fe-19.17Cr-14.8Ni-1.5Be

All exposed to boiling $MgCl_2$

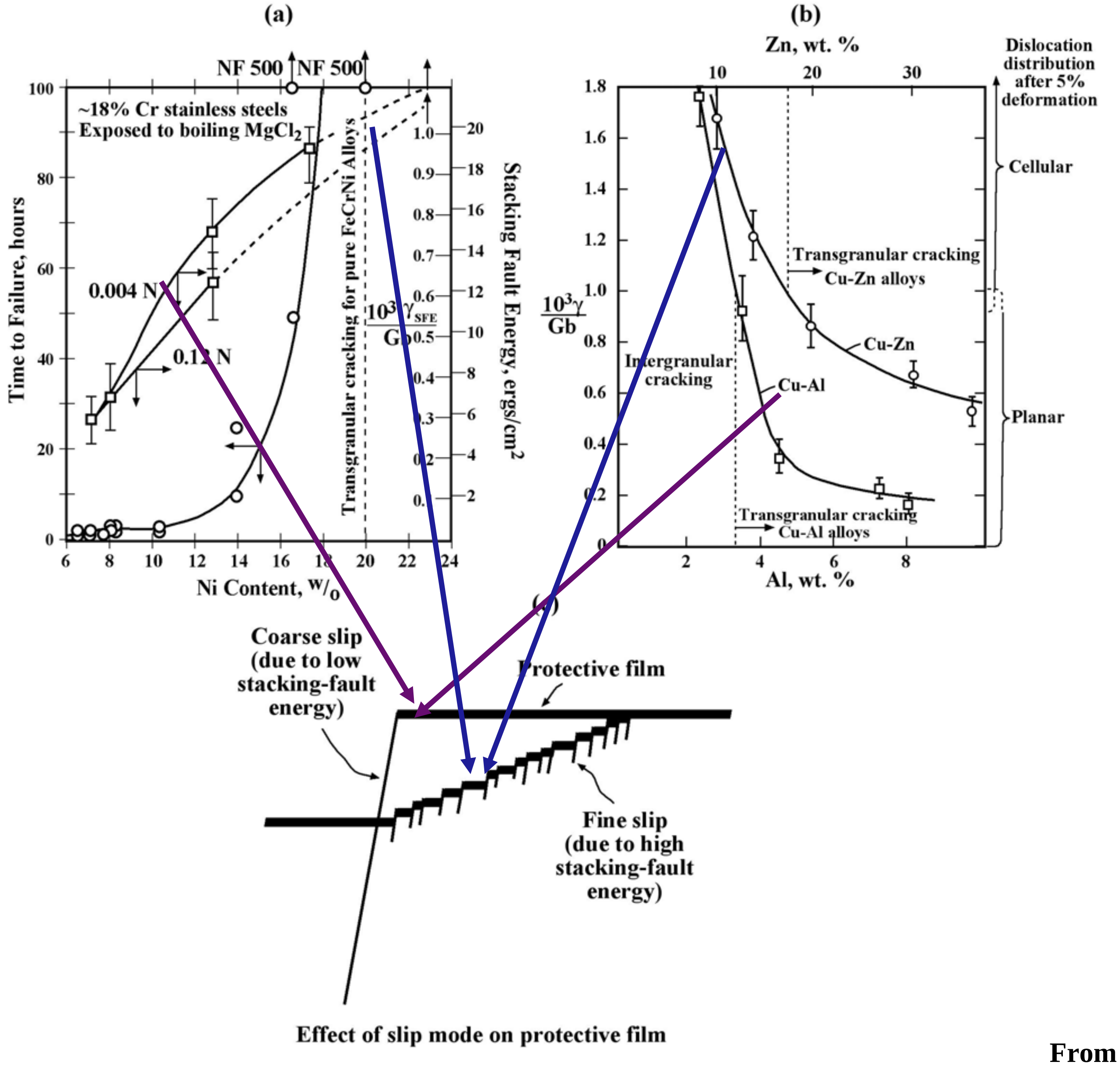
From Smith and Staehle and Davis and Staehle



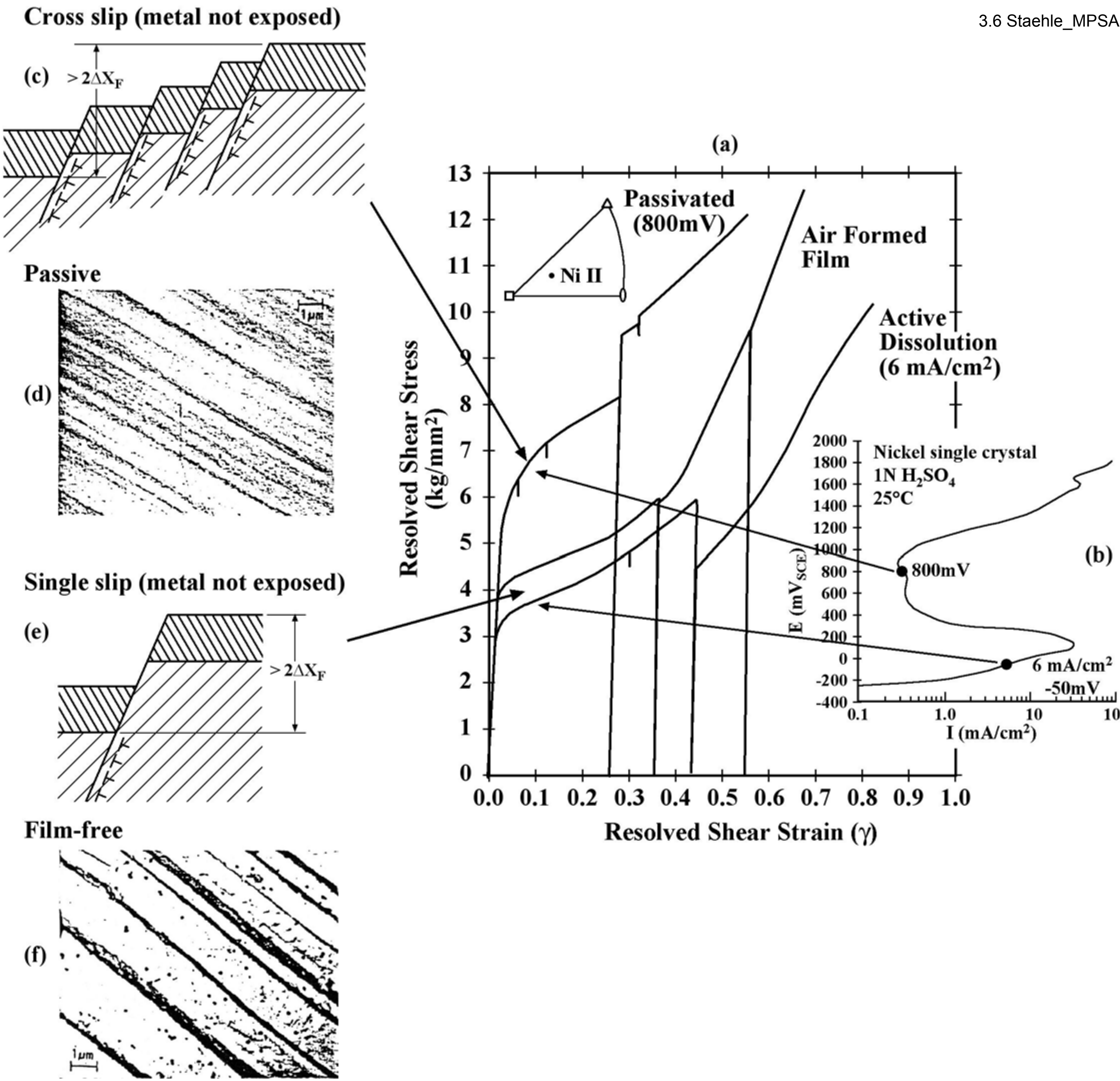
10 minutes
64.5Fe-19.17Cr-14.8Ni-1.5Be


(1) Initial film
30Å
ΔX_F (Fe in borate)
(a)
σ
σ
Single slip
(2) Film not sufficiently displaced
< 2ΔX_F
(3) Bare surface exposed
(b)
> 2ΔX_F
(4) Metal dissolves at new bare surface
M++
M++
(1) Multiple slip (cross slip)
(c)
ΔX_F
(2) No bare metal exposed despite displacement > 2ΔX_F
> 2ΔX_F
(d)
304 ELC stainless steel
25°C
641 mV_H
0.15N boric acid
0.15N sodium borate
Passivation times in sec.
2.5
11
100
600
I (A/cm²)
ε (%)
0
1.0
2.0
3.0
1
2
3

Stacking fault energy, sfe, related to slip and morphology of SCC

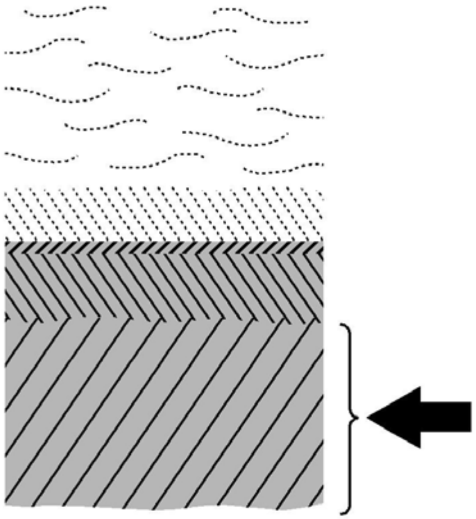


From Swann and Embury

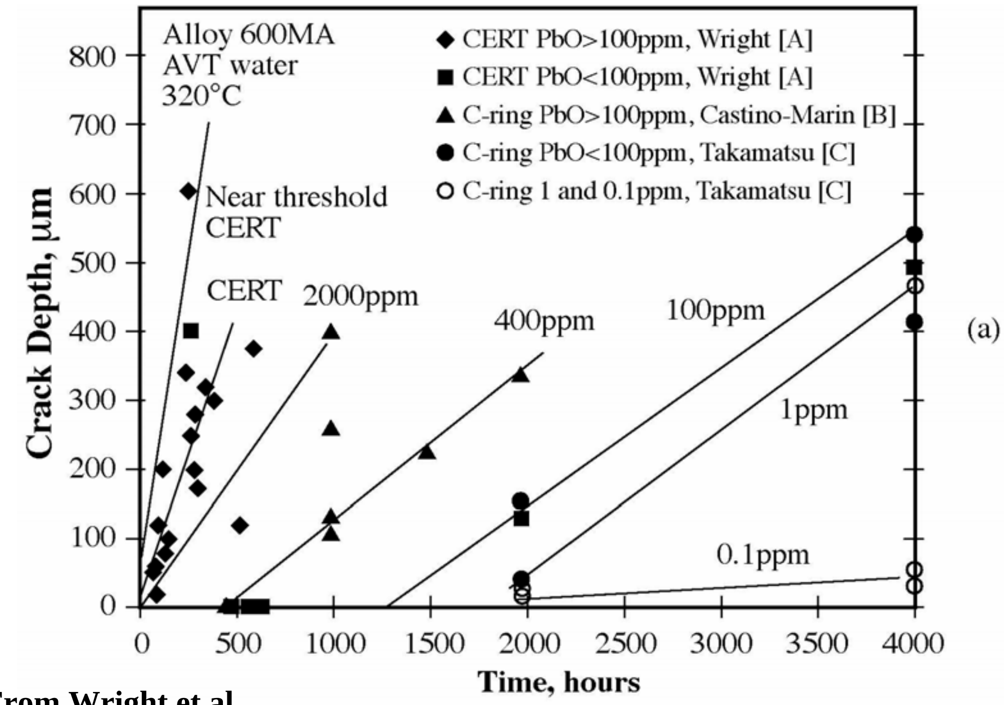

Cross slip (metal not exposed)
(c)
> 2ΔX_F
Passive
(d)
1μm
Single slip (metal not exposed)
(e)
> 2ΔX_F
Film-free
(f)
1μm
(a)
Passivated (800mV)
Ni II
Air Formed Film
Active Dissolution (6 mA/cm²)
Resolved Shear Stress (kg/mm²)
Resolved Shear Strain (γ)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13
Nickel single crystal
1N H₂SO₄
25°C
(b)
800mV
6 mA/cm²
-50mV
E (mV_SCE)
I (mA/cm²)
0.1 1.0 10 100
-400 -200 0 200 400 600 800 1000 1200 1400 1600 1800 2000

Examples of microprocesses and effects in bulk metal domain

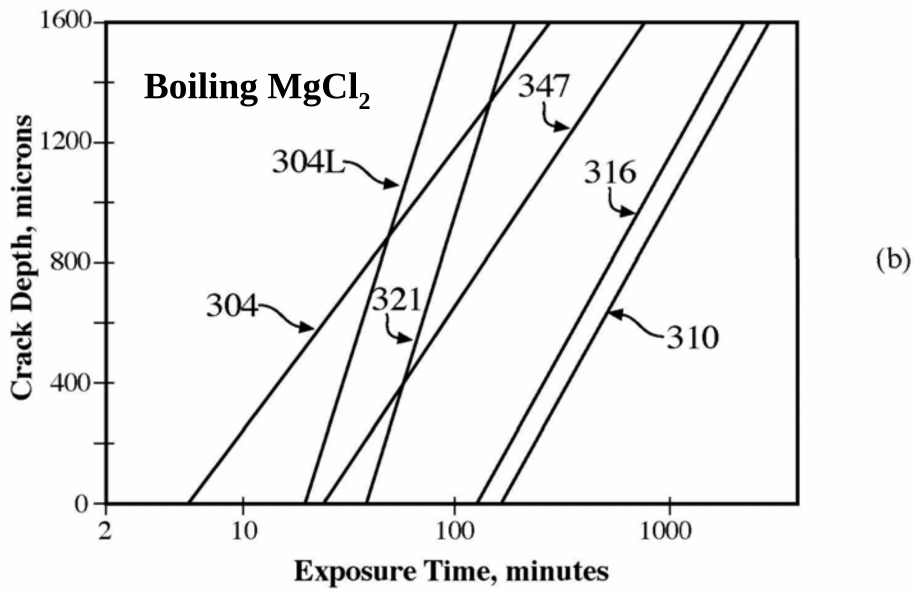
Bulk Metal Domain



Microprocesses (Time Related)	Effects
1. G.B. composition, ppt	• Grain rotation • Grain shedding
2. G.B. composition, adsorb/desorb	• Preferential dissolution, diffusion
3. G.B. diffusion (O_2, N_2, C, ...)	• Embrittlement
4. G.B. movement, slip, isolate	• Pounds or decimal
5. G.B. pile-up site for dislocation-induced stresses	• Promotes IGSCC, SCC
6. G.B. bubble formation (CH_4, NH_3)	• Promotes SCC
7. G. matrix - early precipitation	• Promotes slip coplanarity
8. G. matrix - transformation	• Promotes slip coplanarity
9. G. matrix - slip coplanarity	• Pile up stress
10. G. matrix - voids nucleation	• Stress



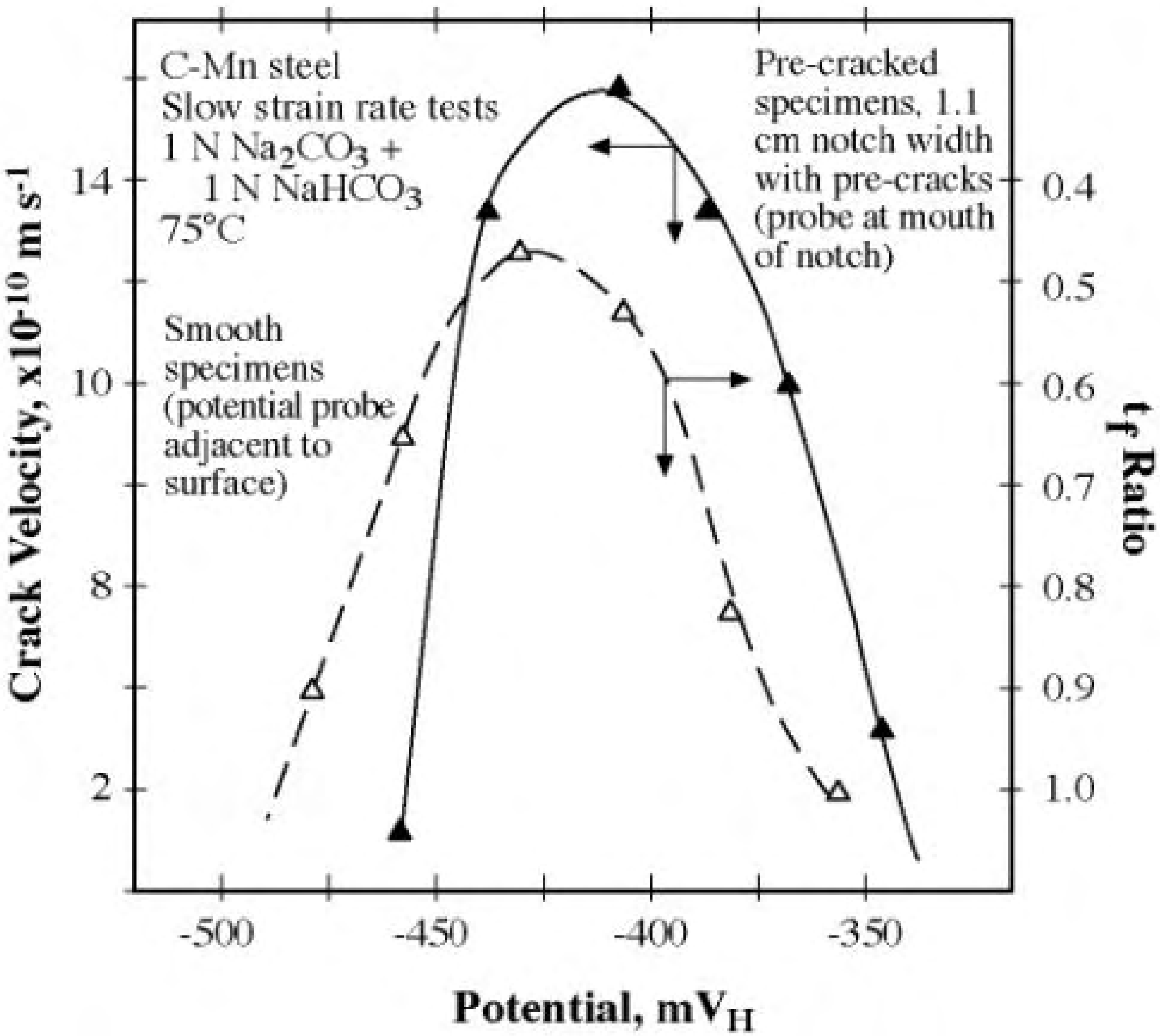
From Wright et al.



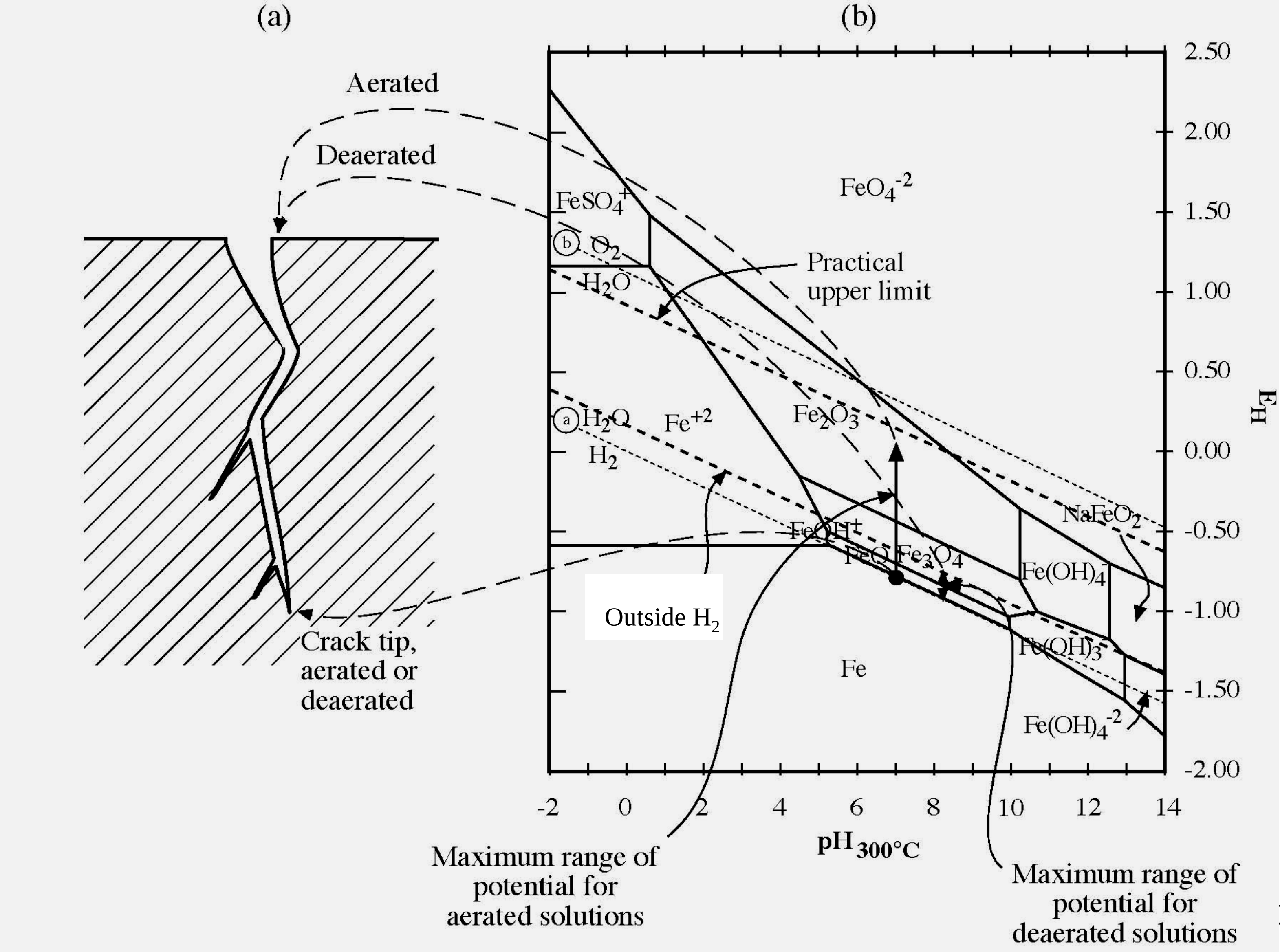
From Eckel

Relative dependences of initiation and propagation on environmental species and alloy composition

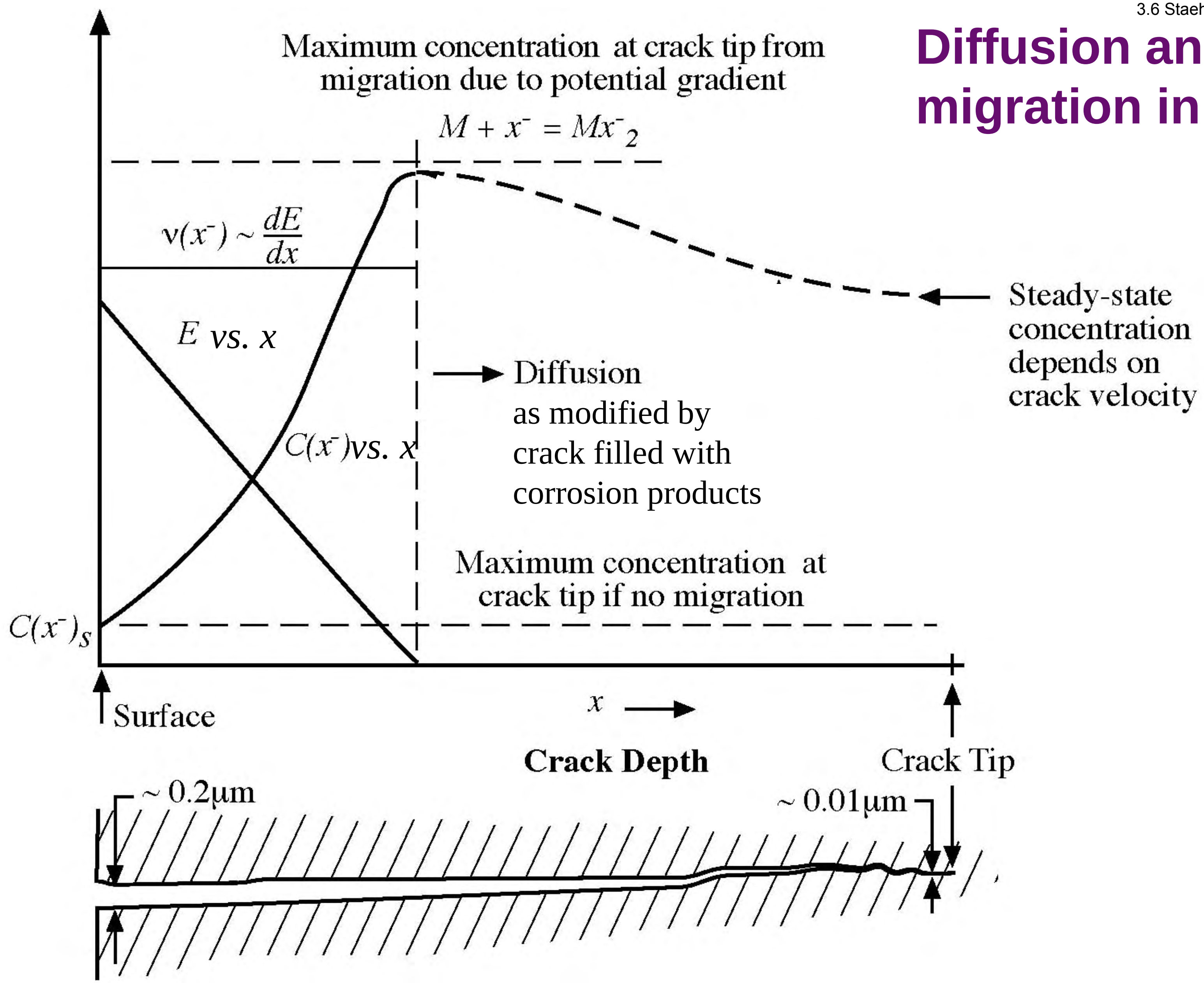
Dependence of initiation and propagation of low alloy steels on potential



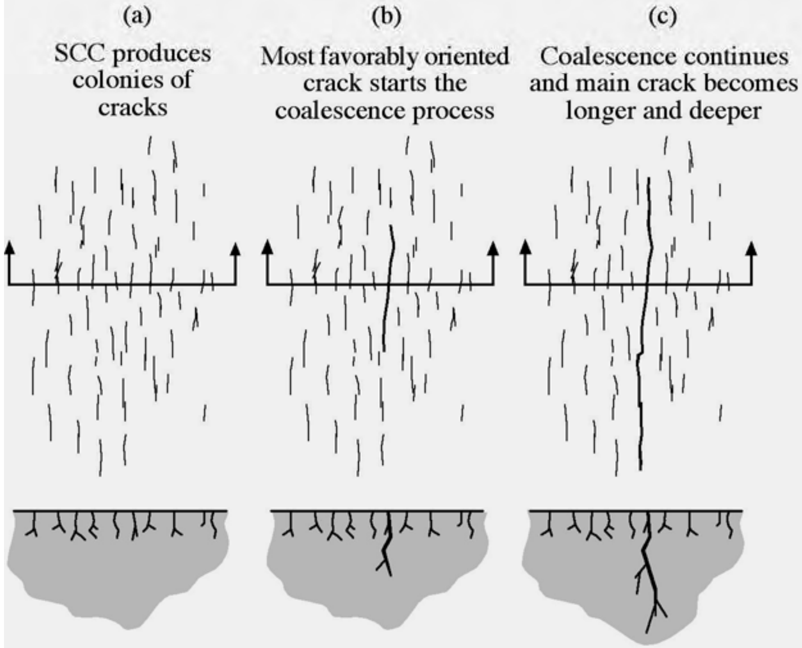
Electrochemical constraints to initiation and propagation

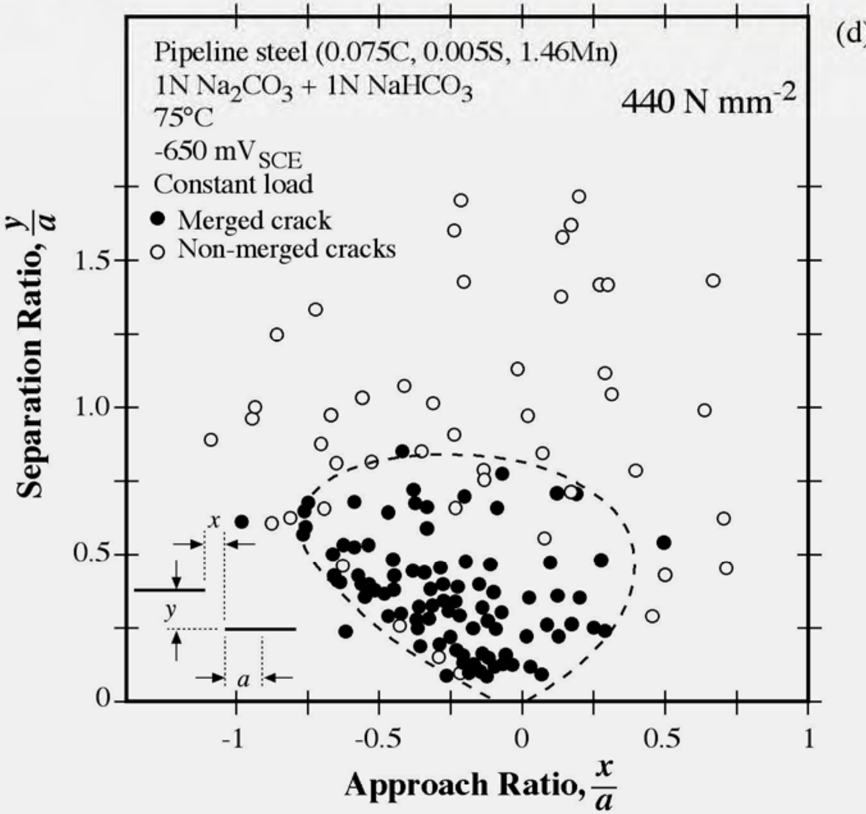


Diffusion and/or migration in an SCC



Initiation morphology and evolution



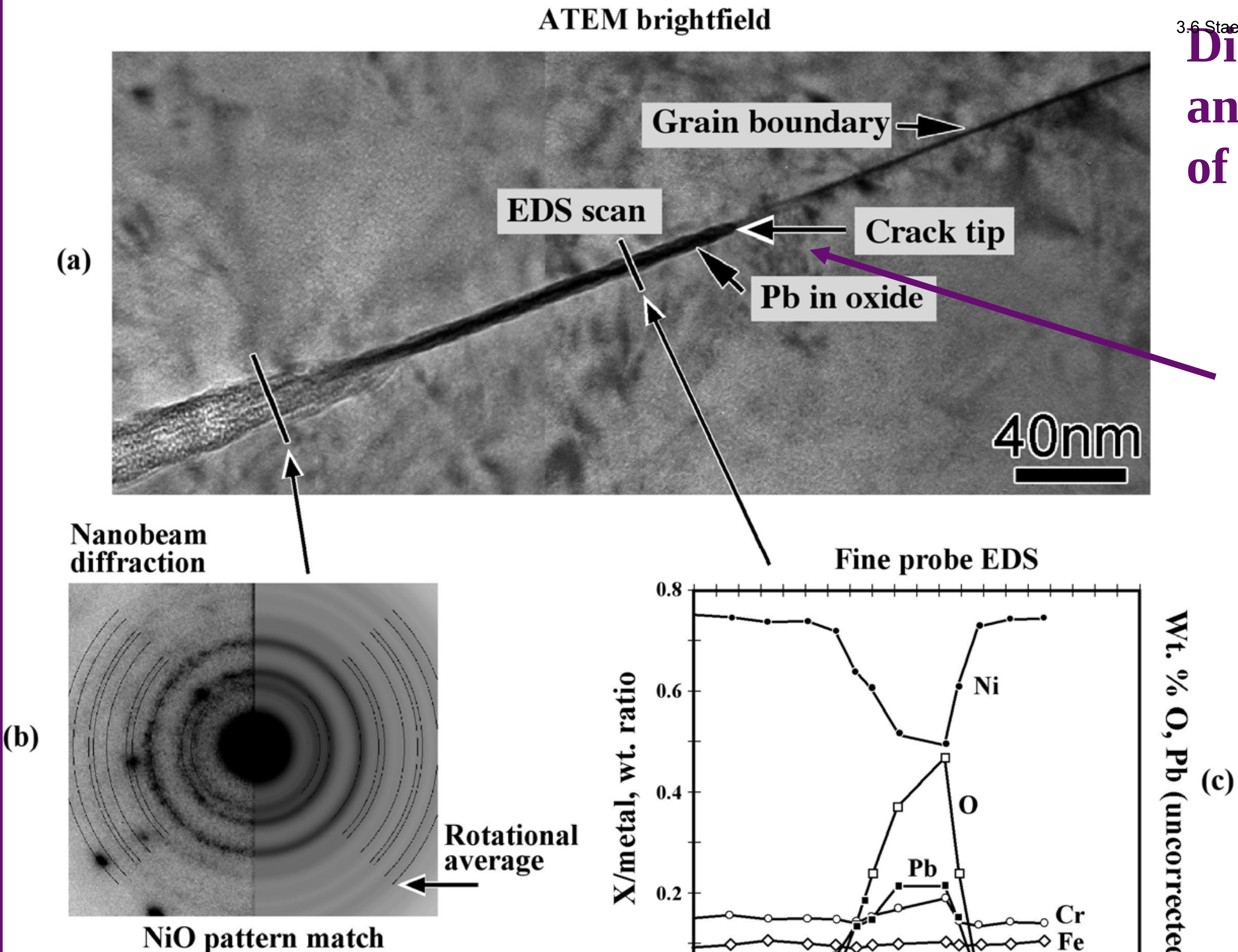


[From Parkins]

Colony of SCC on T304 SS at 204°C in dilute NaCl solution

[From Staehle]

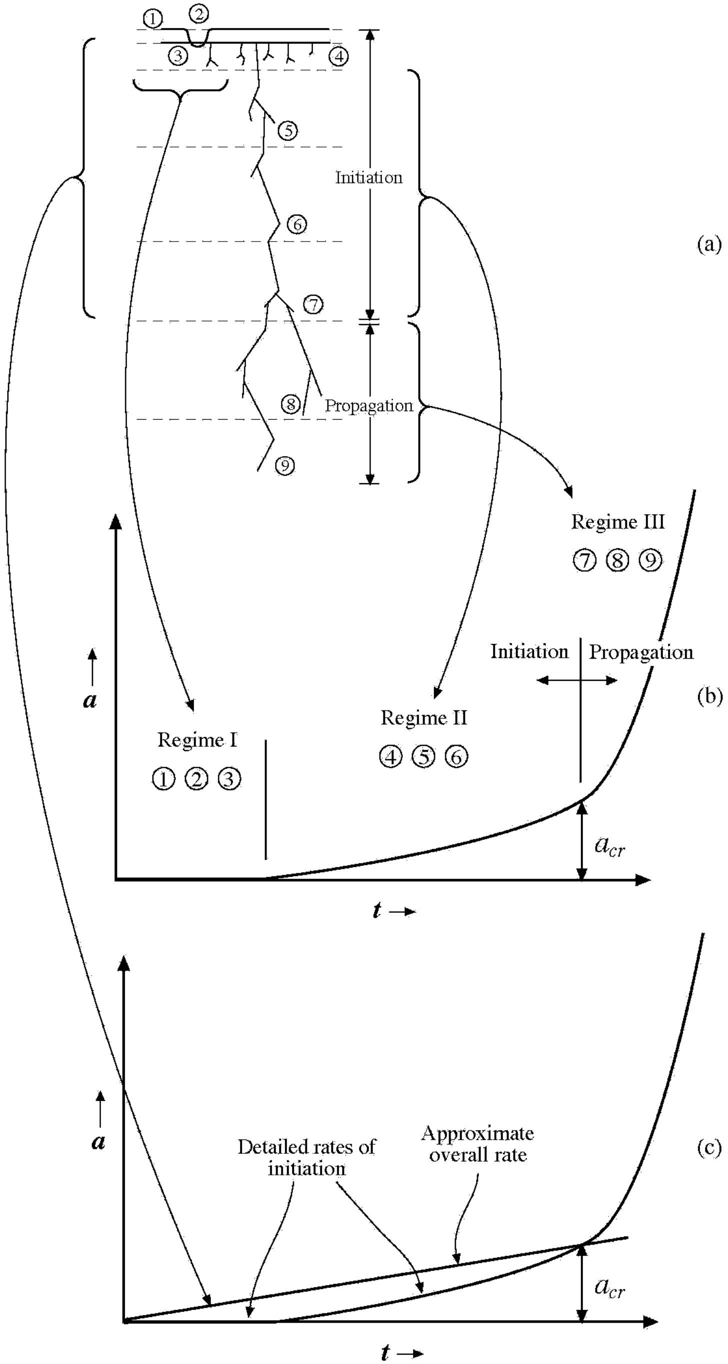
Dimensions and chemistry of SCC tip



Alloy 600MA
CIEMAT (Spain) test with Pb
AVT water+0.002M PbO
320°C

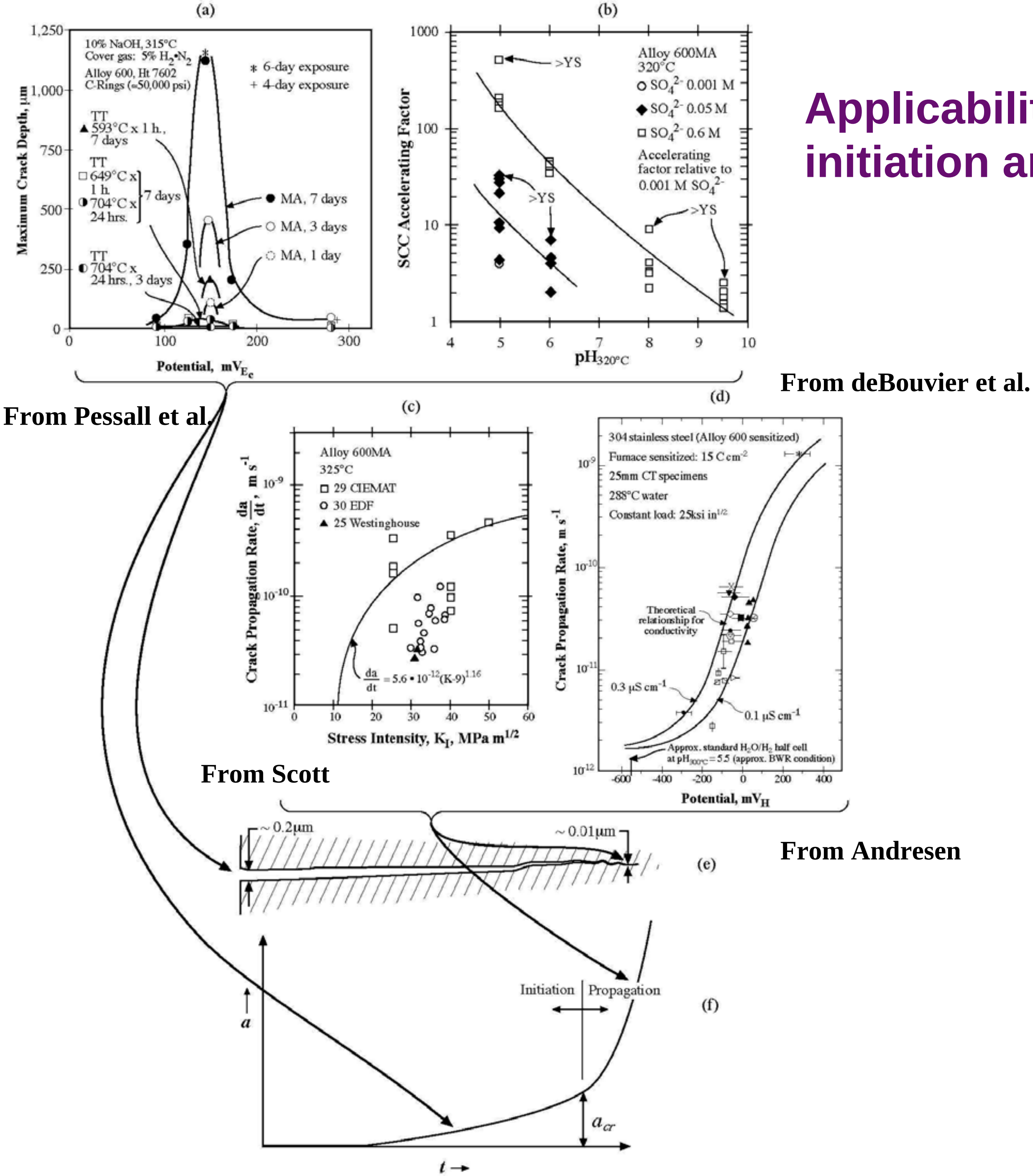
No dislocations associated with crack tip regardless of view of foil

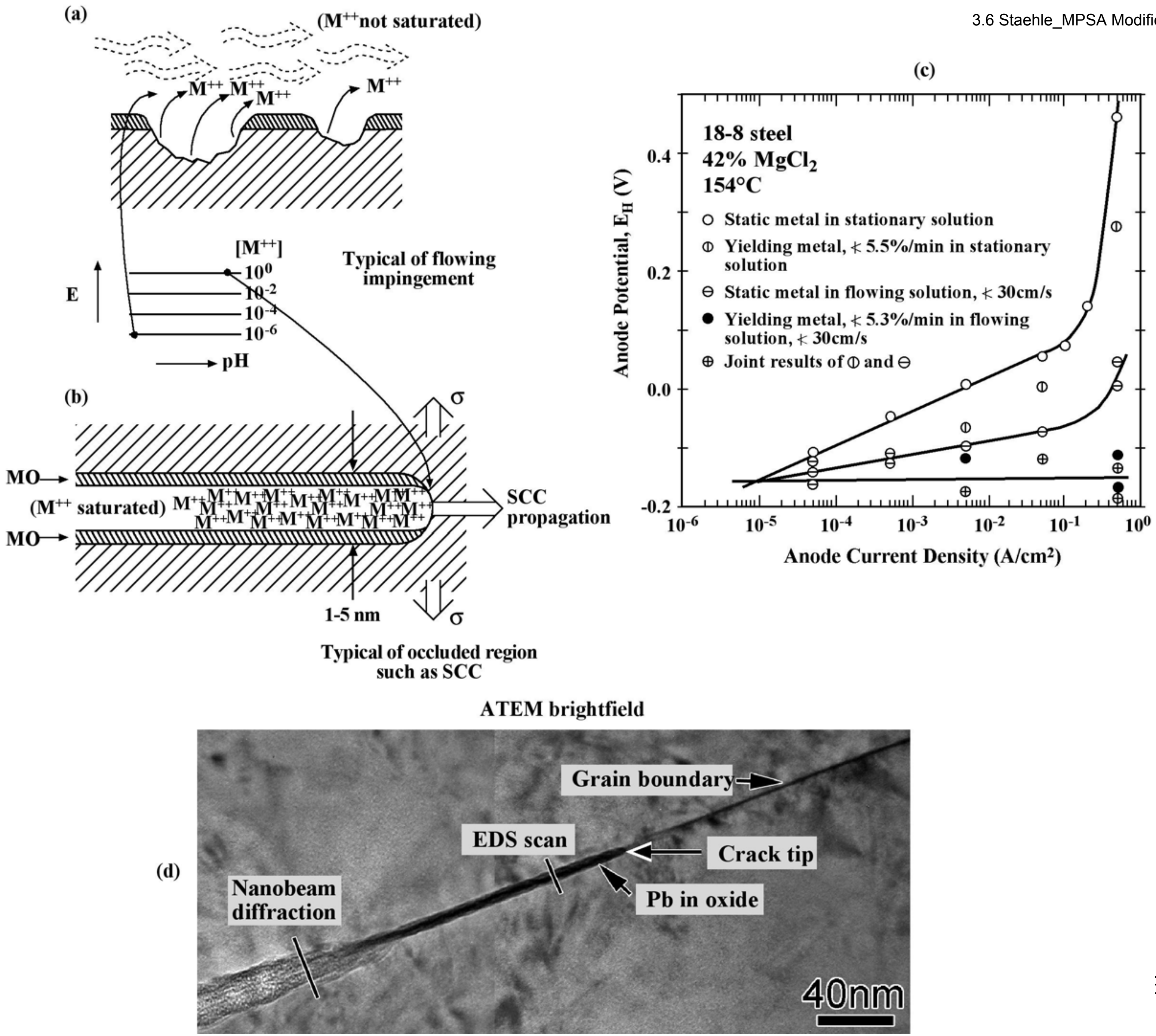
From Thomas and Bruemmer



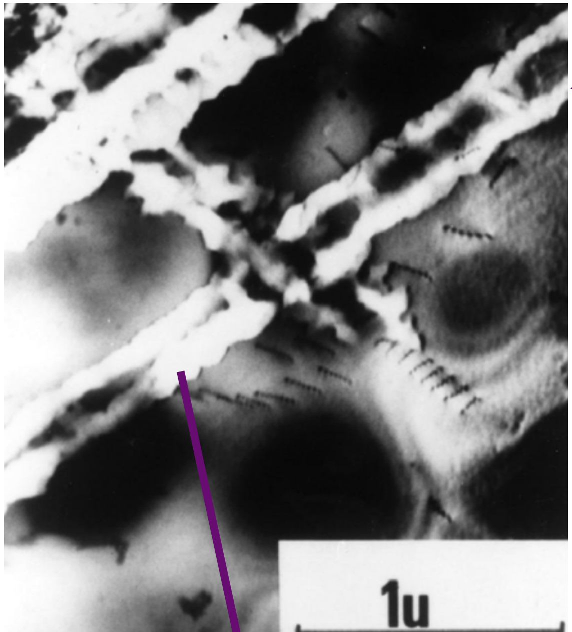
Nine segments of SCC in terms of initiation and propagation

Applicability of data to initiation and propagation

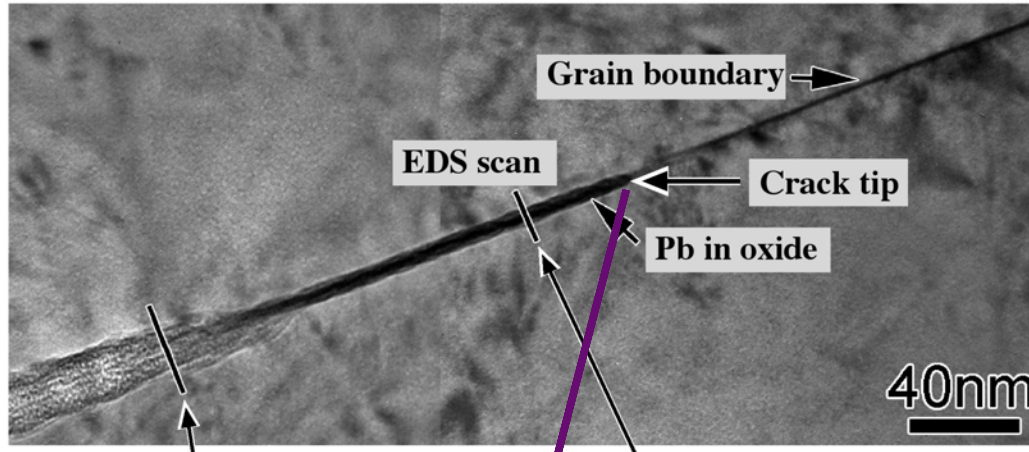



(a)
(M++not saturated)
M++ M++ M++
M++
[M++]
10^0
10^-2
10^-4
10^-6
E
pH
Typical of flowing impingement
(b)
σ
MO
(M++ saturated)
MO
SCC propagation
1-5 nm
σ
Typical of occluded region such as SCC
(c)
18-8 steel
42% MgCl2
154°C
Static metal in stationary solution
Yielding metal, ⋞ 5.5%/min in stationary solution
Static metal in flowing solution, ⋞ 30cm/s
Yielding metal, ⋞ 5.3%/min in flowing solution, ⋞ 30cm/s
Joint results of ⦶ and ⊖
Anode Potential, E_H (V)
0.4
0.2
0.0
-0.2
10^-6
10^-5
10^-4
10^-3
10^-2
10^-1
10^0
Anode Current Density (A/cm²)
ATEM brightfield
(d)
Grain boundary
EDS scan
Crack tip
Pb in oxide
Nanobeam diffraction
40nm

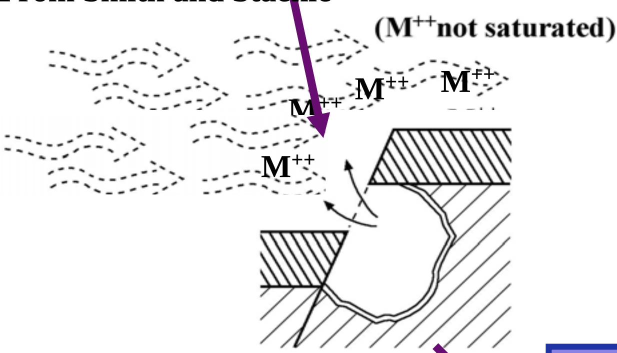
Mass transfer in dissolution at initiation and propagation

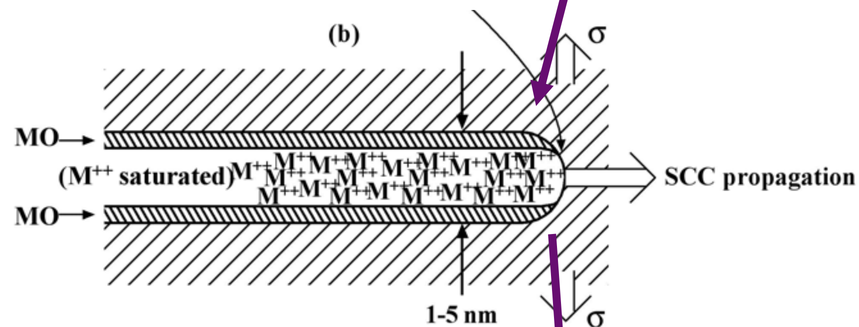


From Smith and Staehle



From Thomas and Bruemmer

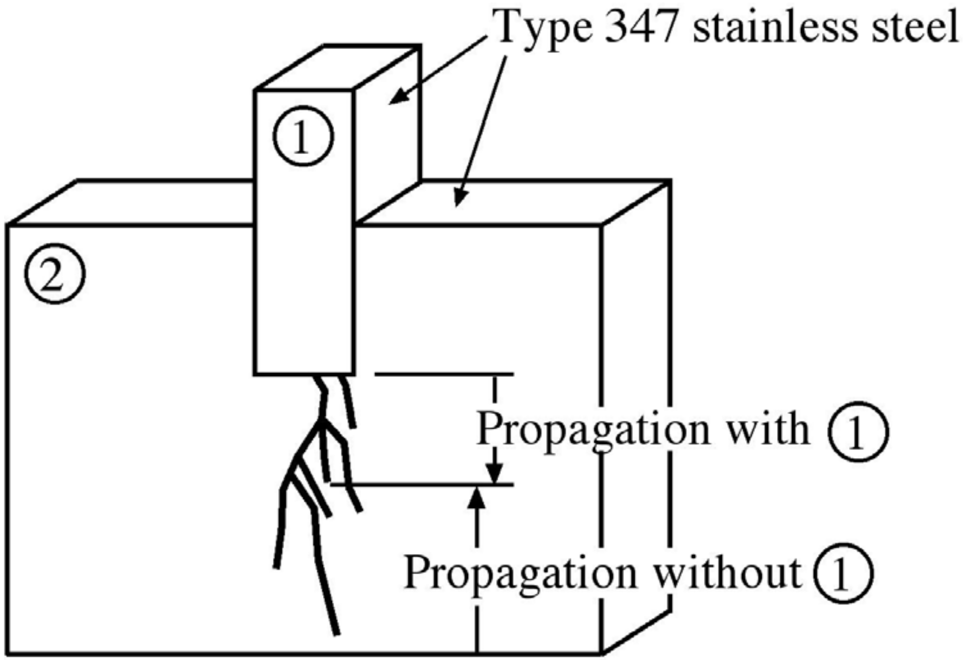




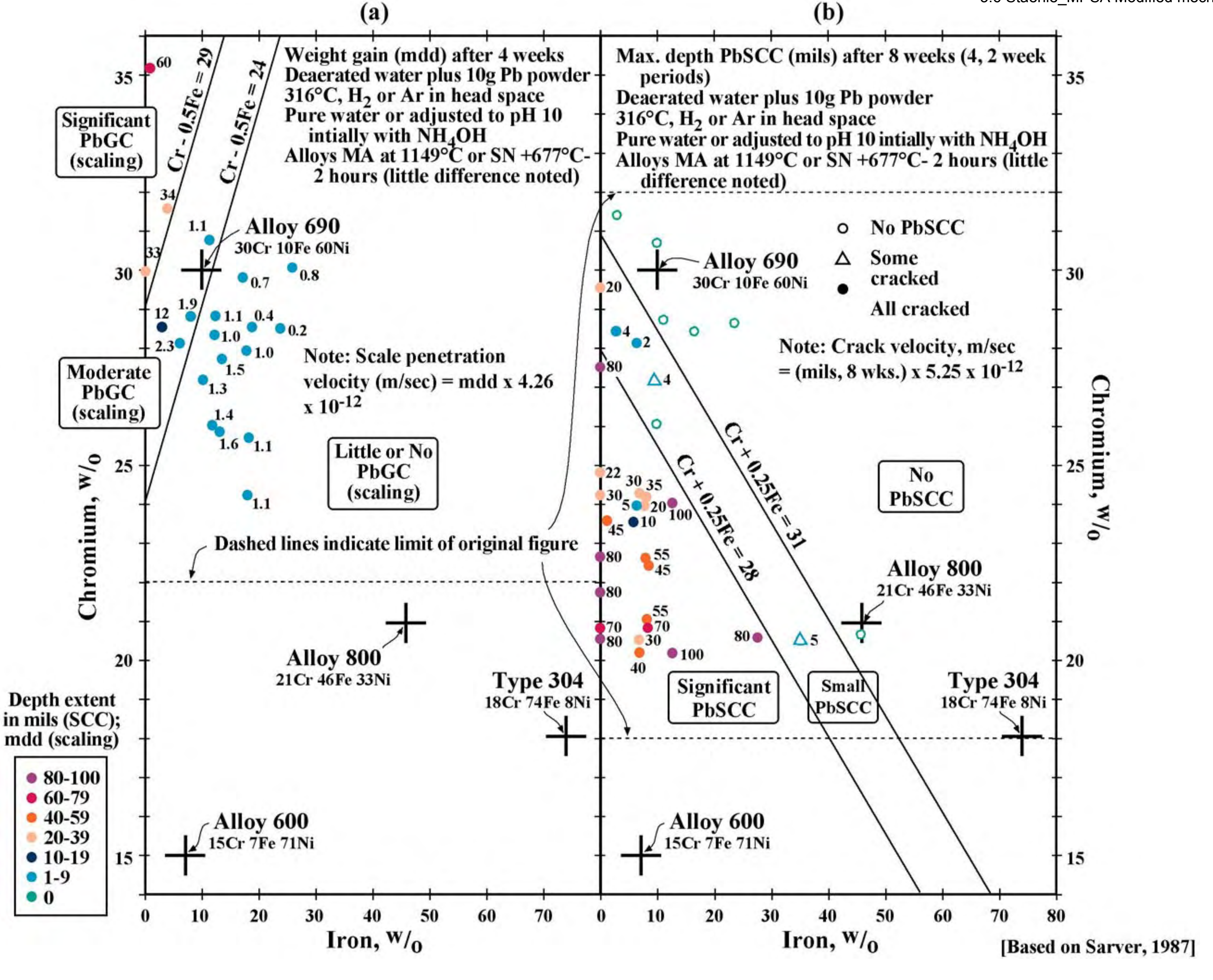
Initiation (Non inhibited mass transport)

Crack tip (Inhibited mass transport)

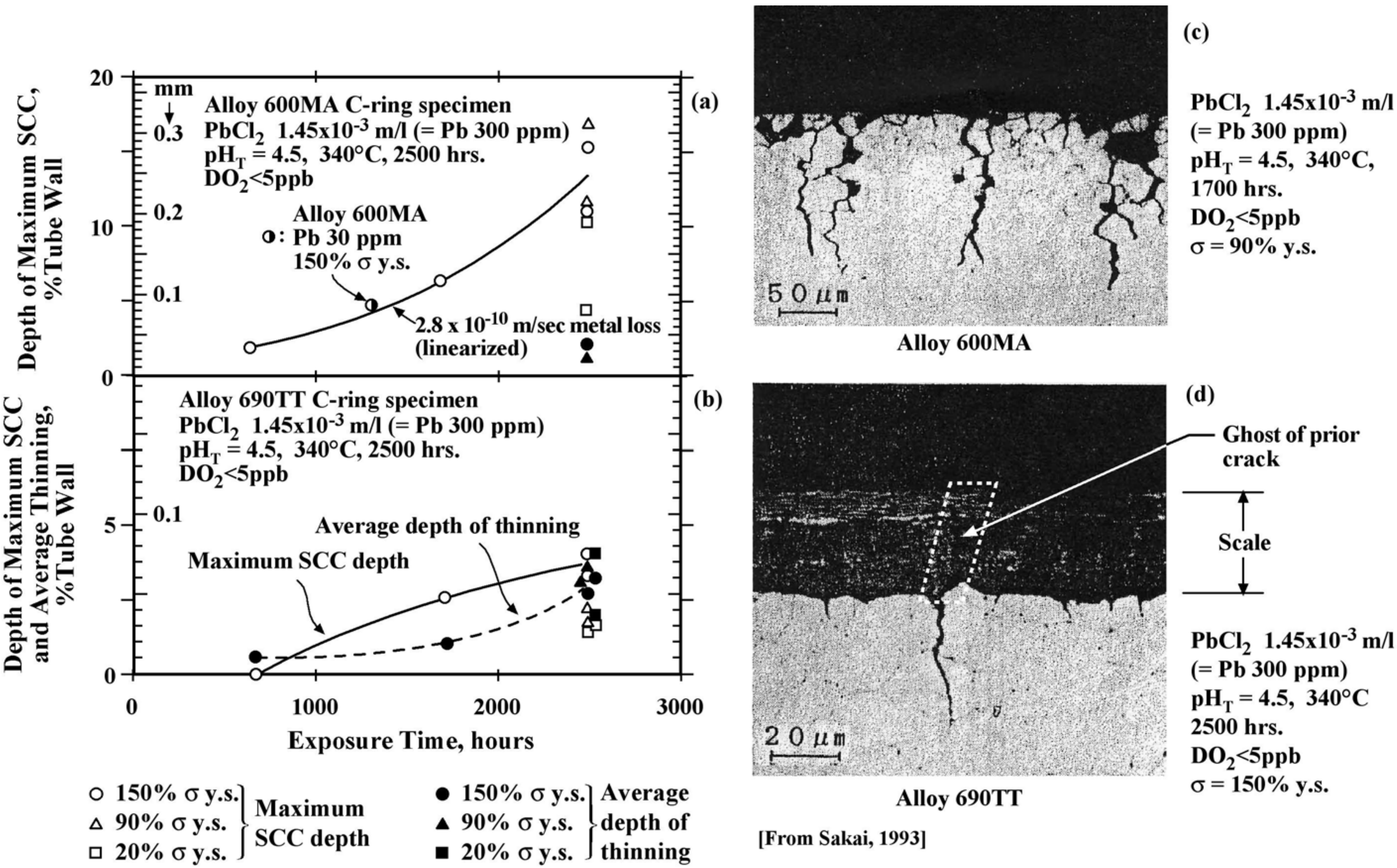
Corrosion products expand to produce stresses in near surface domain

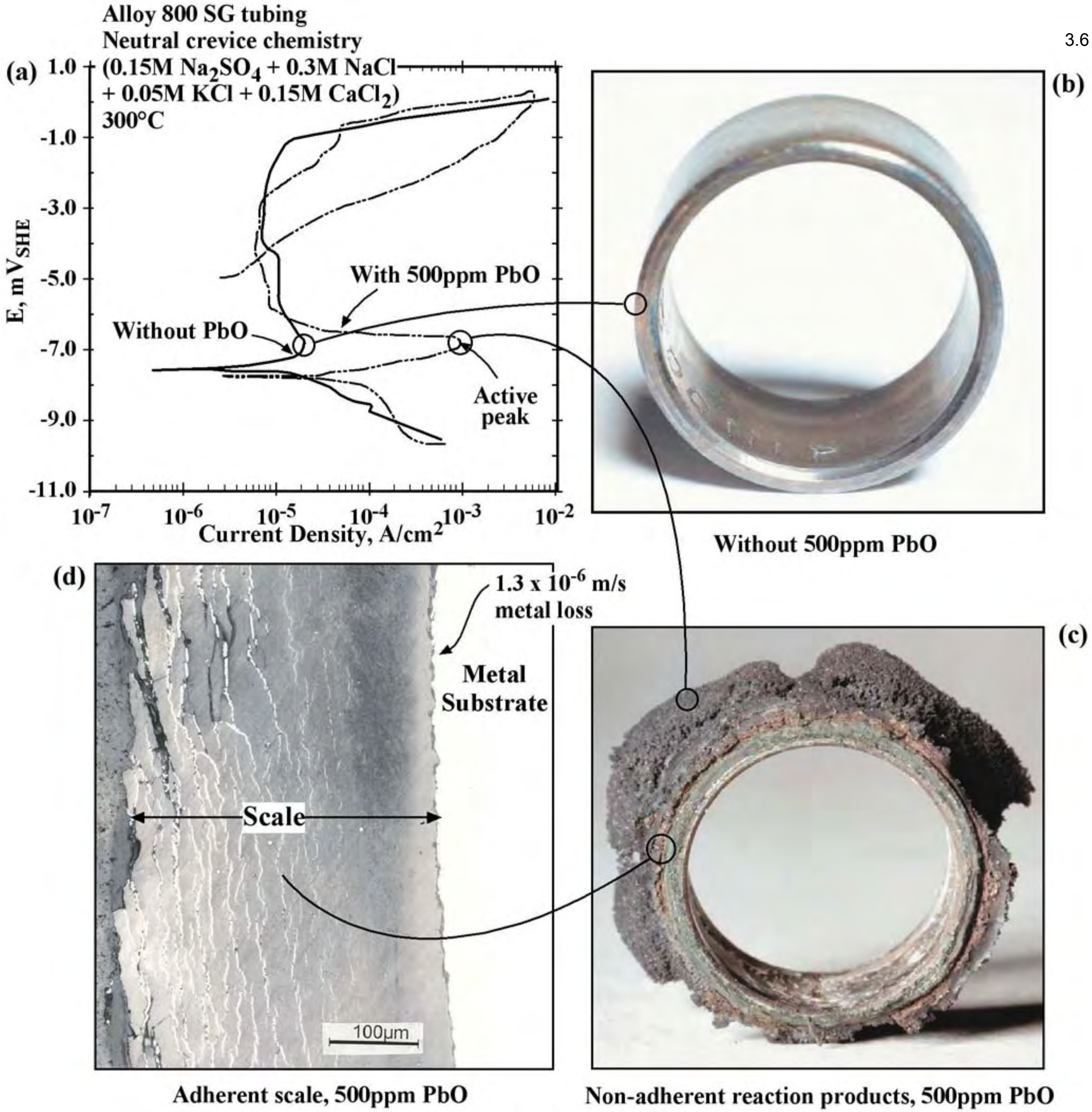


Exposed at 204°C in vapor condensation phase of 2% NaCl + 3% HNO_3 solution



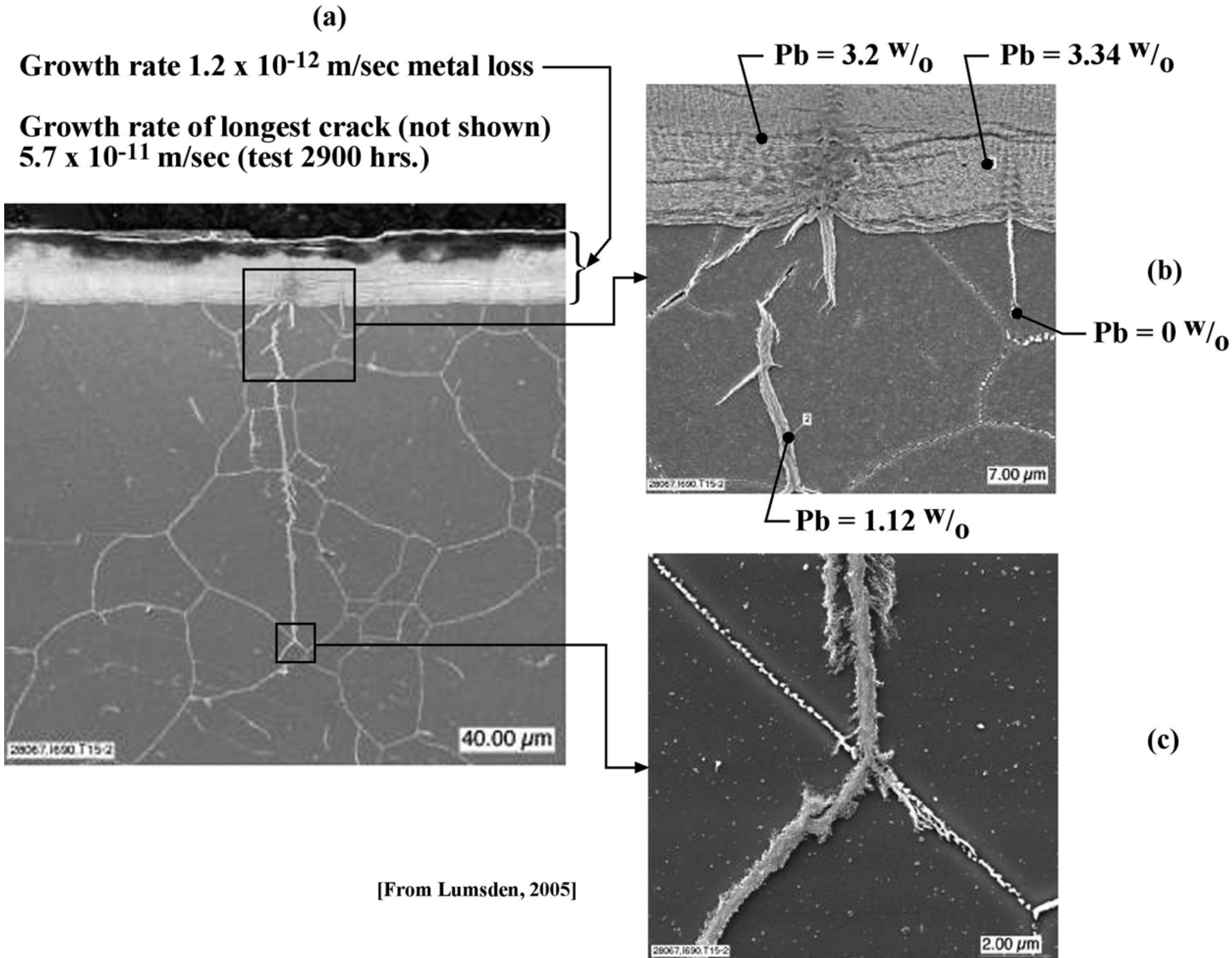
(a)
(b)
Weight gain (mdd) after 4 weeks
Deaerated water plus 10g Pb powder
316°C, H_2 or Ar in head space
Pure water or adjusted to pH 10 intially with NH_4OH
Alloys MA at 1149°C or SN +677°C- 2 hours (little difference noted)
Cr - 0.5Fe = 29
Cr - 0.5Fe = 24
Significant PbGC (scaling)
Moderate PbGC (scaling)
Little or No PbGC (scaling)
Alloy 690
30Cr 10Fe 60Ni
Note: Scale penetration velocity (m/sec) = mdd x 4.26 x 10^{-12}
Dashed lines indicate limit of original figure
Alloy 800
21Cr 46Fe 33Ni
Type 304
18Cr 74Fe 8Ni
Alloy 600
15Cr 7Fe 71Ni
Depth extent in mils (SCC); mdd (scaling)
80-100
60-79
40-59
20-39
10-19
1-9
0
Max. depth PbSCC (mils) after 8 weeks (4, 2 week periods)
Deaerated water plus 10g Pb powder
316°C, H_2 or Ar in head space
Pure water or adjusted to pH 10 intially with NH_4OH
Alloys MA at 1149°C or SN +677°C- 2 hours (little difference noted)
No PbSCC
Some cracked
All cracked
Note: Crack velocity, m/sec = (mils, 8 wks.) x 5.25 x 10^{-12}
Cr + 0.25Fe = 31
Cr + 0.25Fe = 28
No PbSCC
Significant PbSCC
Small PbSCC
Chromium, w/o
Iron, w/o
[Based on Sarver, 1987]


(a)
Alloy 600MA C-ring specimen
PbCl2 1.45x10-3 m/l (= Pb 300 ppm)
pHT = 4.5, 340°C, 2500 hrs.
DO2<5ppb
Alloy 600MA
Pb 30 ppm
150% σ y.s.
2.8 x 10-10 m/sec metal loss
(linearized)
mm
0.3
0.2
0.1
Depth of Maximum SCC, %Tube Wall
20
10
0
(b)
Alloy 690TT C-ring specimen
PbCl2 1.45x10-3 m/l (= Pb 300 ppm)
pHT = 4.5, 340°C, 2500 hrs.
DO2<5ppb
Average depth of thinning
Maximum SCC depth
Depth of Maximum SCC and Average Thinning, %Tube Wall
5
0.1
0
1000
2000
3000
Exposure Time, hours
150% σ y.s.
90% σ y.s.
20% σ y.s.
Maximum SCC depth
150% σ y.s.
90% σ y.s.
20% σ y.s.
Average depth of thinning
(c)
50 μm
Alloy 600MA
PbCl2 1.45x10-3 m/l
(= Pb 300 ppm)
pHT = 4.5, 340°C,
1700 hrs.
DO2<5ppb
σ = 90% y.s.
(d)
Ghost of prior crack
Scale
20 μm
Alloy 690TT
PbCl2 1.45x10-3 m/l
(= Pb 300 ppm)
pHT = 4.5, 340°C
2500 hrs.
DO2<5ppb
σ = 150% y.s.
[From Sakai, 1993]

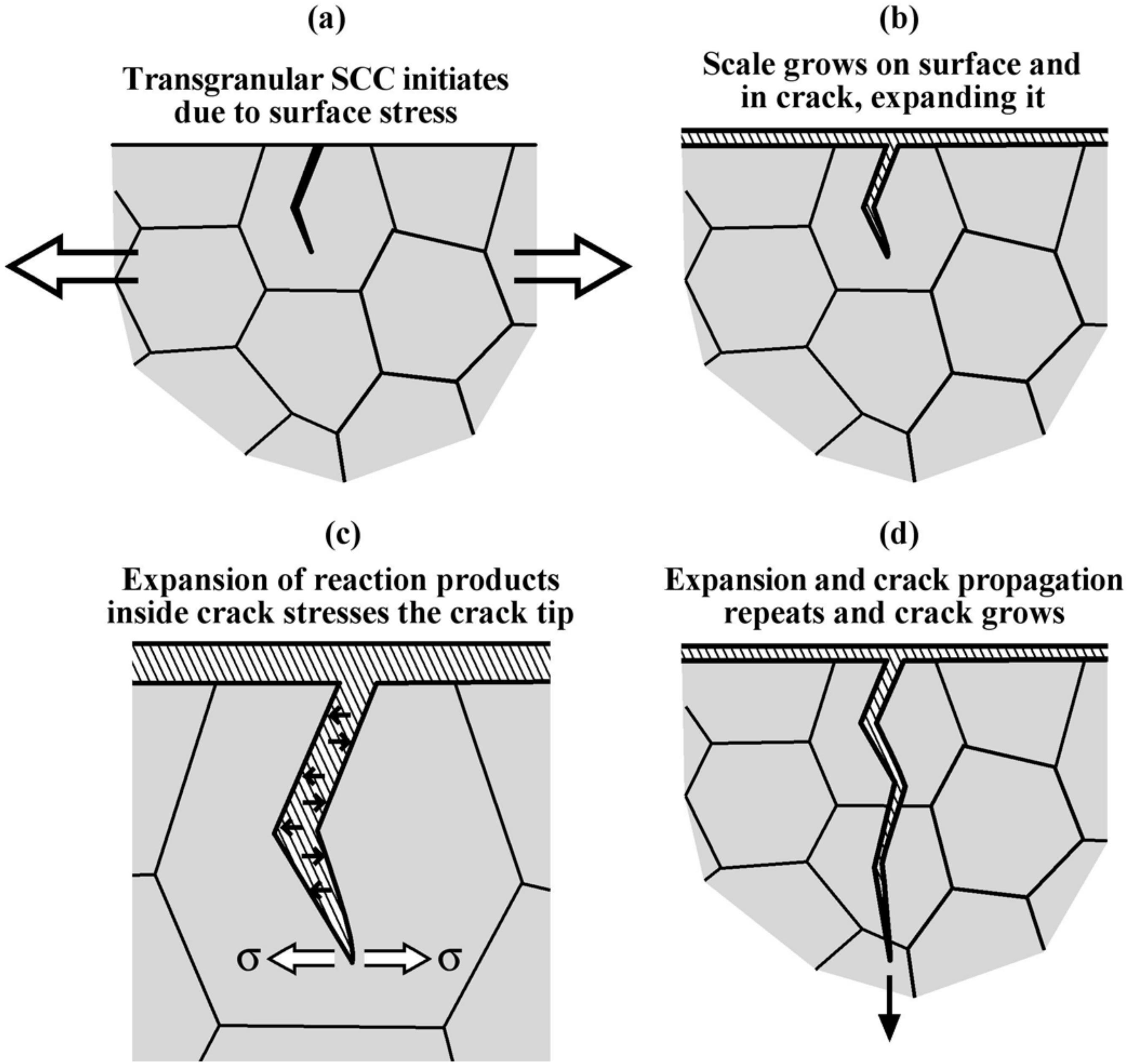


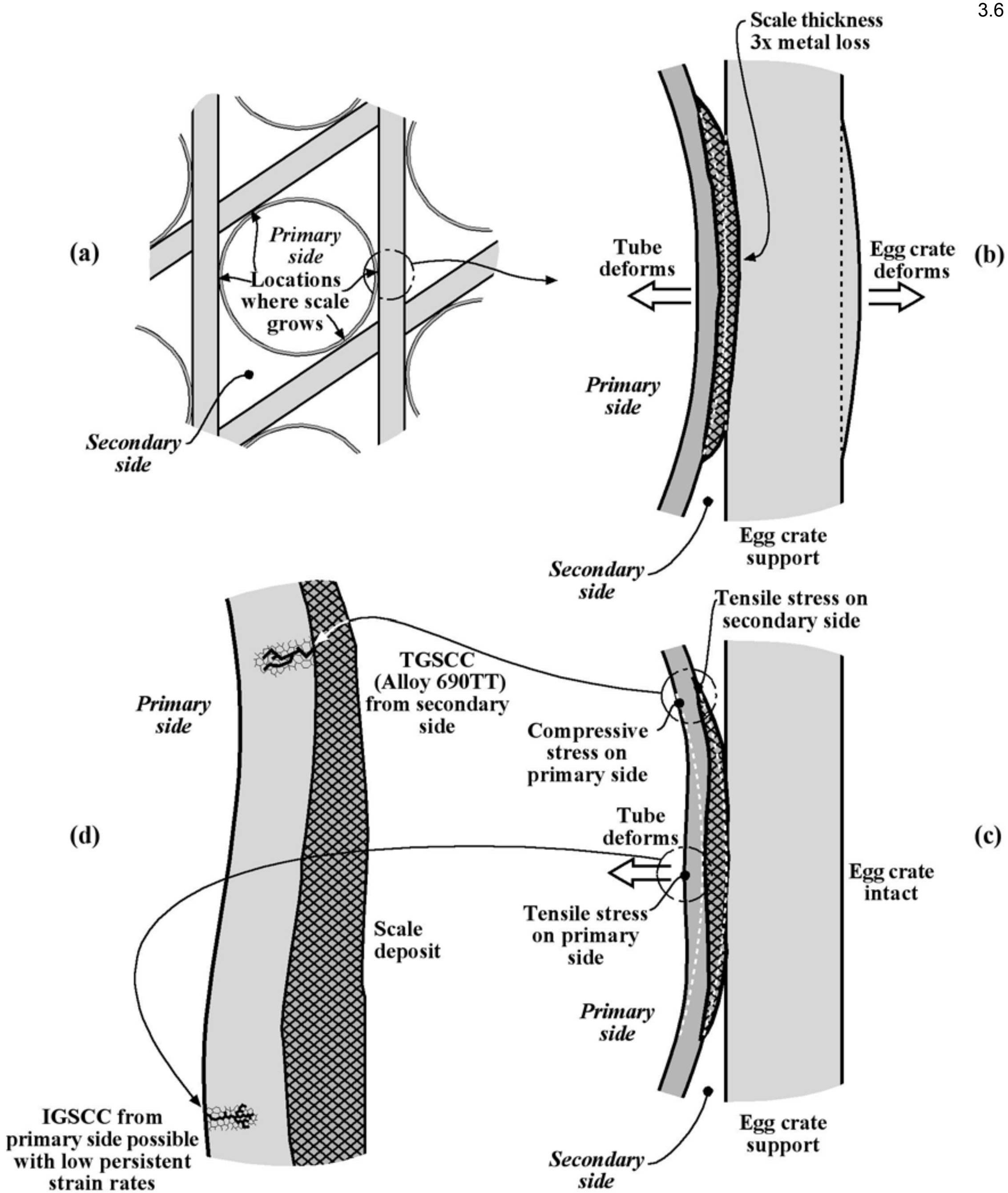
Alloy 800 SG tubing samples, near active peak for 24 hrs.
Neutral crevice chemistry (0.15M Na_2SO_4 + 0.3M NaCl + 0.5M KCl + 0.15M $CaCl_2$), at 300°C

[From Lu, 2005]



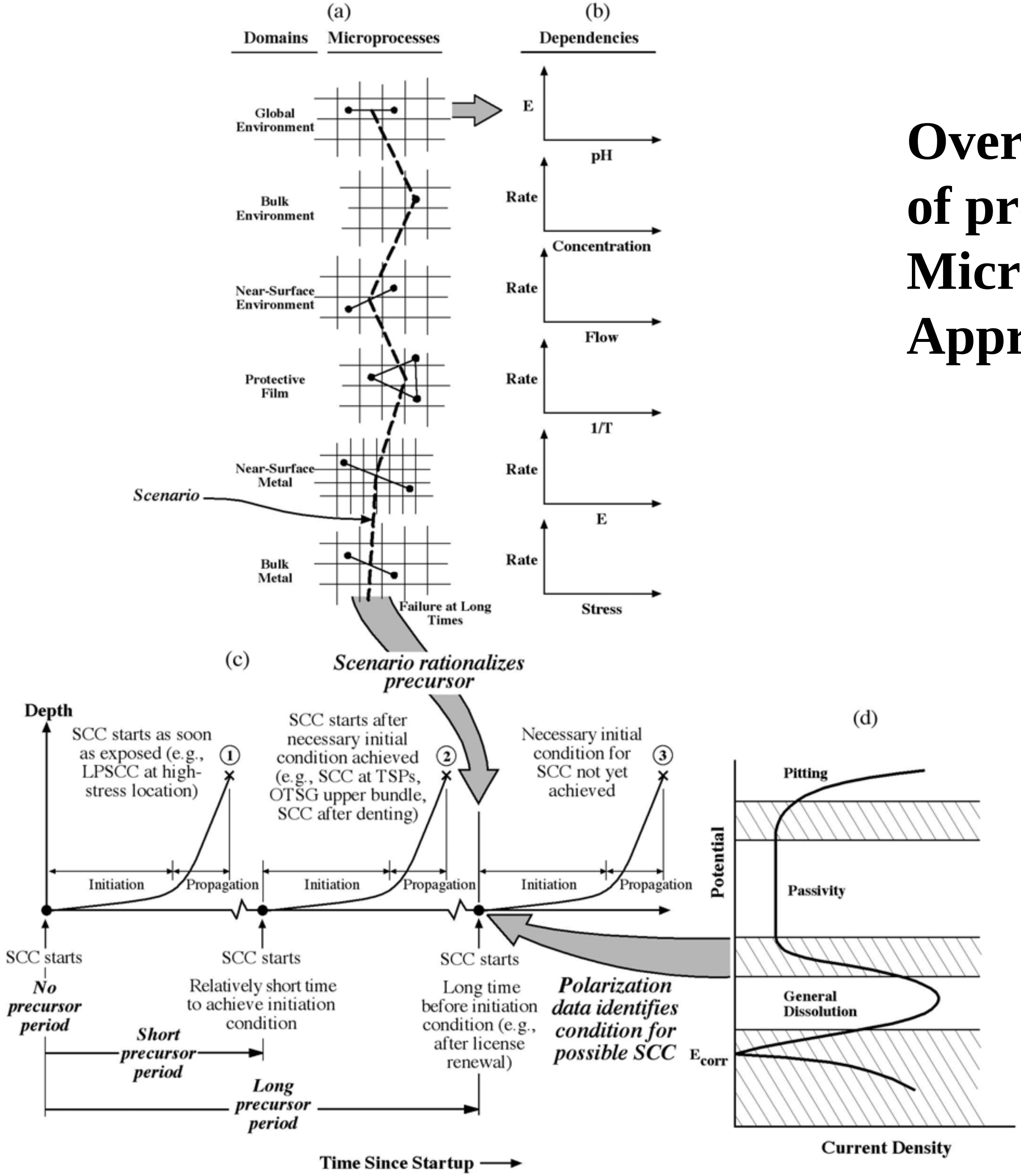
[From Lumsden, 2005]


(a)
Transgranular SCC initiates due to surface stress
(b)
Scale grows on surface and in crack, expanding it
(c)
Expansion of reaction products inside crack stresses the crack tip
σ
σ
(d)
Expansion and crack propagation repeats and crack grows



(a)
Primary side
Locations where scale grows
Secondary side
Scale thickness 3x metal loss
Tube deforms
Egg crate deforms
(b)
Primary side
Secondary side
Egg crate support
Tensile stress on secondary side
TGSCC (Alloy 690TT) from secondary side
Primary side
Compressive stress on primary side
Tube deforms
(d)
(c)
Egg crate intact
Tensile stress on primary side
Scale deposit
Primary side
IGSCC from primary side possible with low persistent strain rates
Secondary side
Egg crate support

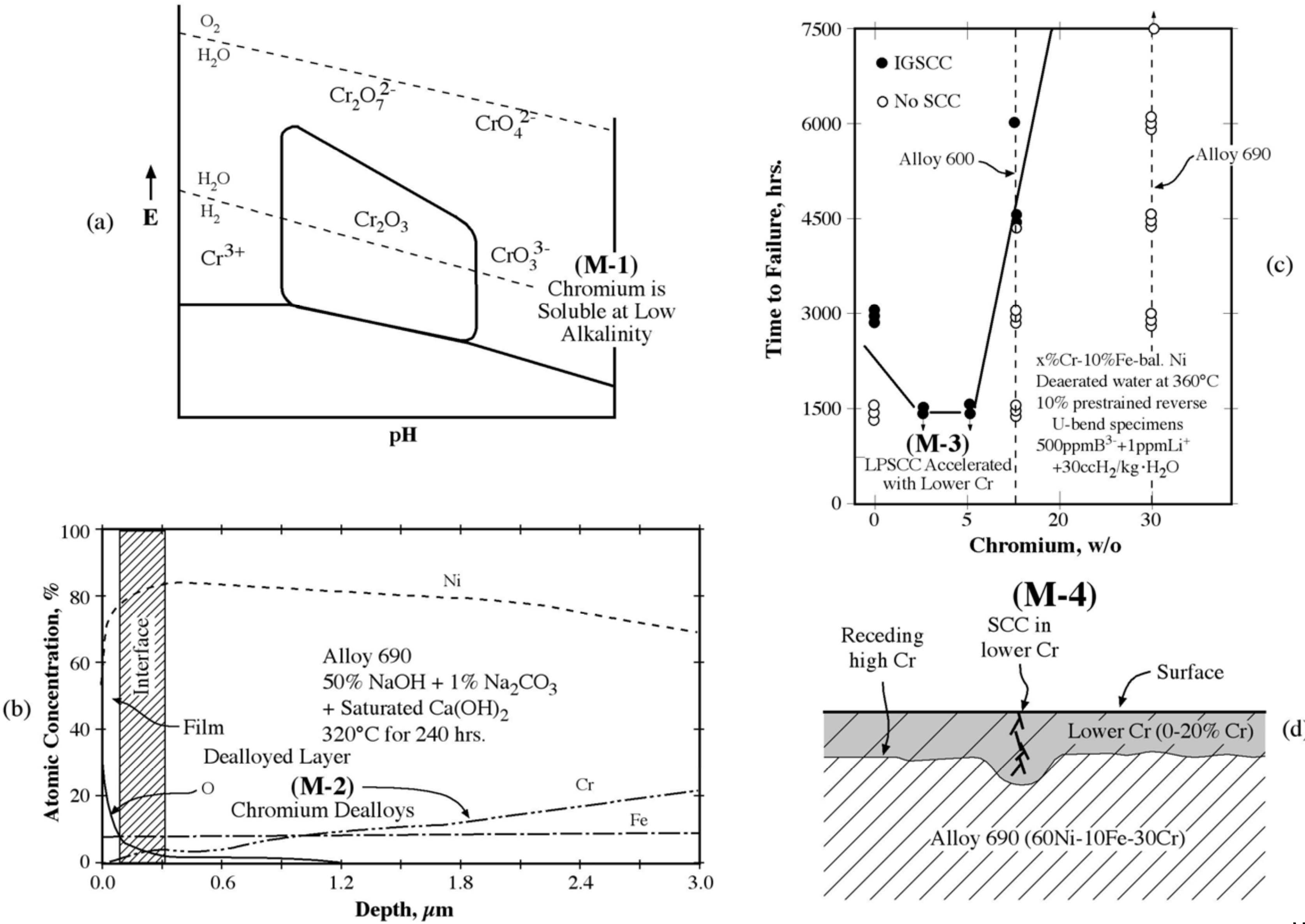
Overall sequence of prediction in Microprocess Sequence Approach (MPSA)



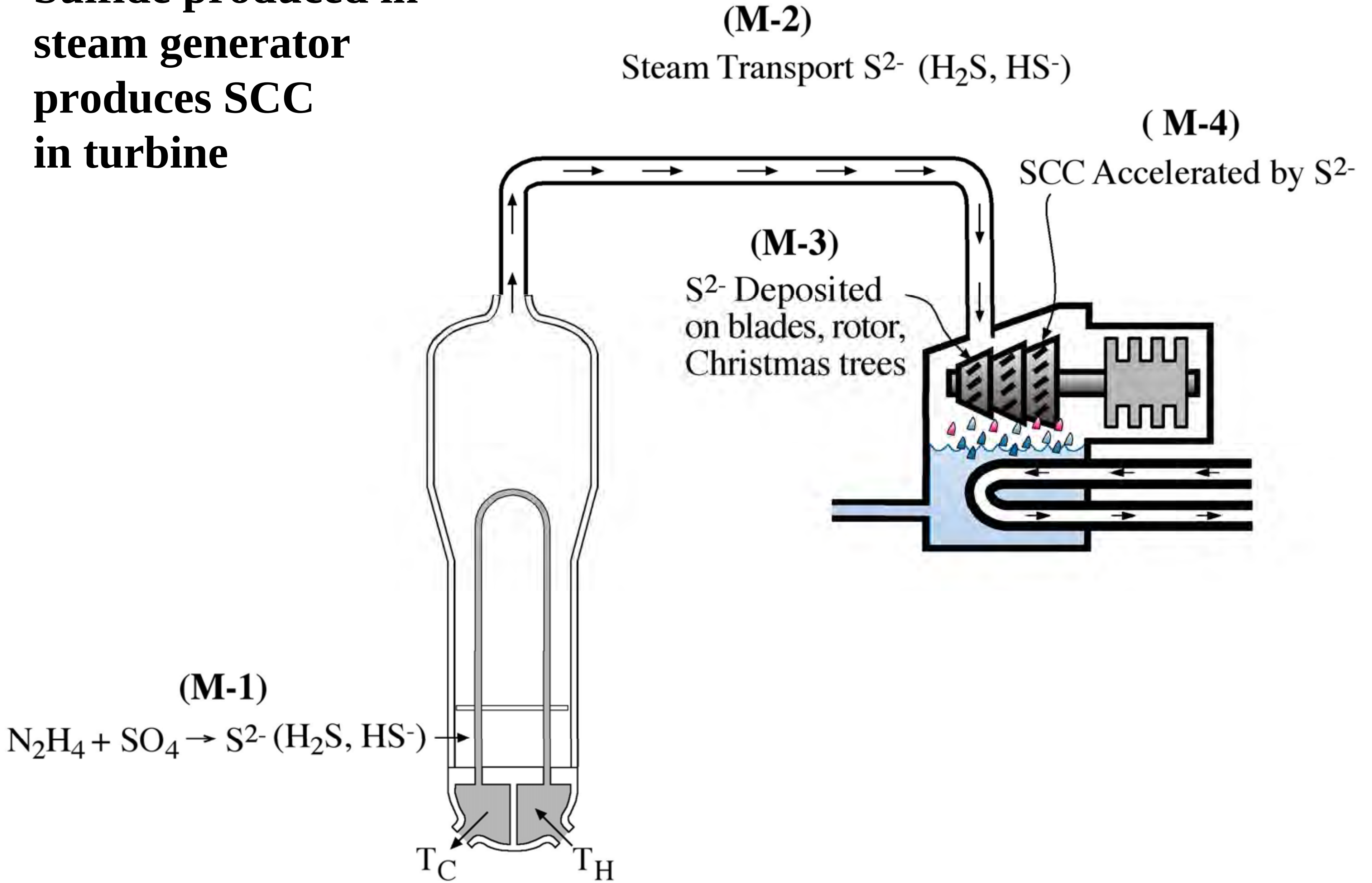
Examples of Predictions

- **Sulfide carryover from SG to turbine related to reduction of sulfates by hydrazine.**
- **Depletion of chromium produces SCC in Alloy 690**
- **Pb accumulation and release produces massive SCC**
- **Changing FAC rate increases SCC probability**

Alloy depletion changes surface composition in Alloy 690 and promotes LPSCC



Sulfide produced in steam generator produces SCC in turbine



Conclusions

1. **Very long time predictions are most probably related to the development of precursor conditions.**

2. **The formation and effects of precursor conditions can be assessed by identifying domains and their microprocesses followed by the selection of scenarios. This requires expert judgment**

3. **The target or objective of scenarios that lead to accelerated failures can be assessed by scoping experiments that identify possible conditions for fast failures.**

4. **Predicting failure at long times then is based on identifying likely scenarios for precursors and connecting them with critical conditions for rapid failures.**

3.6 Staehle_MPSA Modified mech PMDA

Topics for Proactive Materials Degradation Assessment

May 2006

Allen Baum

PMDM Materials and Mechanisms Topics

- SG Tubing SCC
- Weld SCC
- Fatigue
- Thick-wall A600 SCC
- Pressure Vessel SCC and BAC
- IASCC
- SCC of Main Steam and Feed Lines (BWR)

SG Tubing SCC

- **Pb + NaOH**
  - **Determine stress dependence for reference chemistries and tubing materials**
    - **Is there a threshold stress for no SCC?**
    - **Is there a threshold degree of cold work for SCC at hydraulically expanded tubesheet joints?**
      - **If so, can NDE identify these locations?**
  - **Quantify Pb transport process between bulk and crack face (ppt to % concentrations)**
    - **Does chemical cleaning promote or prevent further transport?**
  - **Quantify extent of buffering in SG crevices compared to tests**

SG Tubing SCC (continued)

- **Sulfur-species SCC**
  - **Quantify cold work required for SCC at tubesheet joints**
    - **A600SR (OTSG) tubes (mechanically rolled?)**
    - **A600TT and A690TT tubes (hydraulically expanded)**
- **PWSCC (or LPSCC)**
  - **Quantify cold work required for SCC at hydraulically expanded tubesheet joints**

Weld SCC

- Evaluate conditions for crack propagation
  - Apply equally to PWRs and BWRs (vary ECP & temperature)
  - Inconel and stainless
  - Residual and applied stress; applied strain
  - Fabrication and metallurgical anomalies
    - Conditions for crack propagation in 52/152
      - Low-temperature propagation under transient conditions
- Relate identified conditions to NDE capability
- Mitigation techniques

Fatigue

- **Improved quantification of fatigue limits**
  - Effect of environment (ECP, chemistry)
  - Effect of flow
  - Aging effects
- **Detailed identification of plant locations potentially subject to thermal fatigue**
- **Improve FIV technology**
  - Confirmation that developing fixity of SG tubes will not lead to fatigue
  - Confirm that uprate effects are manageable

Thick-Walled A600 SCC

- Characterize weld defect conditions necessary for promoting SCC propagation
  - Surface finish
  - Residual and applied stress/strain
- Aging effects on SCC

Pressure Vessel SCC and Boric Acid Corrosion

- Vessel SCC technology is mature
  - Challenge comes from increased service life
- Dynamic strain aging
- Weld heat-affected zones

- (no additional boric acid testing)

Irradiation Assisted SCC

- Extend database to higher temperatures and fluences
- Effect of Si segregation on crack growth
- Reduced fracture toughness in water compared to air

SCC of Low-Alloy Steel Piping (BWR Feed and Steam Lines)

- Improved quantification of mechanism kinetics
  - Pit formation
  - Microcrack initiation
  - Crack coalescence
- Quantify single effects
  - Ripple loading
  - Dynamic strain aging
  - Heat-affected zones

Some suggested PMDM projects
R. W. Staehle

Topic #1: Initiation and propagation of SCC in cold worked stainless steel and Alloys 600 and 690: Fundamental assessments of crack tips

Topic #2: Measurement of accumulation of Pb, as well as S^{y-} in line contact crevices of steam generators

Topic #3: Reduction of high valence sulfur species to lower valence aggressive species

Topic #4: Long term LPSCC of Alloy 690TT

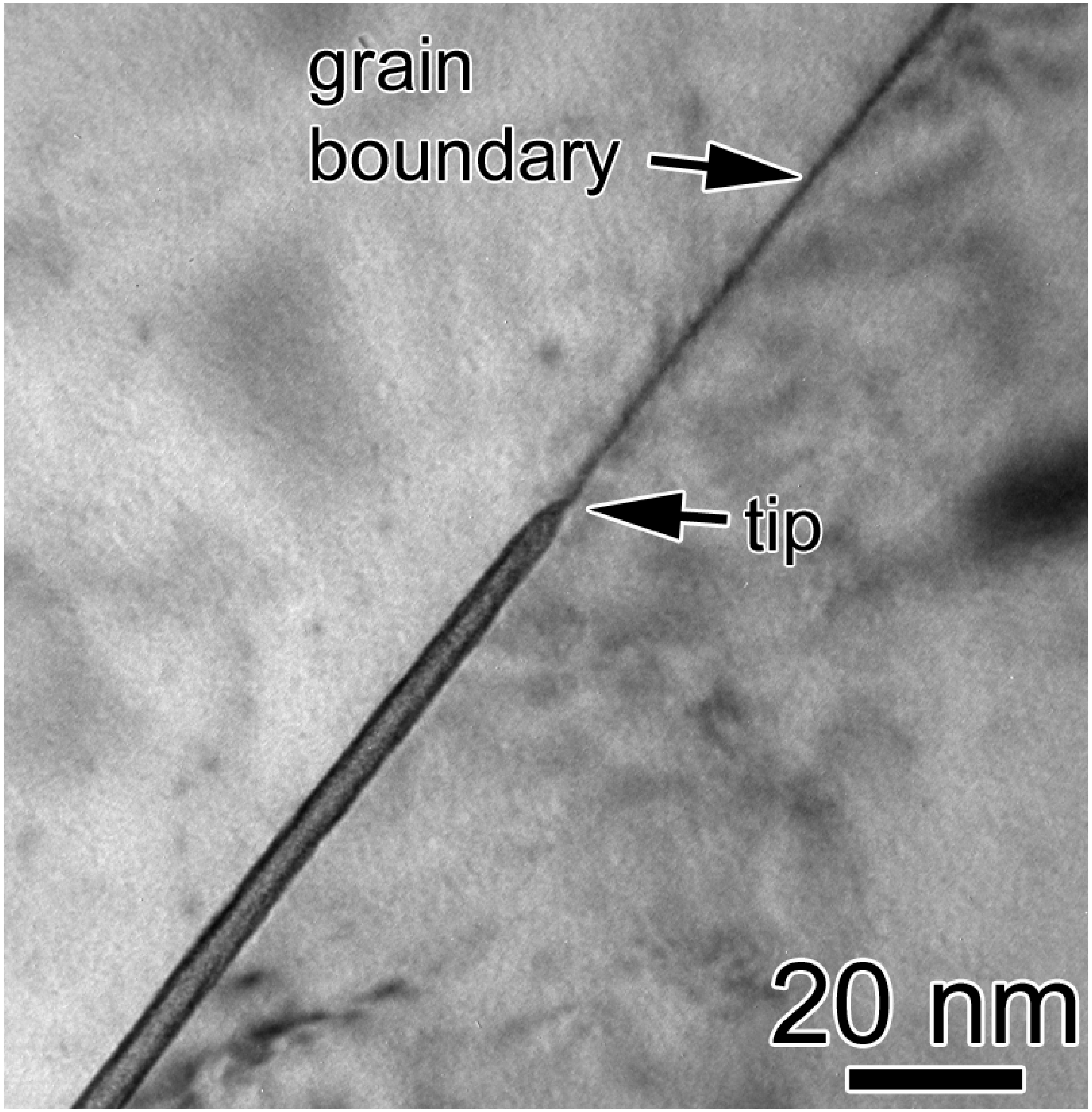
Topic #5: SCC and mitigation for Alloy 600TT and 690TT in Pb^{-} and S^{y-} contaminated solutions

Topic #6: Scaling of Alloy 690TT in Pb-containing environments

A paradigm shift--the “tight crack”

(based on some ATEM evidence from Bruemmer and Thomas)

Bright field



Crack tip in range of 1-5 nm

Alloy 600, 320°C PbO experiment

From Bruemmer and Thomas

The past framework--

The mechanics definition of crack dimensions

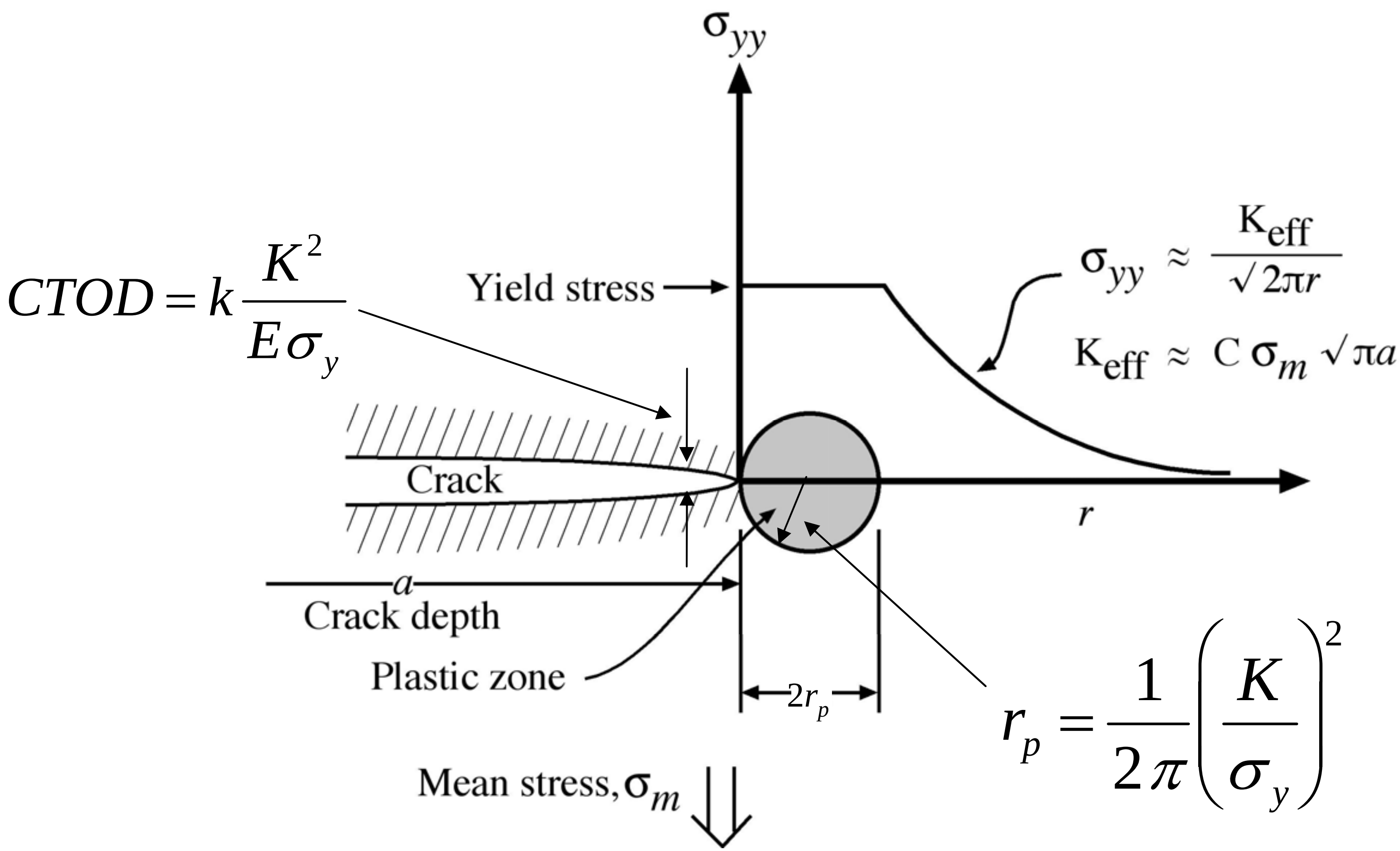
- **Plastic zone size**
- **Crack tip opening displacement, CTOD**

Sample calculations (then converted to metric):

- σ_y = 40 ksi
- σ_m = 20 ksi
- E (Ni) = 16×10^3 ksi
- a = 0.1 in

r_p = 100μm

CTOD = 2.5×10^3nm



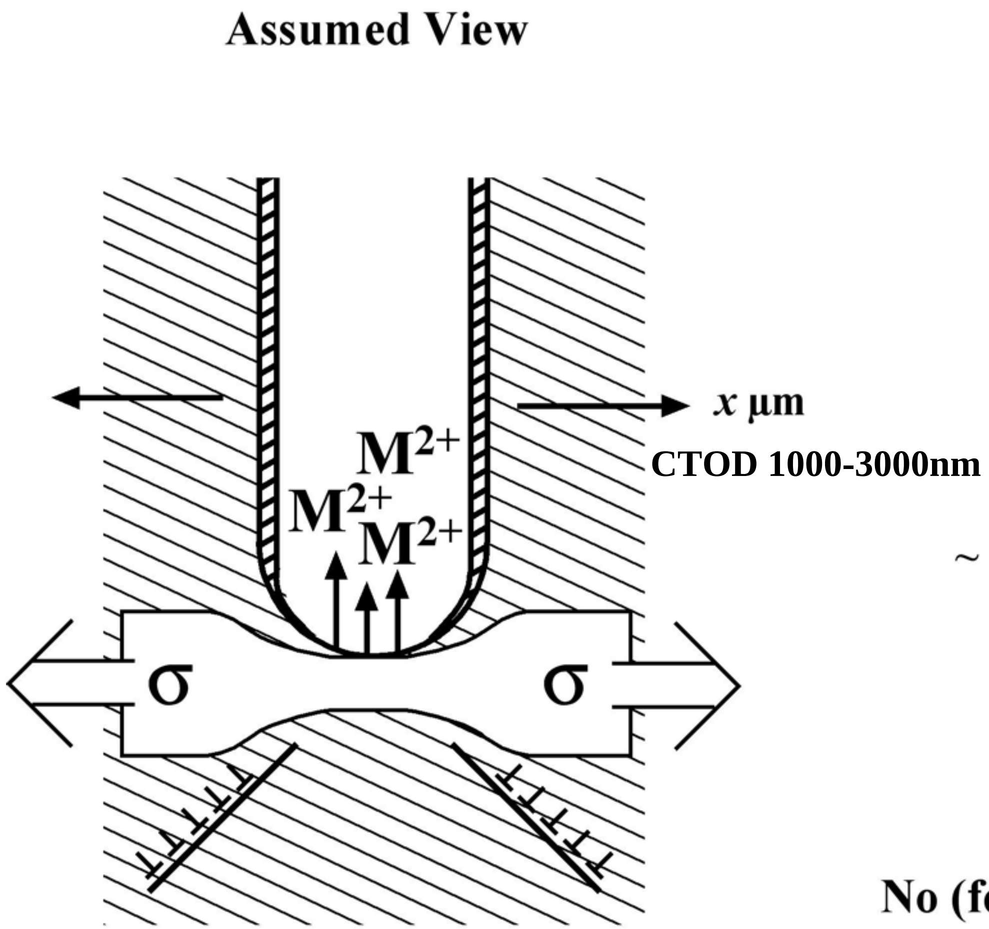
r_p = 100μm

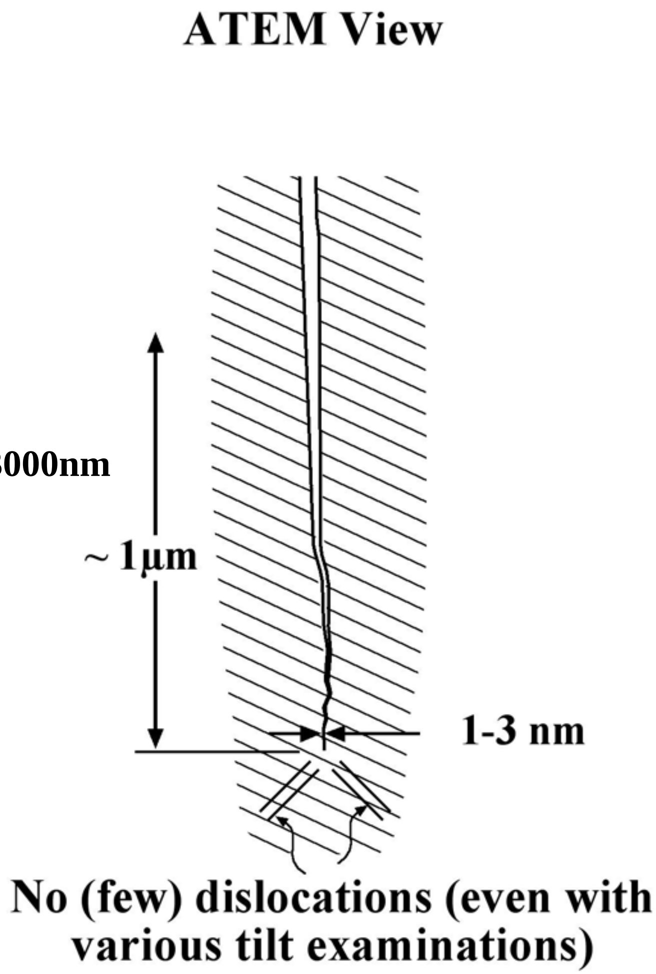
CTOD = 2.5x10^3nm

The paradigm shift

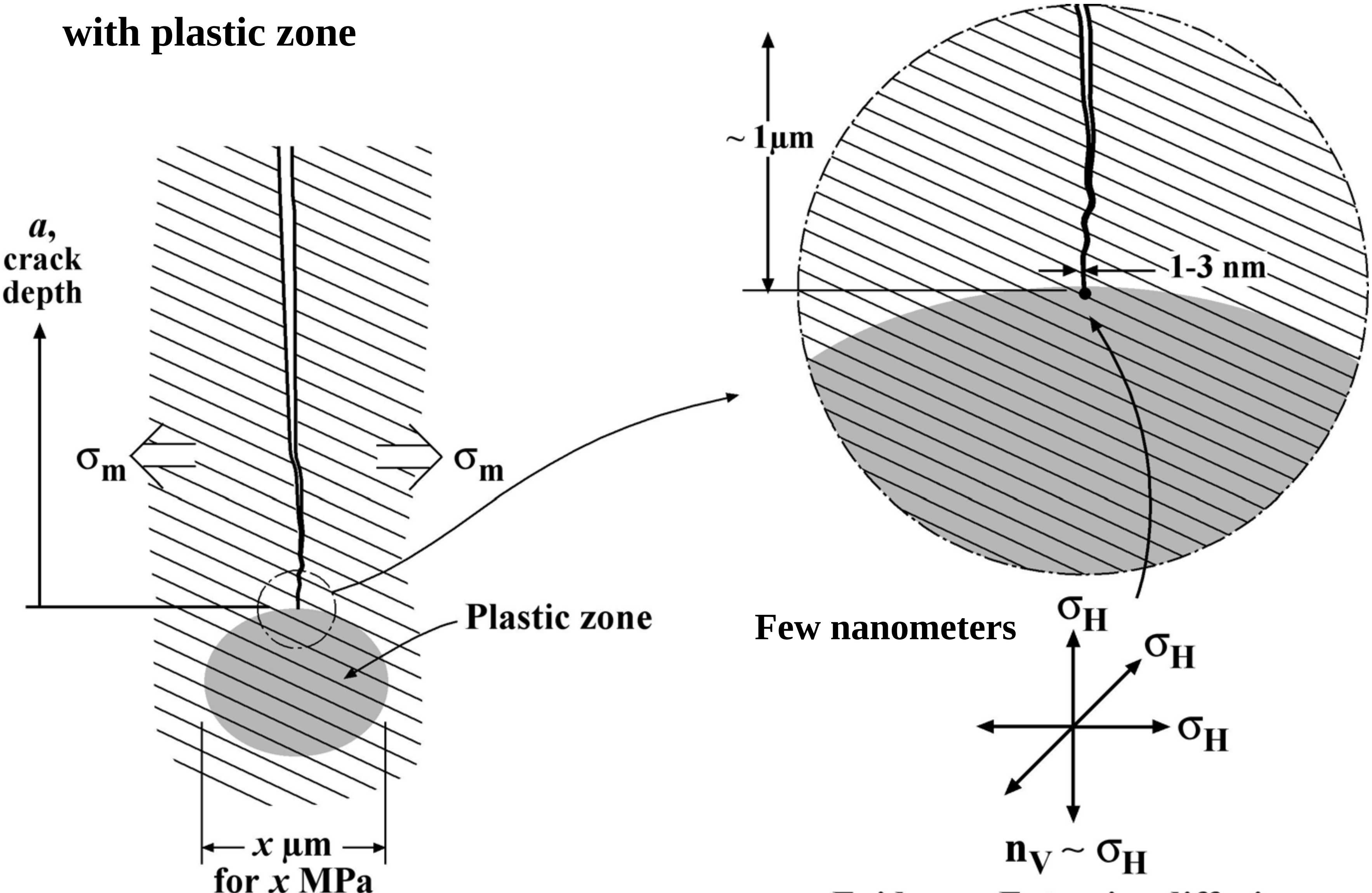
Crack tip width
in range of 1-5 nm

Past assumptions on SCC size relative to ATEM views





Narrow crack interactions with plastic zone



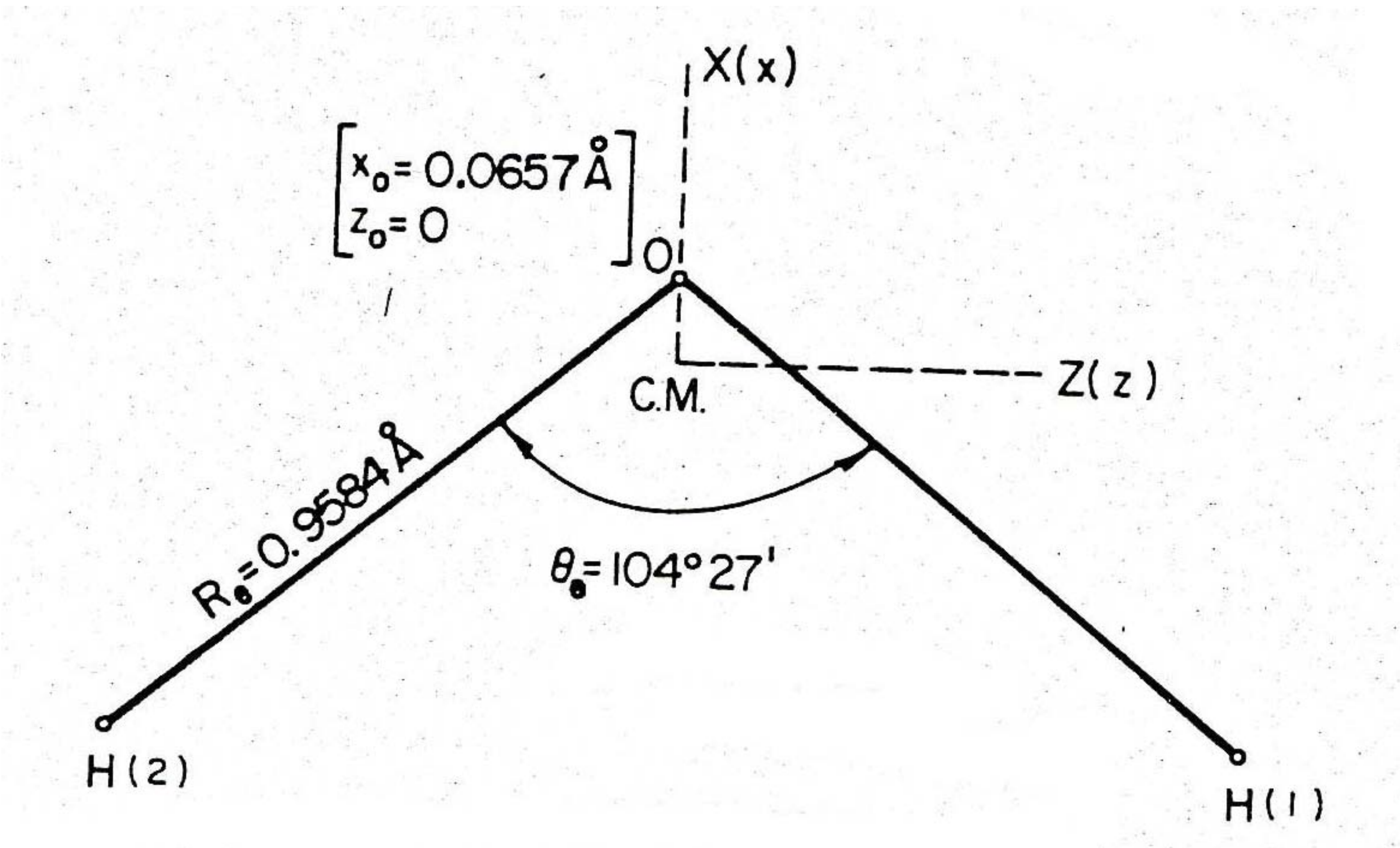
Hundreds of microns

Few nanometers

$n_V \sim \sigma_H$

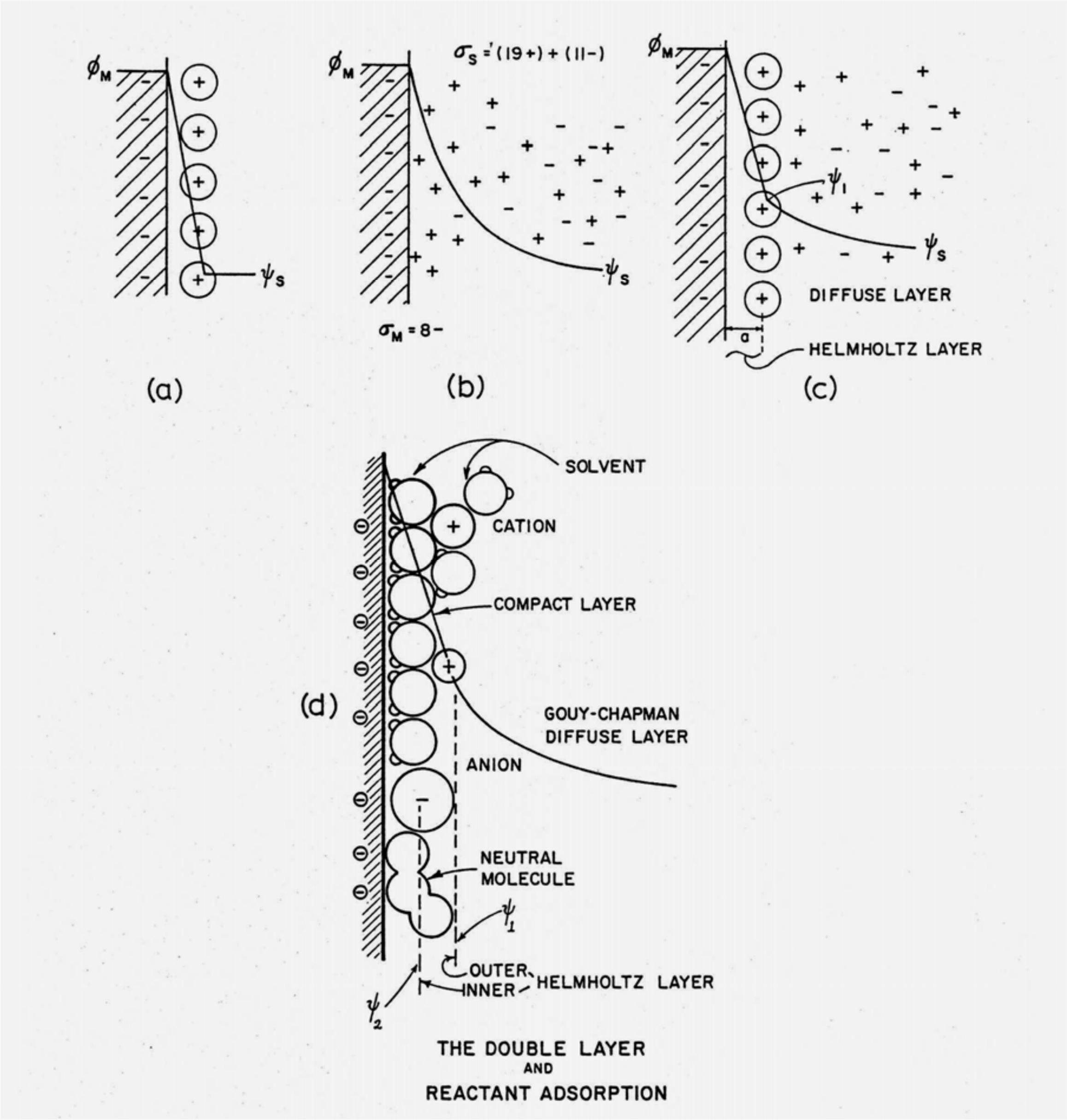
Evidence: Extensive diffusion ahead of tip

Equilibrium geometry of water molecules



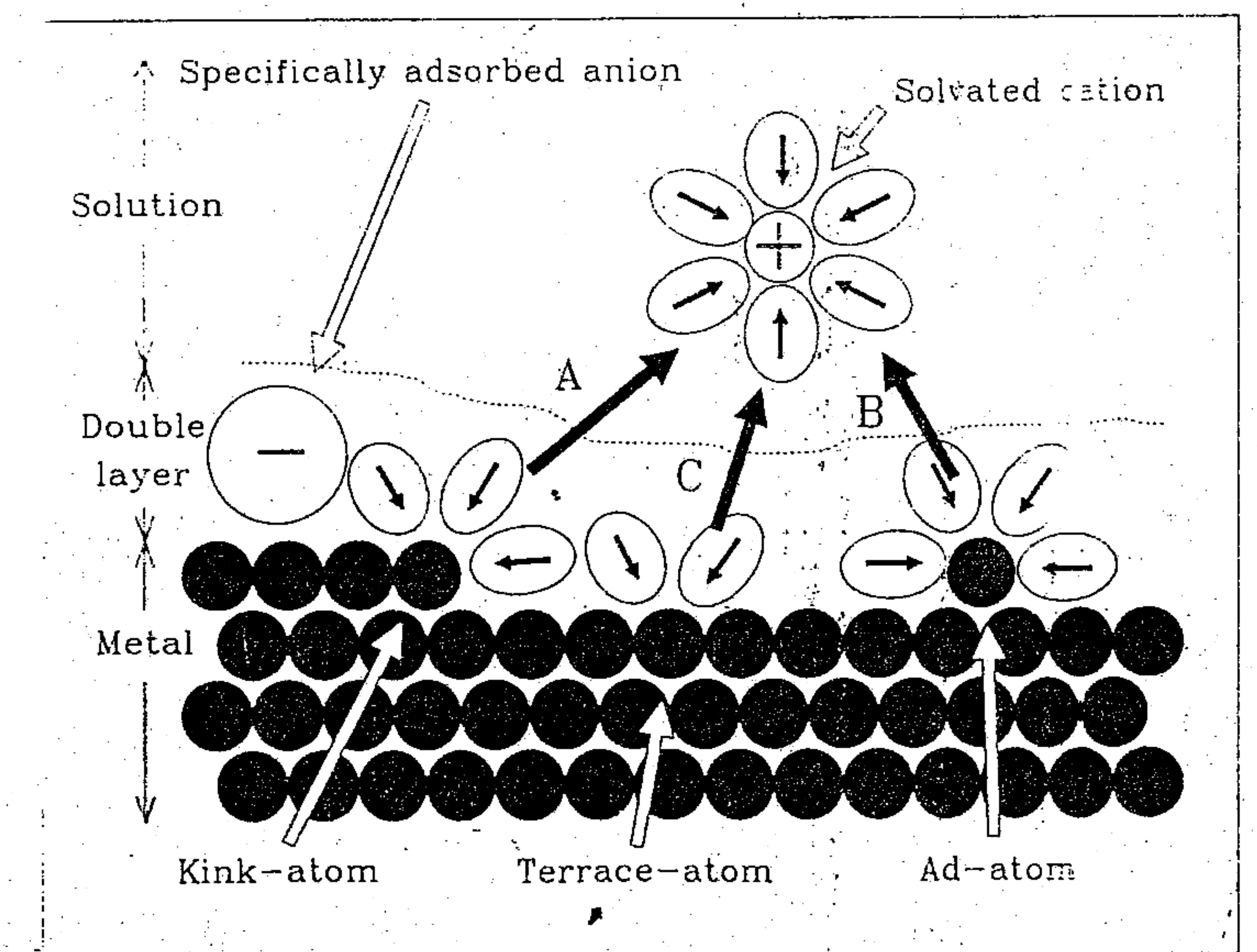
Franks, text

Thicknesses of charged surfaces



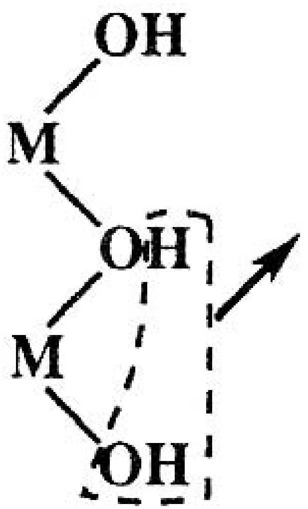
Conway, text

Dimensions associated with solvated and adsorbed species

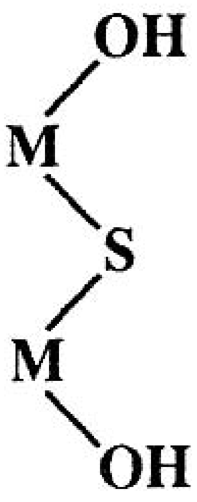


Galvele, 1993

Effect of adsorbed sulfur on the passivation of metals : blocking or retarding effect



In this configuration, passivation is favoured.



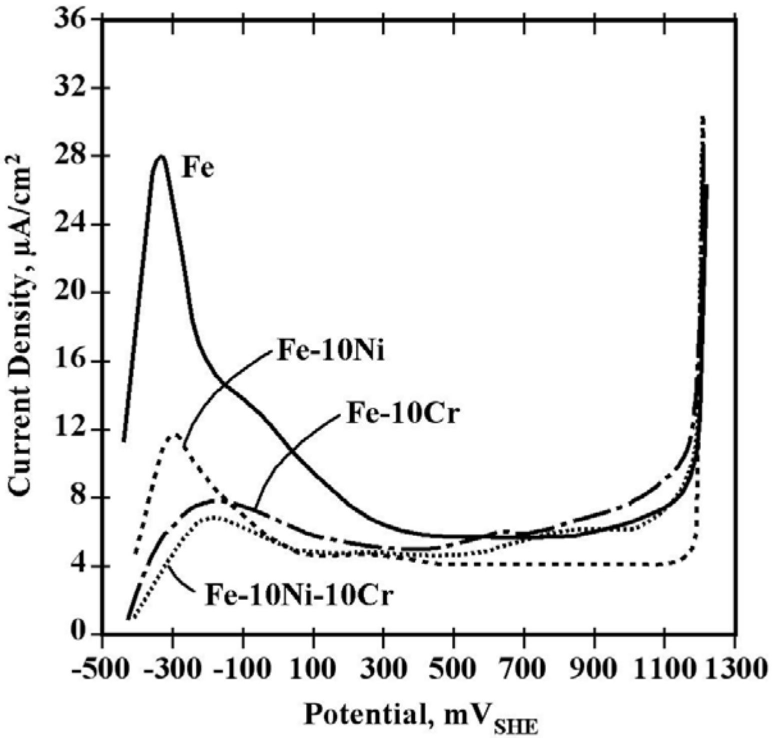
In this configuration, passivation is precluded.

Marcus, Kuwait, 2005

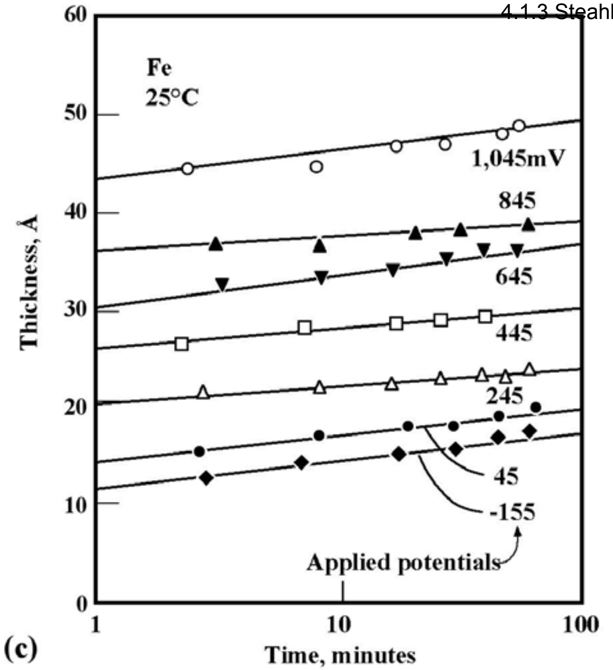
Passive films on iron-base alloys in borate solutions

(Ellipsometric and electrochemical study)

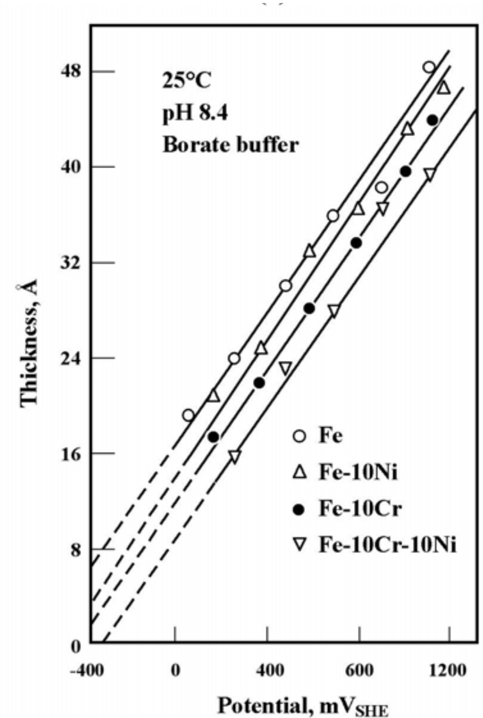
(a)



(b)

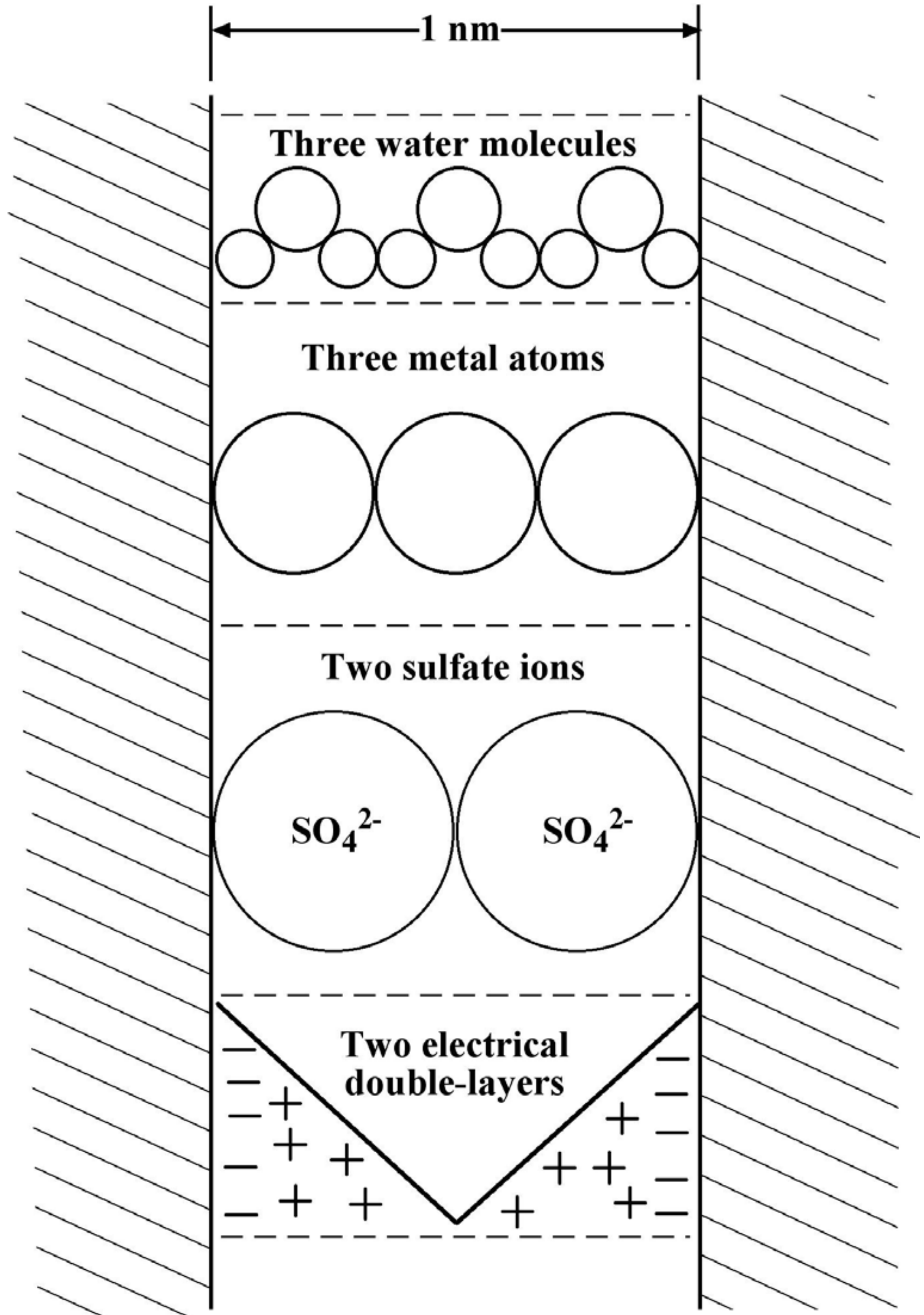


(c)

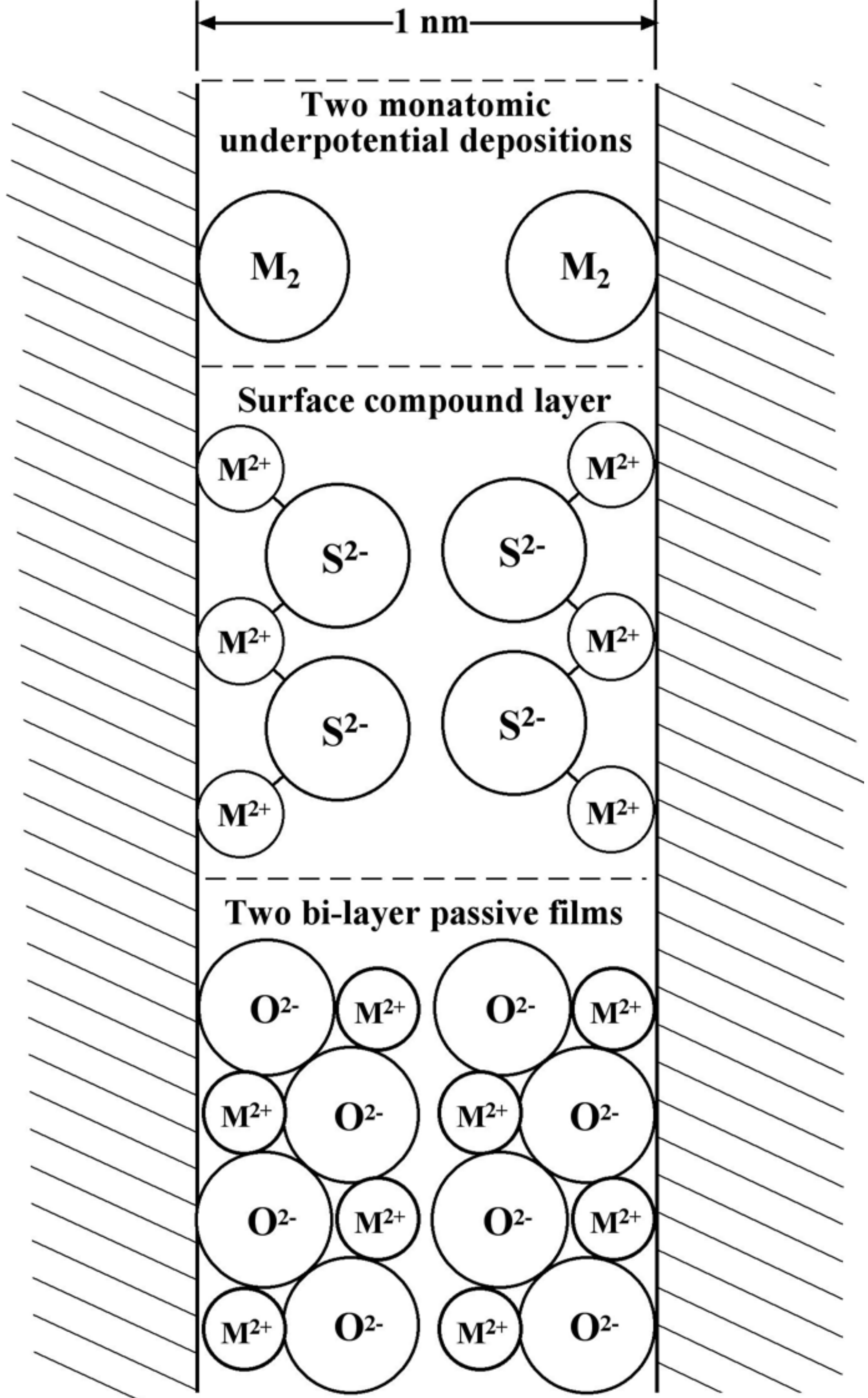


From Goswami and Staehle

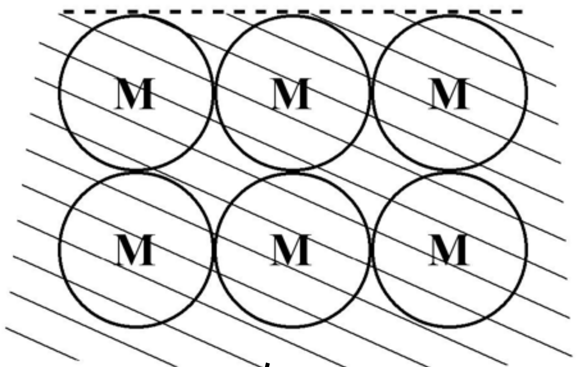
Dimensional comparison of SCC and constituents



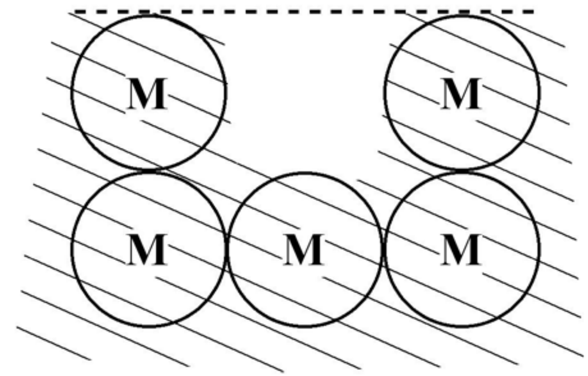
Dimensional comparison of SCC and constituents



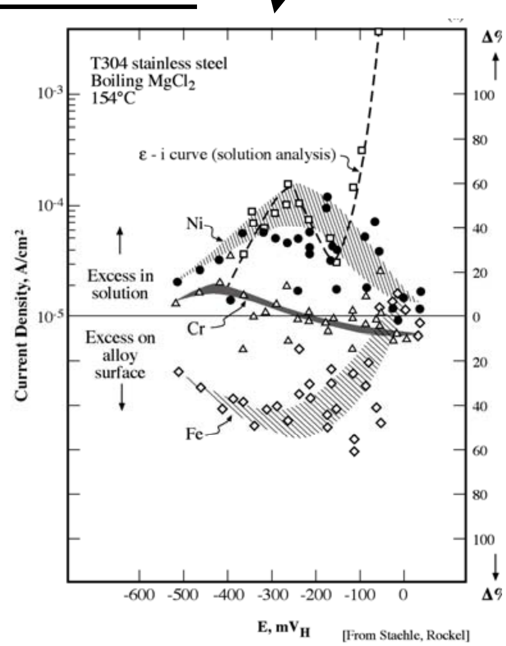
Some possible modes of decohesion



Vacancy Formation



Surface enrichment

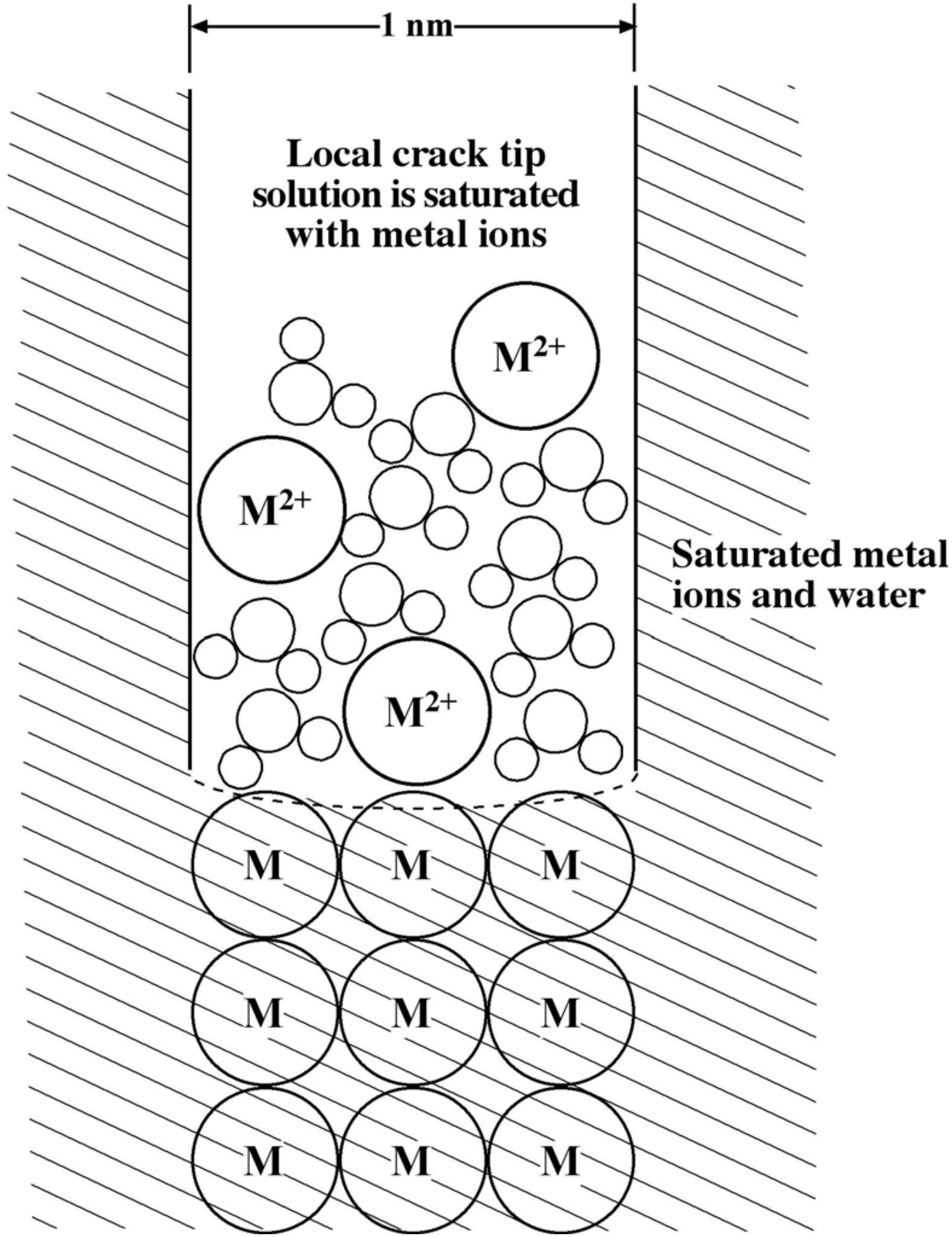


Chemical Reactions

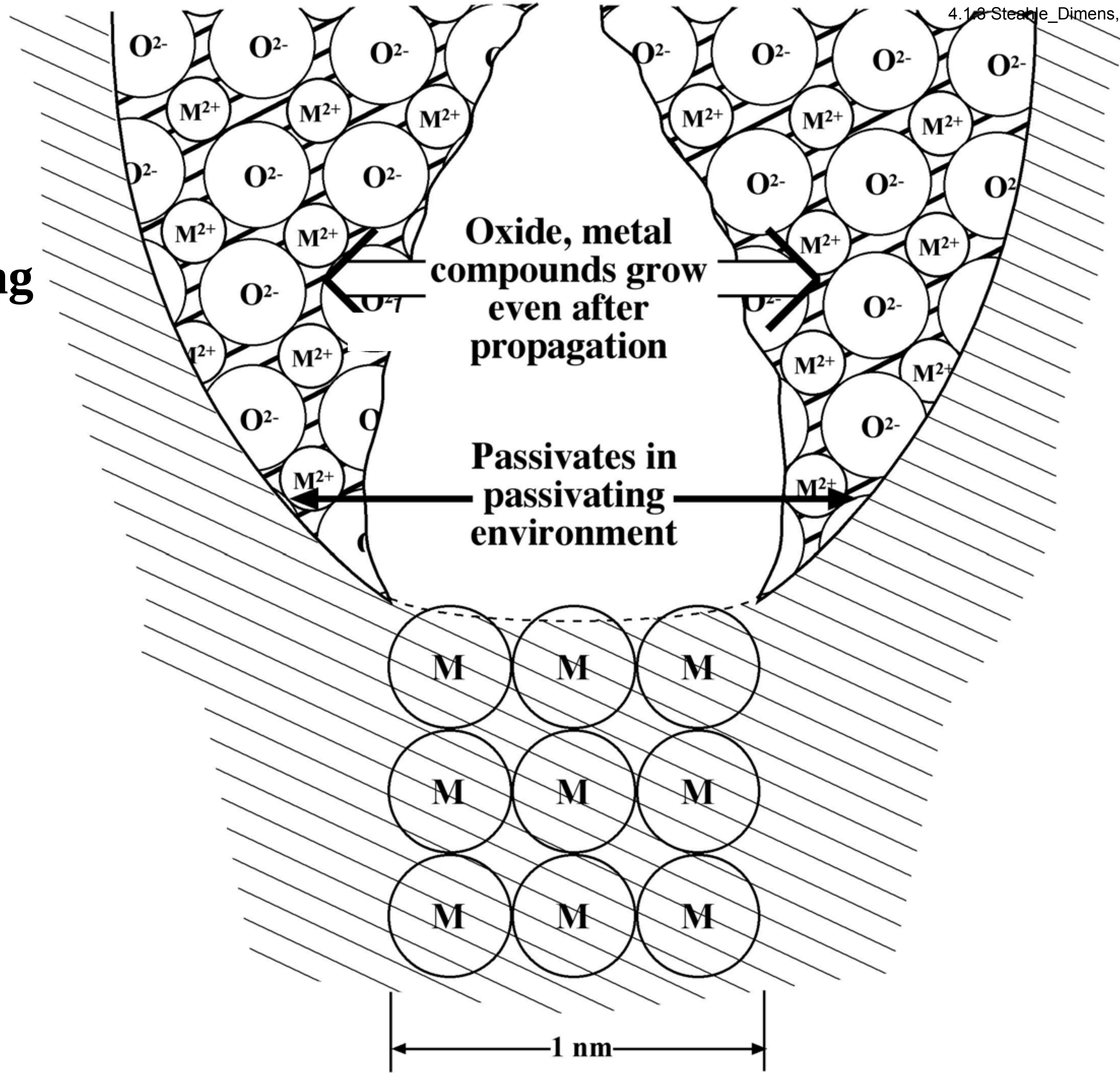
MX →
- MO
- MS layer
- M* underpotential deposition
- M* adsorbed
- MH bond

Formation of vacancies also leads to change in concentrations of species ahead of crack tip, i.e. changes by factors up to 2-3x for stainless steel.

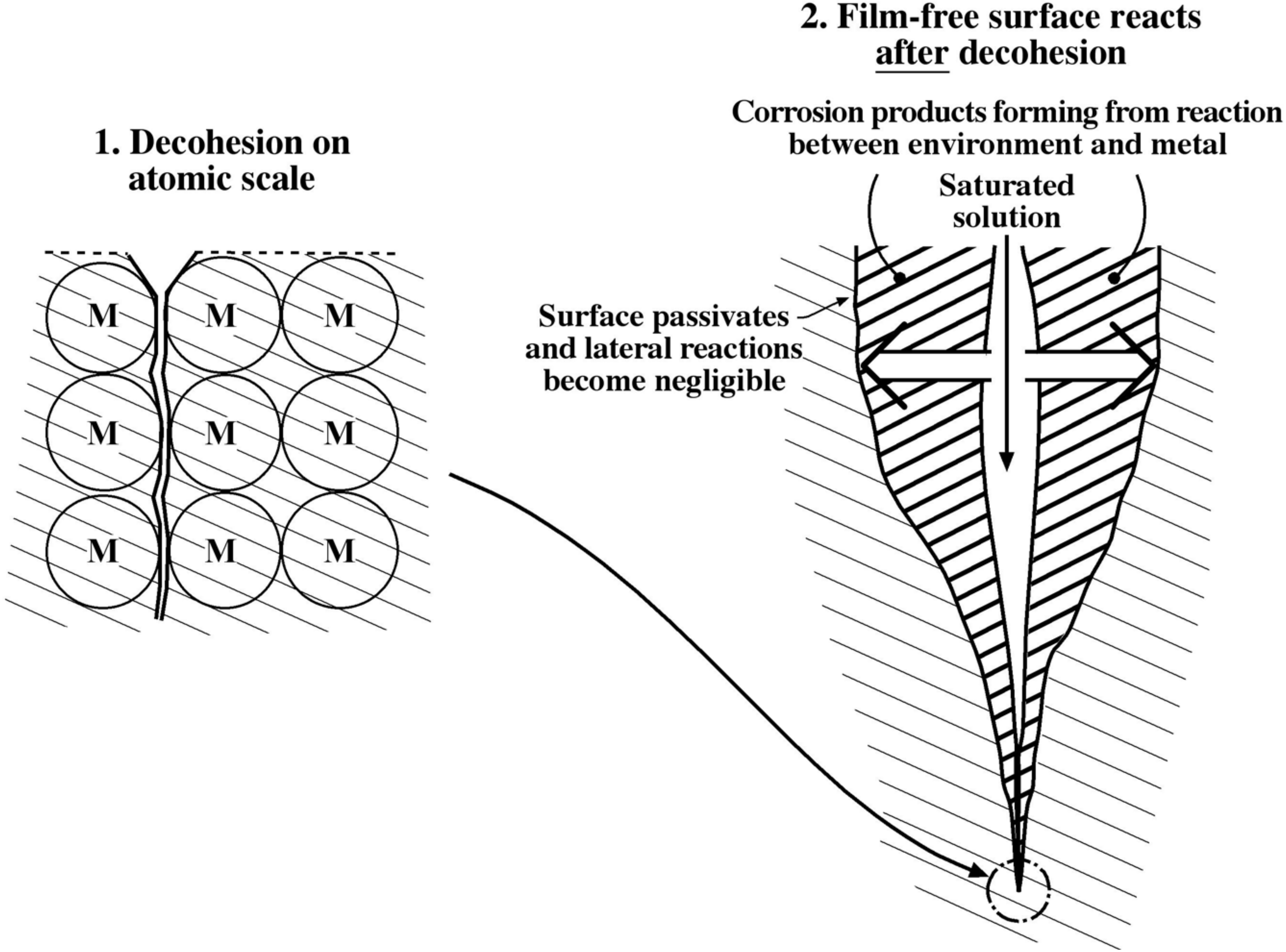
Crack tip of SCC relative to the local saturation of species in local environments

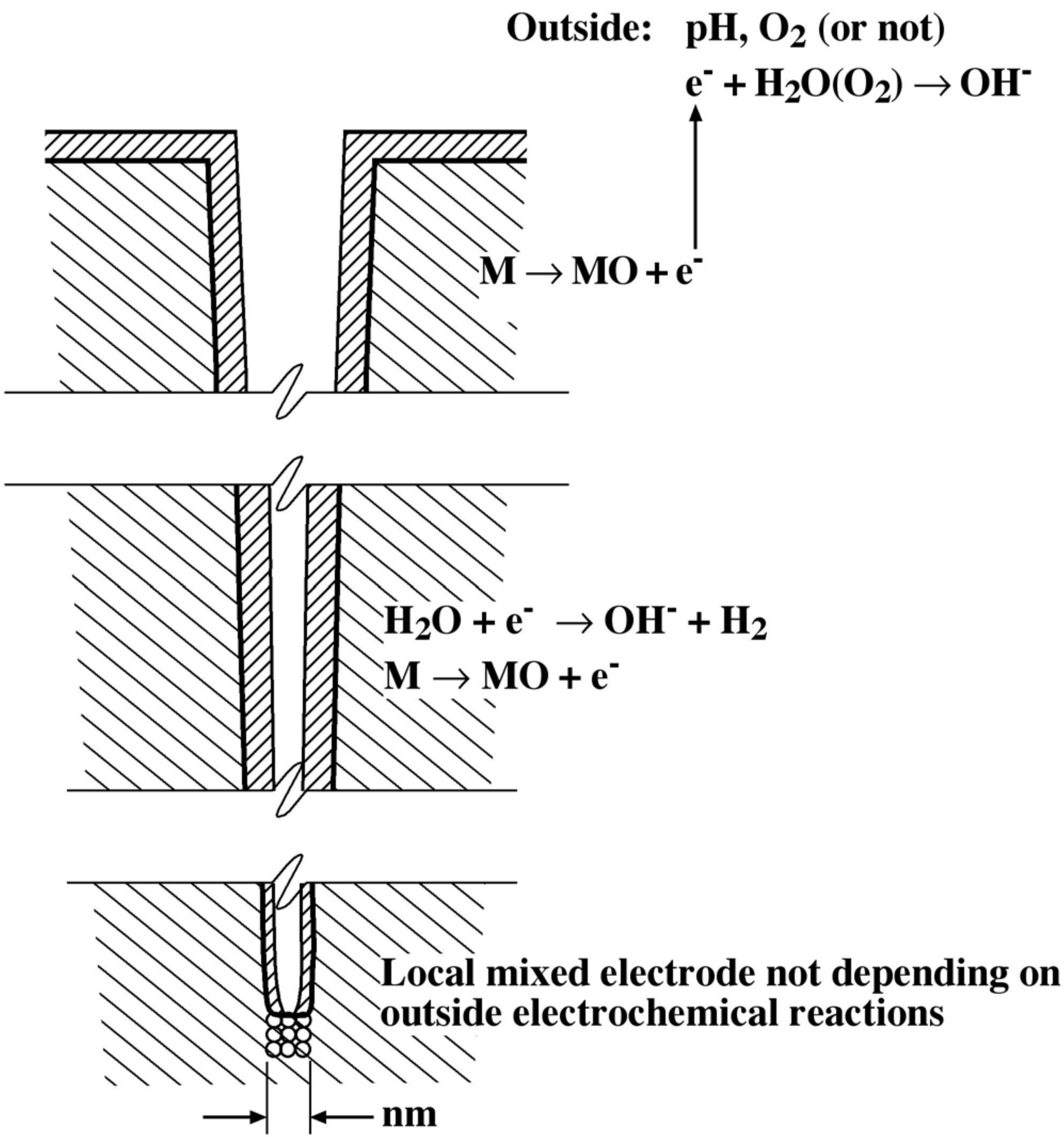


Reactions along flanks after decohesions



Two Steps

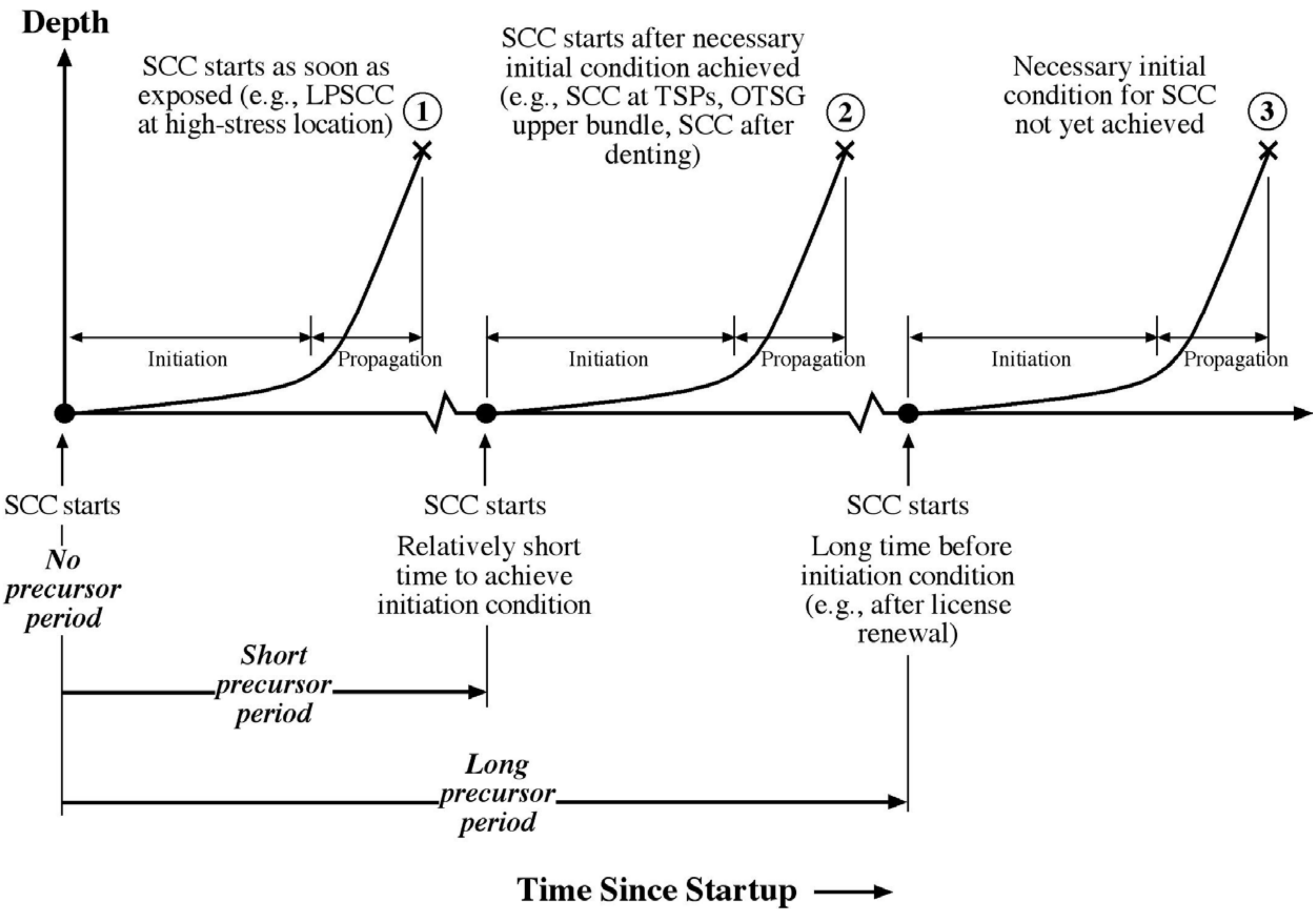

1. Decohesion on atomic scale
M
2. Film-free surface reacts after decohesion
Corrosion products forming from reaction between environment and metal
Saturated solution
Surface passivates and lateral reactions become negligible


Outside: pH, O_2 (or not)
$e^- + H_2O(O_2) \rightarrow OH^-$
$M \rightarrow MO + e^-$
$H_2O + e^- \rightarrow OH^- + H_2$
$M \rightarrow MO + e^-$
Local mixed electrode not depending on outside electrochemical reactions
nm

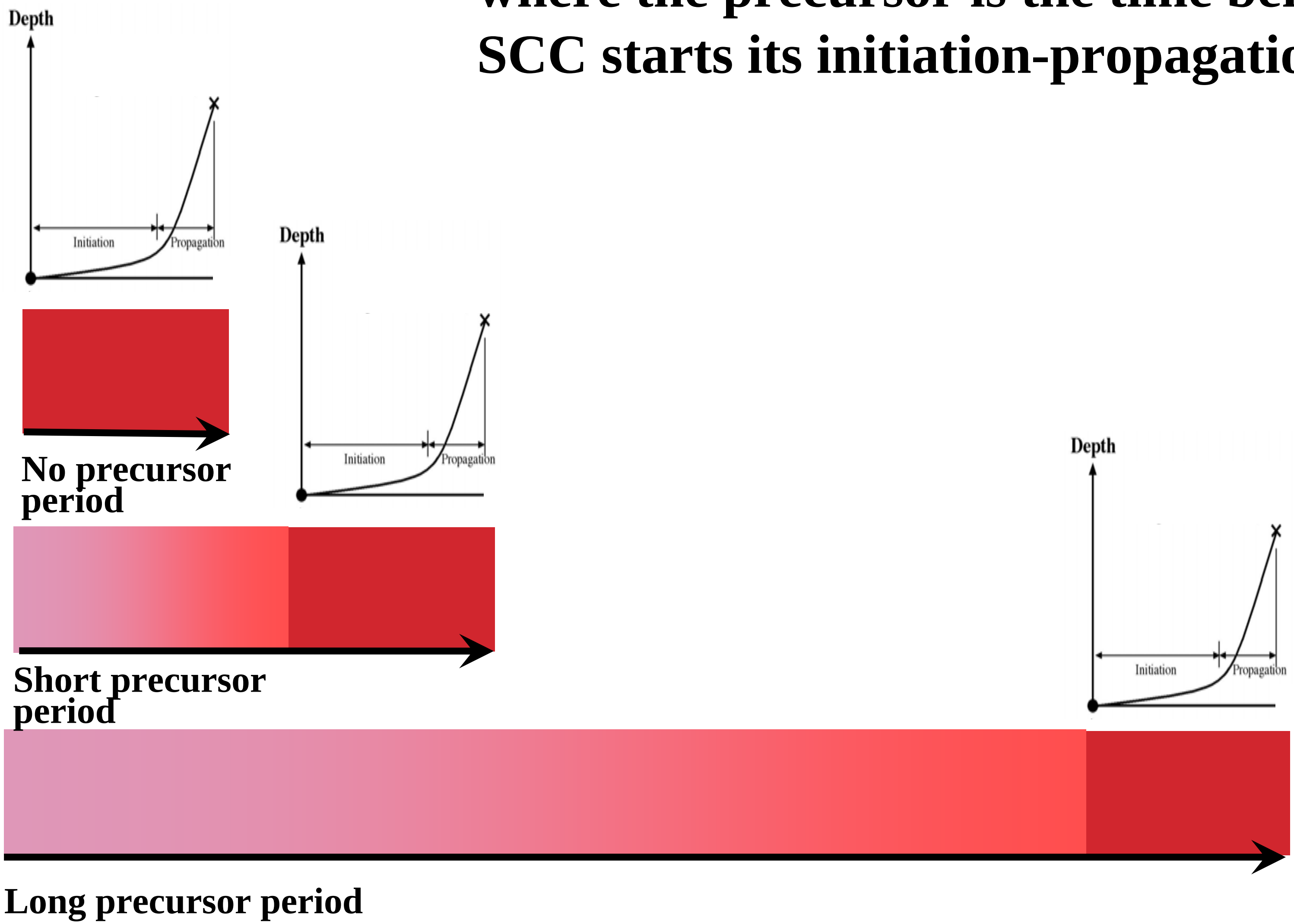
Predictions for long times

Analyzing “precursors”

Three cases for prediction of SCC



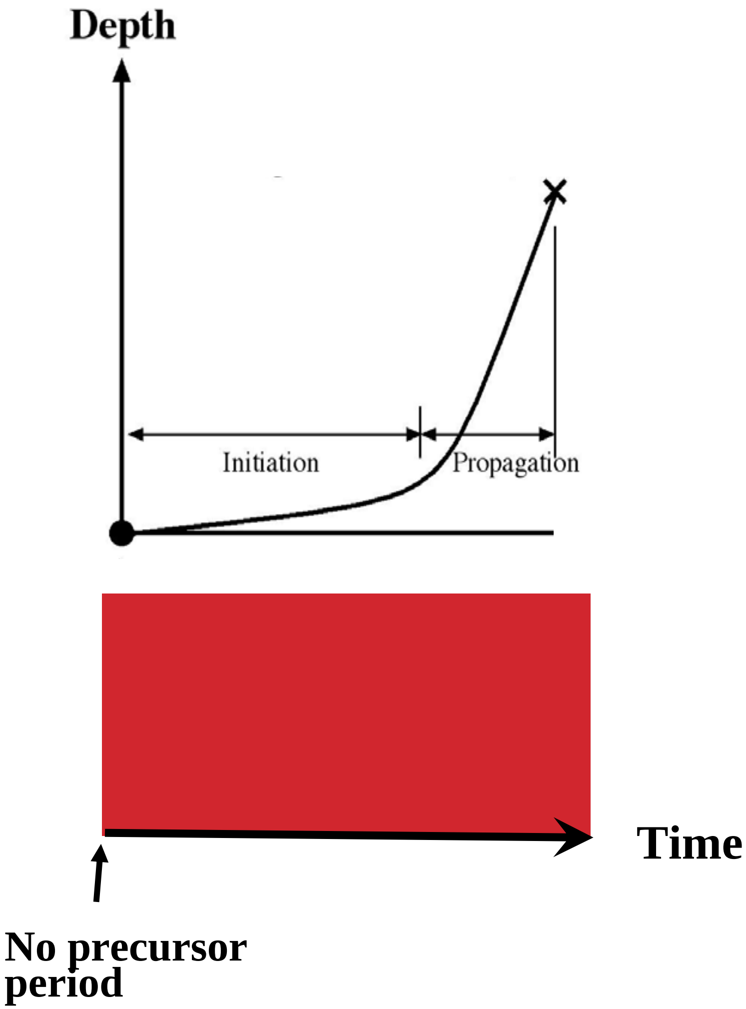
Predicting corrosion (e.g. SCC failure) at long times is progressively more a problem of predicting the "precursor" where the precursor is the time before SCC starts its initiation-propagation process



No precursor period

Examples

- IDSCC in SG tubing (LPSCC)
- ODSCC at scratches in cold leg of SG tubing
- FAC, e.g. Mihama 3, secondary system
- BWR sensitized piping and non-sensitized core structurals



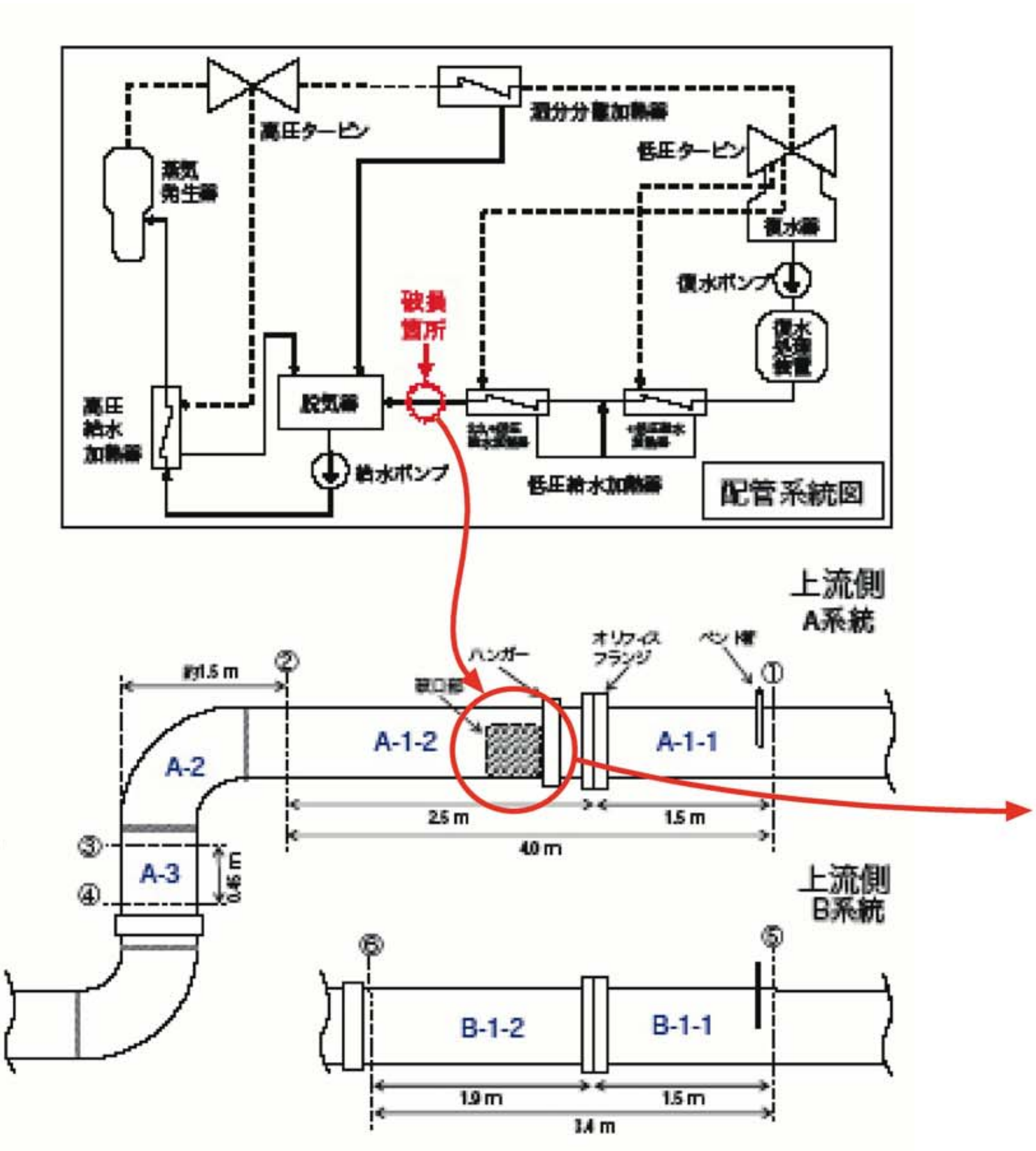
No precursor

FAC on secondary side

- 560mm diam, 10mm wall
- 22 m/s, 0.93MPa, 142°C, 8.6-9.3pH
- 185,700hr operation

(a)

(b)



(c)

Short precursor period

Examples

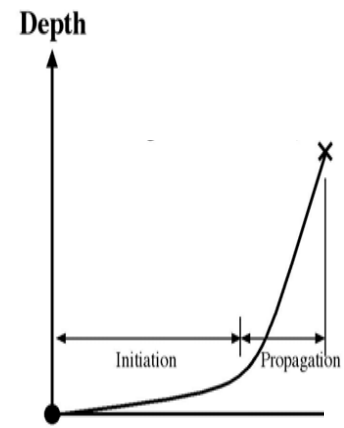
- Accumulation of aggressive chemicals on heat transfer surfaces

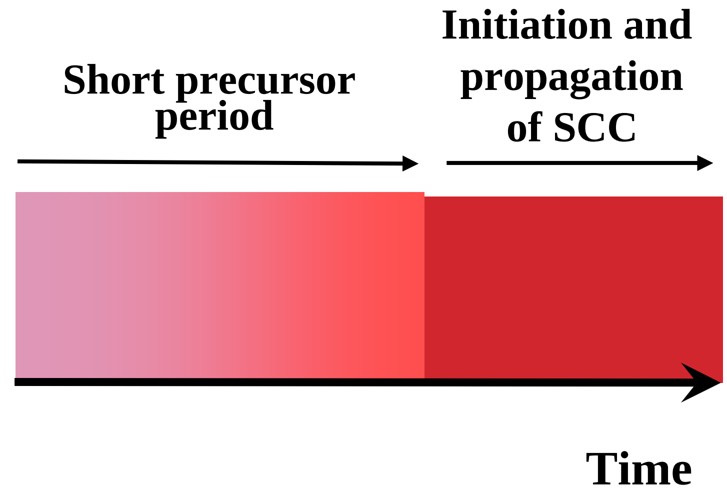
- "Denting" resulting from the expansion of growing corrosion products in tube supports and TTS

- Accumulation of chemicals on superheated surfaces of upper bundle of OTSG

- Accumulation of deposits and corrosion products leading to increased thermal resistance and then to perforation of fuel cladding (not SCC but rapid perforation).

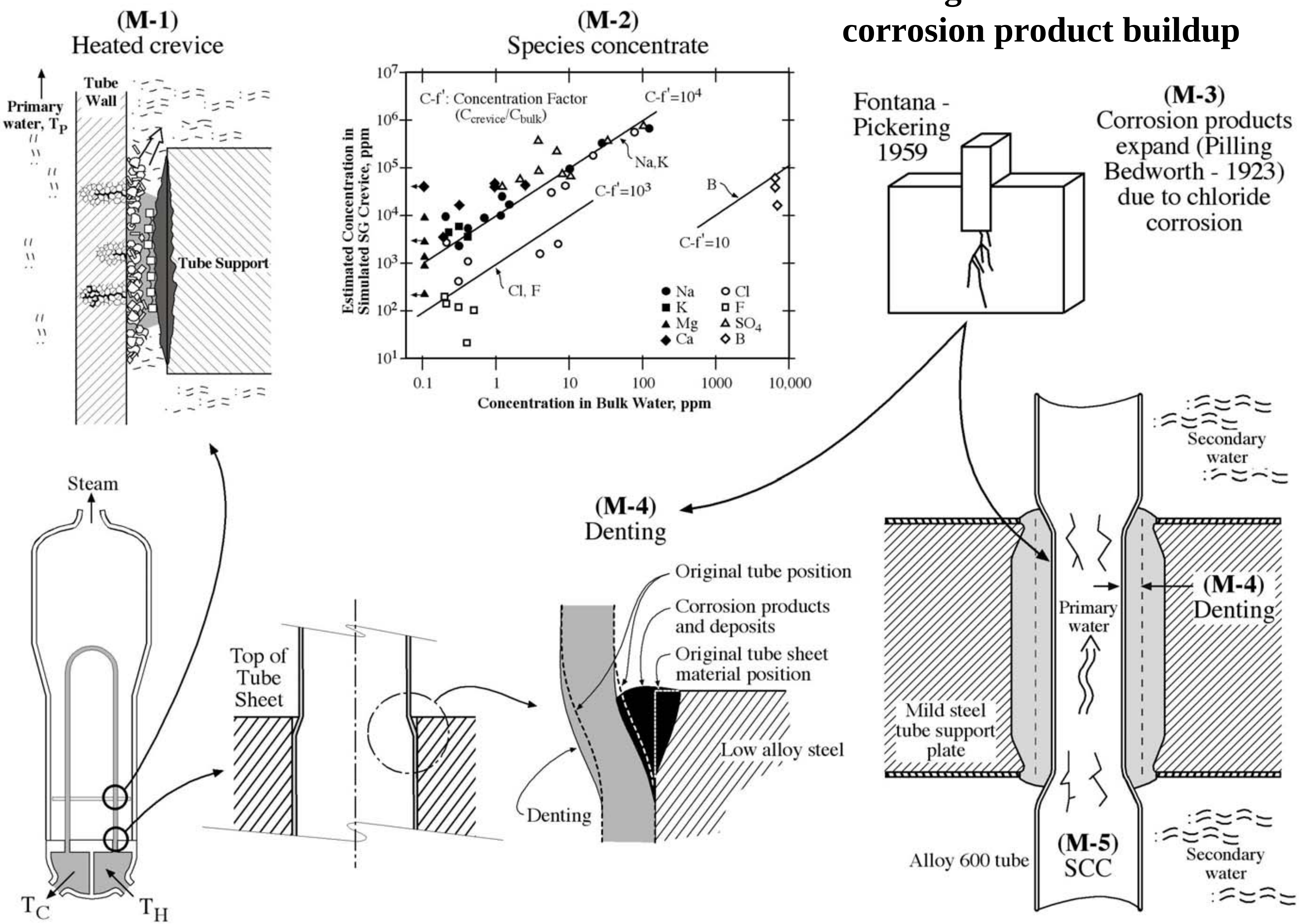
- Vessel head perforation at Davis Bessie



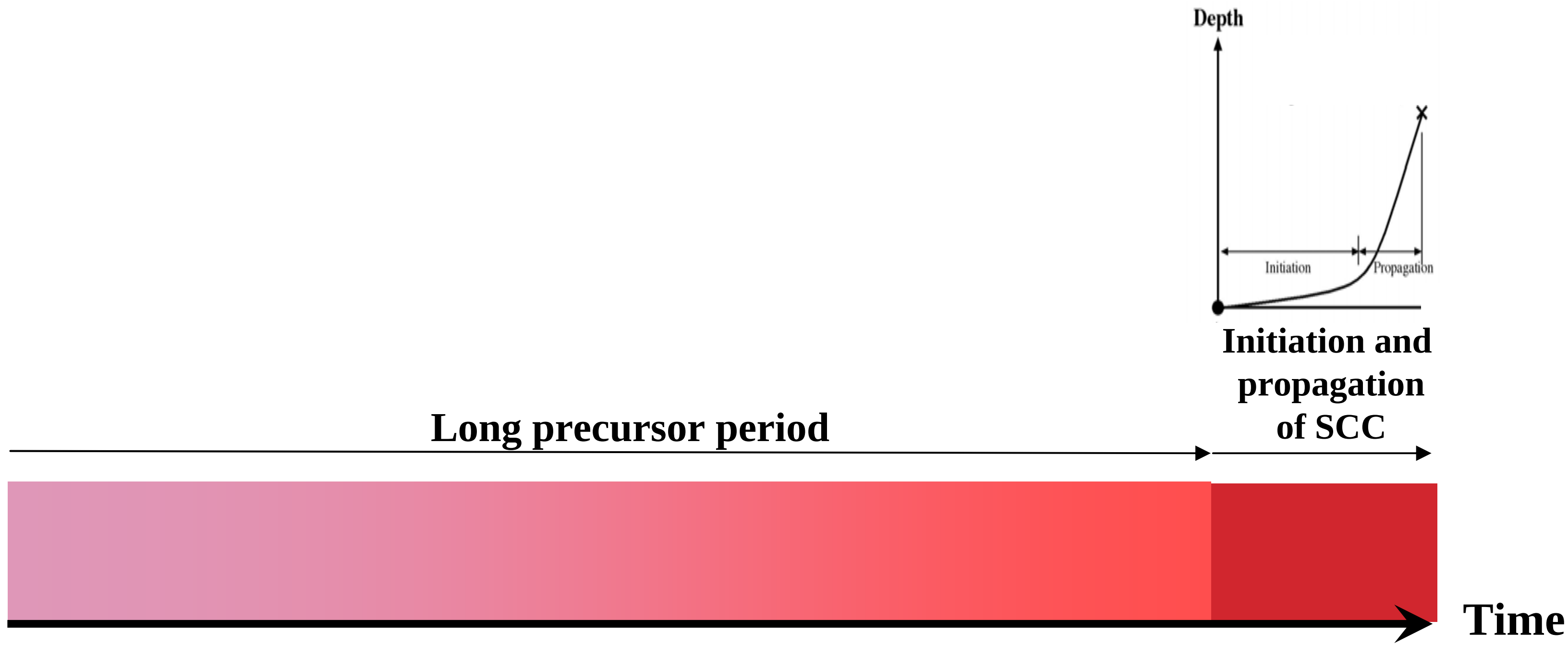


Short precursor period

Denting due to stresses from corrosion product buildup



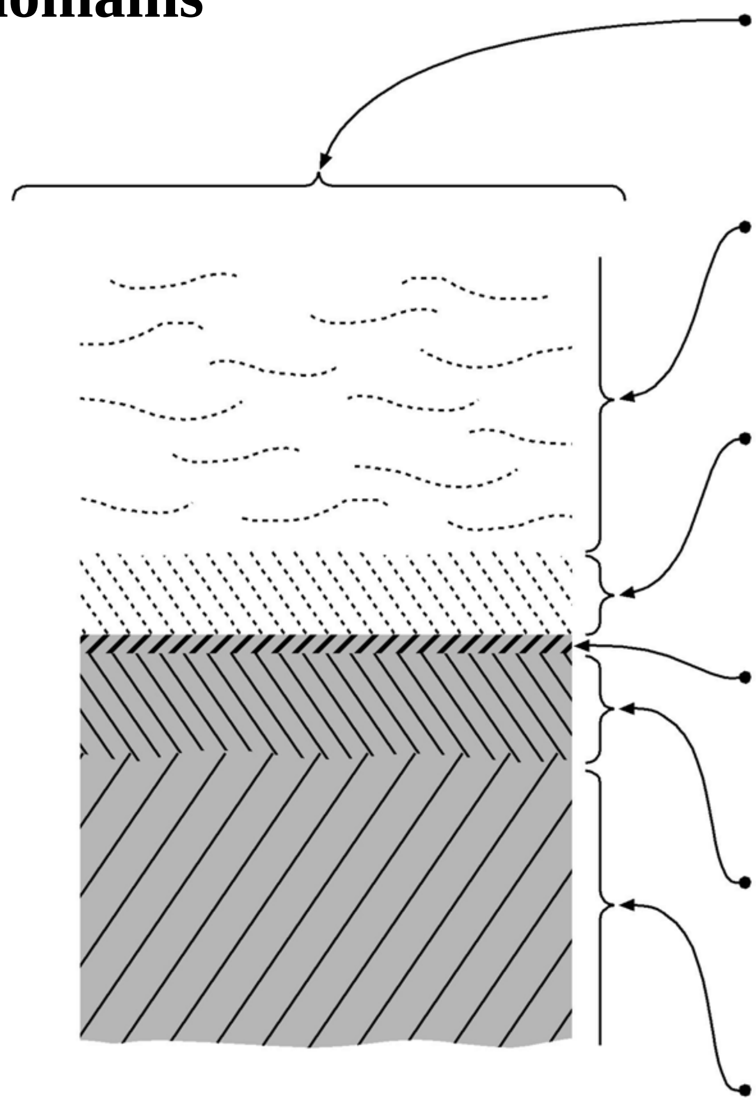
Predicting failures associated with a long precursor period– Failures that have not occurred in the past



The approach →

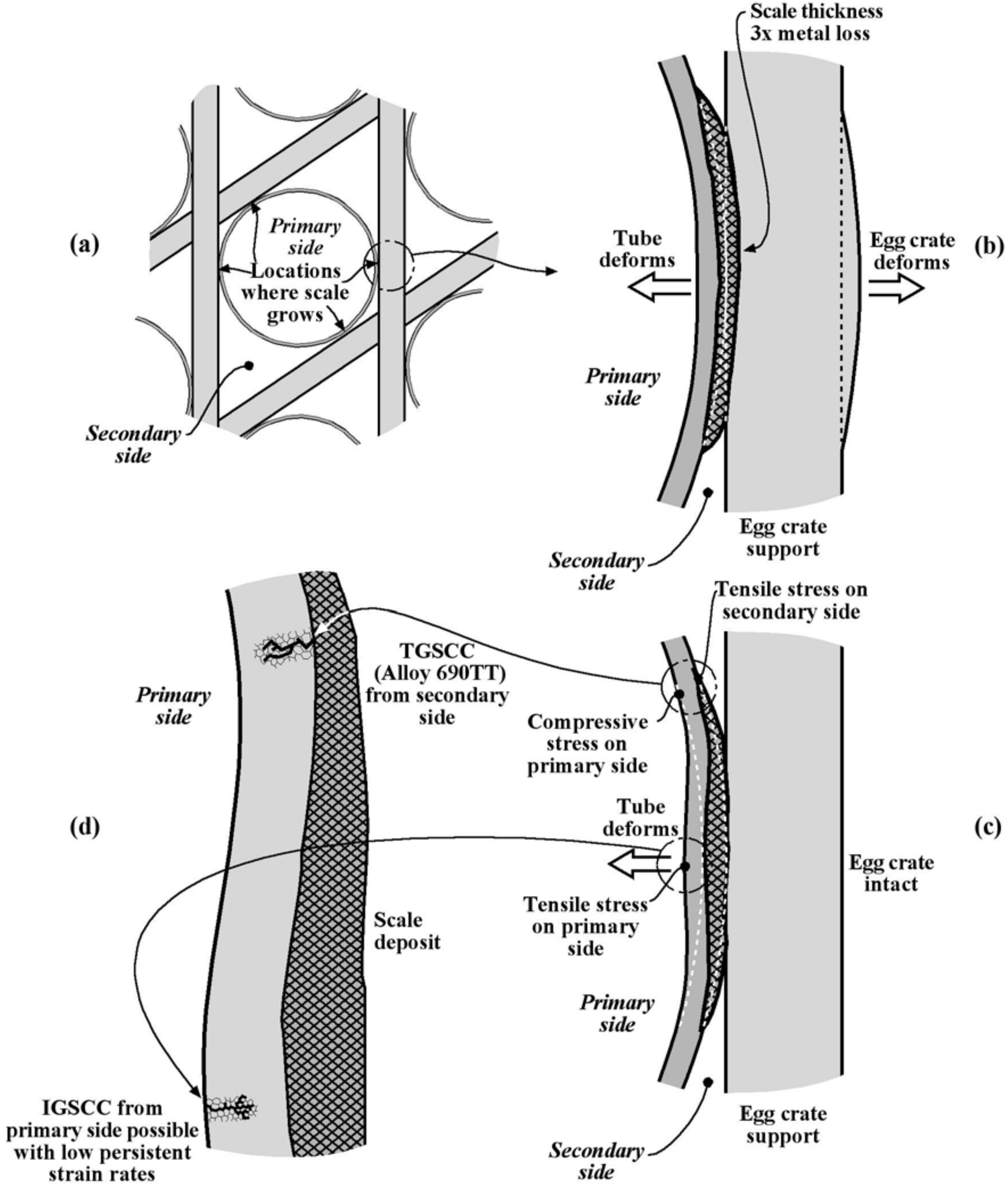
- **Develop long precursor period on physical bases using the six domains from bulk environment to bulk metal**
- **Elaborate on domains with "microprocesses"**
- **Develop a scenario period based on a sequence of microprocesses within each domain**
- **Identify "targets" for the critical conditions of SCC to be approached by the scenarios.**

First step in MPSA: Identify "domains"

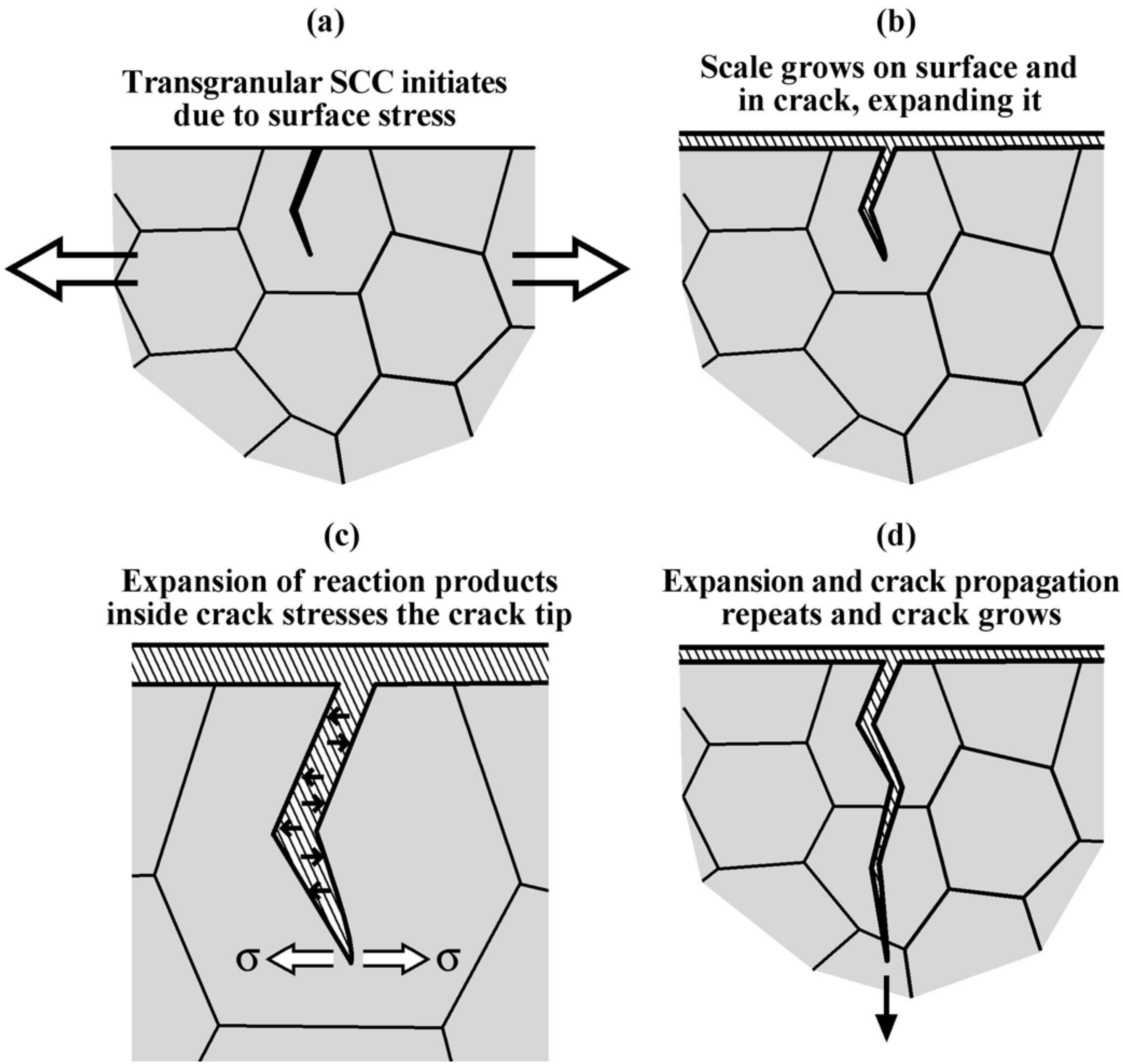


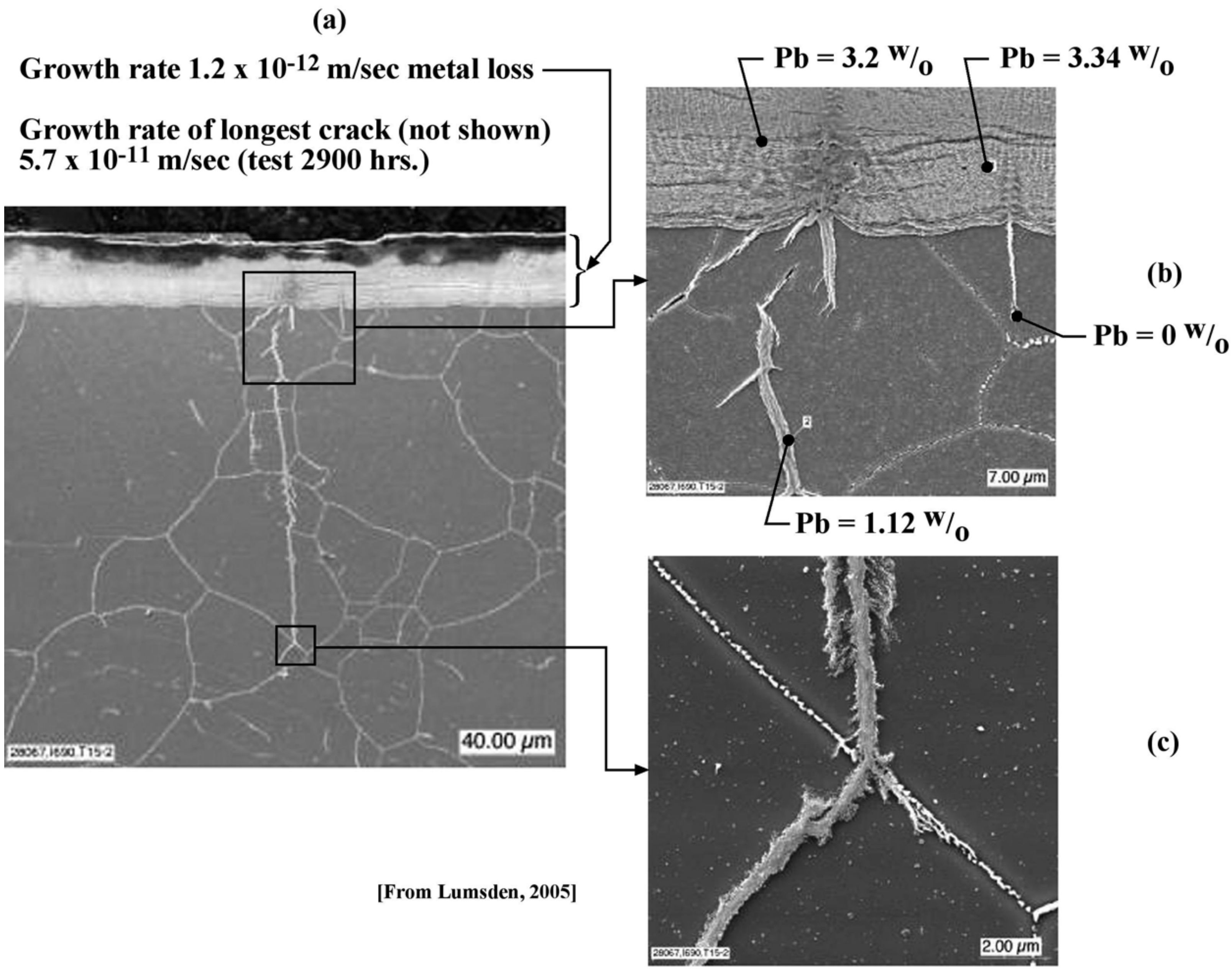
Domains
(Examples of microprocesses)

- **Global Environment**
  - ΔG
  - Temperature
  - Nuclear radiation
  - . . .
  - . . .
- **Bulk Environment**
  - H_2 concentration
  - N_2H_4 concentration
  - O_2 concentration
  - . . .
  - . . .
- **Near-Surface Environment**
  - Deposits
  - Electrochemical cells
  - Heat transfer
  - Concentration
  - . . .
  - . . .
- **Protective Film**
  - Thickness
  - Epitaxial
  - Surface slip interaction
  - . . .
  - . . .
- **Near-Surface Metal**
  - Depletion of alloy
  - Tunnel formation
  - Hydrogen entry
  - . . .
  - . . .
- **Bulk Metal**
  - Grain boundary composition
  - Grain boundary sliding
  - Grain matrix precipitation
  - . . .
  - . . .



(a)
Primary side
Locations where scale grows
Secondary side
Scale thickness 3x metal loss
Tube deforms
Egg crate deforms
(b)
Primary side
Secondary side
Egg crate support
TGSCC (Alloy 690TT) from secondary side
Primary side
(d)
Scale deposit
IGSCC from primary side possible with low persistent strain rates
Tensile stress on secondary side
Compressive stress on primary side
Tube deforms
Tensile stress on primary side
Primary side
Secondary side
Egg crate support
Egg crate intact
(c)


(a)
Transgranular SCC initiates due to surface stress
(b)
Scale grows on surface and in crack, expanding it
(c)
Expansion of reaction products inside crack stresses the crack tip
σ
σ
(d)
Expansion and crack propagation repeats and crack grows



[From Lumsden, 2005]

NDE & Monitoring: Brainstorming Ideas

May 11, 2006

Brainstorming on Research Ideas

- Detection of degradation Precursors
  - Changes in material properties
  - Changes leading to crack initiation
- Detection of SCC nano-crack formation
- Micro-cavities formation on grain boundaries linking to form fatigue crack
- For fast growing cracking, where precursors can't be measured, or where access is limited then apply AE monitoring
- Life cycle of degradation from virgin material to macro cracking with conventional NDE
  - What physical basis exists/is needed for each phase of the degradation life cycle

Brainstorming on Research Ideas cont'd

- Determine if precursors exist for degradation and can they be measured using NDE
- Are we using all of the information available from conventional NDE data?
- Need a listing and ranking of precursors relating to the importance of LWR degradation
- Need a listing and ranking of material changes relating to the various stages of degradation in LWRs to cover the entire life cycle
- Screening method for large areas so that very sensitive measurements in localized areas can be performed
- Life cycle of fatigue and SCC seem to be at the top of the list of degradation to fully understand
- Precursor versus actual cracking may be the only life cycle changes??
- Precursor versus cracking and then accelerated cracking are the stages in degradation life cycle????

Things we Missed

- Crack growth rate monitoring for predicting remaining life
- What more can be learned from conventional NDE
- NDE can lead the way
- Screening method for large areas so that very sensitive measurements in localized areas can be performed
- Generic assessment of NDE methods for measuring stages of degradation – survey other technologies in other fields for use
- Diagnostics and prognostics for managing degradation
- Laser acoustics using fiber optics
- Guided waves
- Absorption spectroscopy
- Stand off remote systems
- Acoustic microscopy for surface studies
- Field deployment Issues
- Coordination activities with materials and degradation as well as repair, replacement and mitigation research activities

Avoid Failures--What needs doing

Identify and Scope

Mechanistic basis for Crack growth

Objective:

- **Understand mechanisms of propagation**
- **Experimental verification**
- **Identify important variables and dependencies**
- **Transition from initiation**
- **Determine causes of data scattering**
- **Develop predictive capability for PMDM for license renewal lifetimes**

– **Scope**

- **Materials of construction**
- **Bulk environments & Local environments**
- **Primary and secondary systems**
- **Normal and transient operation**
- **Major degradation mechanisms**
- **Static and dynamic loads**
- **Develop technology for accelerating aging**
- **Define and bound important variables**
  - **Temperature, stress, chemistry, alloy macro and micro chemistry and structure, radiation,**

Mechanistic basis for Crack growth *duplicate*

Objective:

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  - **Ballinger, Bruemmer, Van Dyck, Lu**

Mech basis for crack growth, specifics

- Weld microstructure interaction with fracture and SCC, hot cracking during welding (microhot cracking), bi-metallic, HAZ/weld, residual stresses
- Make crack growth rate specific for inspection
- Analyze the implications of tight crack tips
- Lead--init, prop, heat trans crevices
- Mechanism of LPSCC (PWSCC)
- Matrix hardening, cold work, irradiation
- Low temp cracking
- Mechanistic basis for Kic including environmental effects

Initiation

- **- Objective:**
  - **Determine if SS can initiate SCC and fatigue cracks over plant lifetime**
  - **Understand mechanisms of initiation**
  - **Develop experimental methods, atomistic or multi-scale modeling, and verify**
  - **Identify important variables and dependencies**
  - **Transition to propagation**
  - **Determine causes of data scattering**
  - **Develop and validate (including field experience) predictive capability for PMDM including license renewal**
- **Scope:**
  - **Materials of construction**
  - **Develop experimental methods and verify by field experience**
  - **Bulk environments & local environments**
  - **Primary and secondary systems**
  - **Normal and transient operation**
  - **Develop technology for accelerating aging**
  - **Major mechanisms, e.g. surface phenomen (including DECON effects), aging**
  - **Static and dynamic loads**
  - **Define and bound important variables**
    - **Temperature, stress, chemistry, alloy macro and micro chemistry and structure, radiation, surface condition, fabrication, cold work, sensitization,**

Initiation *duplicate*

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    - **Temperature, stress, chemistry, alloy macro and micro chemistry and structure, radiation, surface condition, fabrication, cold work, sensitization,**
    - **Van dyck, Pinhero, Bruemmer, Ballinger, Arioka, Poruks, Kim, Brozova, Yonezawa,**

Mech of initiation

Cracking of CW CS Pipes

- **Objective**
  - **Determine if and when cracking occurs in PWR secondary and BWR piping on inside and outside surfaces**
  - **Characterize the variables under which the cracking occurs, including material condition**
  - **Determine the associated conditions of fabrication**
- **Scope**
  - **Develop experimental methods and verify by field experience**
  - **Bulk environment (water and stream), local environments, outside environments**
  - **Normal and transient operation**
  - **Develop technology for accelerating aging**
  - **Major mechanisms on both surfaces, e.g. surface phenomena, aging**
  - **Static and dynamic loads**
  - **Include effects of hydrogen from FAC**
  - **Define and bound important variables**
    - **Temperature, stress (applied and residual), chemistry, alloy macro and micro chemistry and structure,, surface condition, fabrication, cold work,**

Cracking of CW CS Pipes *duplicate*

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  - **Determine if and when cracking occurs in PWR secondary and BWR piping on inside and outside surfaces**
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  - **Major mechanisms on both surfaces, e.g. surface phenomena, aging**
  - **Static and dynamic loads**
  - **Include effects of hydrogen from FAC**
  - **Define and bound important variables**
    - **Temperature, stress (applied and residual), chemistry, alloy macro and micro chemistry and structure,, surface condition, fabrication, cold work,**
- **Arioka, Poruks, Tapping,**

Bulk Material Aging Processes

- **Objectives**
  - **Identify significant aging processes in irradiated and non-irradiated materials**
  - **Characterize the composition and structural evolution**
  - **Develop methods for predicting aging processes**
  - **Develop modeling capability from atom to macro-scale**
  - **Define relationship between aged bulk mechanical and material properties, and susceptibility to degradation mechanisms**
- **Scope**
  - **Synergistic effects**
  - **Consider processes such as spinoidal decomposition, stacking fault energies; grain boundary and grain matrix and relative grain orientation**
  - **Consider interaction with stress**
  - **Develop means for aging processes, while maintaining prototypicality**

Bulk Material Aging Processes, *duplicate*

- **Objectives**
  - **Identify significant aging processes in irradiated and non-irradiated materials**
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  - **Consider interaction with stress**
  - **Develop means for aging processes, while maintaining prototypicalty**
  - **Ballinger, Bruemmer, Van Dyck, Yonezawa,**

Surface Aging

- **Objectives**
  - **Define process zone at interface between material and environment**
  - **Define rate at which interfacial processes occur**
  - **Define effects of aging process on the interactions between environment (irradiated and unirradiated) and material on surfaces**
  - **Develop methods of measuring surface aging processes**
  - **Develop predictive capability (atomistic to macro-scale) for significant aging**
  - **Define relationship between aged surface and susceptibility to degradation mechanisms**
- **Scope**
  - **Materials of construction**
  - **Initial conditions of surface**
  - **Develop experimental methods and verify by examination of field exposed components**
  - **Bulk environments & local environments**
  - **Primary and secondary systems**
  - **Normal and transient operation**
  - **Develop technology for accelerating aging**
  - **Major mechanisms, e.g. surface phenomena, aging; include enrichment and depletion at surface, FAC, noble metal durability**
  - **Deposition of insoluble compounds**
  - **Static and dynamic loads**
  - **Define and bound important variables**
    - **Temperature, stress, chemistry, alloy macro and micro chemistry and structure, radiation, surface condition, fabrication, cold work, sensitization**

High Nickel Alloys

- **Objectives**
  - **Consider A600MA and TT, A800SP, A690TT in wrought form and welds**
  - **Define degradation modes on various alloys for BWRs and PWRs**
  - **Consider primary and secondary systems**
  - **Define dependencies of important variables on degradation modes**
  - **Understand low temperature cracking**
- **Scope**
  - **Variables:stress, temperature, cold work, environment, metal structure, impurity composition, mechanical properties, heat treatment, weld fabrication defects**
  - **bulk and local chemistry, e.g. pure water, lead, sulfur, mildly acidic,**
  - **Growth of scales**
  - **Dealloying as a function of pH**
  - **Variables affecting low temperature cracking; hydrogen concentration, welded structures, temperature, strain rate, time at higher temperature**

Heat Transfer Crevices

- **Objectives**
  - **Consider SGs**
  - **Define chemical and physical conditions in crevice**
  - **Define degradation processes under these conditions**
  - **Develop predictive capability**
- **Scope**
  - **Consider TSP and TS crevices**
  - **Variables: tube and secondary temperatures, chemical species and boiling point elevation, materials, designs, expansion process, cold work, denting, deposit chemical and physical characteristics, bulk water chemistry (including chemical cleaning residuals), and excursions, crevice chemistry.**
  - **TSP designs: broached (flat and concave), egg crate**

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- **Residual stresses**
- **High strength materials**
- **Radiation damage**
- **Fatigue**
- **Weld materials**
- **Valve stems**
- **Metallurgical variations**
- **IGA**
- **Long times--licensing and precursons**
- **Fracture**
- **Moving into applications**

Proc. 3rd PMDM ICG Planning Meeting – Charleston, SC, USA, May 11-13, 2006
5.2.1 Surface Mod MRR1

Mitigation, Repair and Replacement Subgroup

Topic Area # 1

Surface Modification Techniques to Improve the SCC and Fatigue Resistance

<u>Background and Overall Objective</u>

The stress corrosion cracking (SCC) susceptibility, growth rate and high-cycle fatigue are severely affected by residual stress of the materials and the SCC growth rate and low-cycle fatigue are severely affected by residual strain of the materials. As a result, methods to reduce the residual stress and strain of the materials for pressure boundary equipments are extremely important to mitigate materials degradation. Many techniques have been used effectively for LWR components including local thermal treatments (e.g., a band heater or laser) to reduce stress/strain and mechanical treatments (e.g., peening by shot, water-jet or laser methods) to alter the residual stress. Up to this time, these techniques were basically developed in the individual private companies with details for application techniques different and typically proprietary to each company. Therefore, to properly evaluate and optimize these mitigation techniques to benefit commercial LWRs world wide, fundamental research must be done.

An alternative modification approach to provide protection for SCC and fatigue is to completely remove the surface layers where cracking initiates. A simple method is the removal of the damaged (corroded or cracked) or cold-worked layer or locally heat-affected zone by grinding, machining or another abrasive technique. The application of a thin cladding of a corrosion-resistant alloy to the surface by laser techniques may also be highly beneficial in certain circumstances (e.g., alloy 690 at J-welds in PWR lower-head penetrations). Once again, there is a significant need to properly evaluate the effectiveness of these surface modification approaches.

Two brief descriptions of possible research tasks are given below. These are provided to illustrate a few more specific areas where key work is needed and are not intended to restrict proposed ideas within this general topic.

(A) Quantitative Assessment of Technique Reliability

The effective reduction of the residual stress and strain on the materials by the thermally or mechanically techniques are not always reliable and reproducible. Reliable and reproducible reducing range of the residual stress and strain on the materials by the thermally or mechanically techniques must be clarified by the laboratory and mock-up tests. Quantitative measurements (e.g., x-ray and/or SEM backscatter imaging) of residual stresses and strains should be performed as a function of location in the components of interest. Once the ability to reduce stresses and strains is demonstrated, tests should be conducted to evaluate the effectiveness of the mitigation treatment to significantly improve the materials resistance to SCC and fatigue failure. This evaluation can be done using laboratory and mock-up tests. In order to check the possibility of the detrimental side effects, materials modified by the thermally or mechanically techniques should be tested from the view point of the mechanical properties, microstructure, dimension, corrosion properties, surface roughness and so on.

The research description above for the thermal/mechanical stress/strain reduction techniques also applies for the surface removal approaches. Once the surface damaged or altered layer is removed, the reliability of this mitigation treatment in improving SCC and fatigue performance should be evaluated by laboratory and mock-up tests. Application reliability for the corrosion-resistant cladding is critical and detailed characterizations of the cladding should be done followed by appropriate laboratory and mock-up tests.

(B) Long-Term Effectiveness of Mitigation Techniques

A critical aspect for these techniques to modify stresses and strains will be their long-term stability and effectiveness in mitigating degradation. Accelerated aging should be employed to assess long-term changes in the modified material. Temperature-accelerated corrosion, SCC and fatigue testing may be done under controlled conditions to evaluate the effectiveness for residual stress and strain modification up to the end of plant life.

Mitigation, Repair and Replacement Subgroup

Topic Area #2
Surface Coatings for Corrosion and SCC Mitigation

Background and Overall Objective

The inhibitive treatment or coating of metal-alloy surfaces has been proposed as an effective mitigation of corrosion and stress corrosion cracking (SCC) for BWR components. The approach is to employ the inhibitive nature of ceramic compounds in deterring the redox reactions required for metal corrosion. In theory, this type of coating could deter all major redox reactions (namely the oxidation of H_2, the reduction of O_2, the reduction of H_2O_2, and the oxidation of metals) in the high-temperature water environment. The exchange current densities (ECDs) of these reactions on the base metal surface would accordingly decrease. In a typical, oxidizing BWR environment that usually contains hundreds of ppb O_2 and tens of ppb H_2O_2, corrosion of stainless steel components will be significantly alleviated if the ECDs of the O_2 and H_2O_2 reduction and SS oxidation reactions are effectively decreased. In addition, the effectiveness of HWC could be enhanced in terms of a reduced electrochemical corrosion potential (ECP) accompanied by a lower H_2 consumption or even without any added hydrogen.

The research objective within this topic is the development and quantitative evaluation of inhibitive coatings for corrosion and SCC mitigation. Candidates to be used as the coating material can be different but should bear a common nature of deterring oxidant reduction and metal oxidation. Prominent examples that require further study are zirconium oxide (ZrO_2) and titanium oxide (TiO_2) coating techniques. Preliminary results have demonstrated their positive benefit in terms of comparatively lower corrosion rate and lower corrosion potential. However, there are issues with regard to practical coating application method, coating integrity, and coating durability to resolve. In addition, the TiO2 coating technique was proposed mainly with the simultaneous presence of ultraviolet photon radiations with a certain range of wavelength. The issue of its effectiveness for away-from-core regions should be addressed. For each coating and perhaps alternation application techniques, the influence of long-term, high-temperature exposure on the coatings should be assessed along with the influence component loading/deformation. Quantitative examinations of SCC response should also be included to fully evaluate mitigation capabilities of the coatings. Finally, their impact on the performance of fuel and on the integrity of fuel rod surfaces should also be investigated.

Mitigation, Repair and Replacement Subgroup

Topic Area #3
Modification of Water Chemistry

Background and Overall Objective

The generally oxidizing environment in the primary coolant circuit (PCC) of a boiling water reactor (BWR) exacerbated by the radiolysis process of water in the core region poses a serious threat of stress corrosion cracking (SCC) to structural components. An effective method to mitigate SCC problems is to modify the BWR water chemistry, namely from an oxidizing one to a reducing one, by appropriate techniques. In the past decades, hydrogen water chemistry (HWC) and HWC along with noble metal chemical addition (NMCA) have been widely adopted and generally successful. However, concerns remain for this approach for SCC mitigation with issues of the optimal hydrogen levels, the possibility of incomplete protection and undesirable radiation field buildup.

The PCC of a pressurized water reactor (PWR) also has a critical issue with the selection of an optimal hydrogen level. Recent work has demonstrated a significant variation in SCC crack growth rates for Ni-base alloys with electrochemical potential (with respect to the Ni/NiO line) driven by the amount of injected hydrogen. It is extremely important that this variability be quantitatively understood. The PWR water environment also has other complexities particularly on the secondary side where significant off-normal chemistries can develop in crevices. Water chemistry modifications (e.g., B/Li ratios) and additions (e.g., Zn) have been used without a clear definition on their influence on SCC susceptibility.

The research objective within this topic is focused on an improved understanding of normal and off-normal water chemistry effects on SCC resistance of BWR and PWR components. In particular, quantitative evaluations of water chemistry on SCC are needed in several areas. This should include the influence of hydrogen levels and electrochemical potentials on SCC of Ni-base alloys and stainless steels (in and out-of-core) for both systems. Solution chemistry additions for mitigation are of direct interest ranging from Zn to more complex alternative chemistries.

Several brief descriptions of possible research tasks are given below. These are provided to illustrate a few more specific areas where fundamental understanding is needed and are not intended to restrict proposed ideas within this general topic.

Task A: BWR Issues

For BWRs, further research on HWC/NMCA is recommended to ensure effective mitigation is obtained. For example, continuous injection of noble metals into a BWR or other approaches to restore the catalytic activity of already present noble metals could be eligible for a further in-depth study since the impurities in the BWR coolant may contaminate the deposited noble metals and thus reduce their catalytic activities over an operation cycle gradually. There is also a concern that platinum or other noble metals may catalyze the oxygen reduction reaction in the absence of sufficient hydrogen and may promote accelerated SCC in a BWR. A possible solution to this problem is to find a different catalyst that would catalyze only the oxidation reaction of hydrogen and be inert to oxygen reduction. Alternate water chemistry is an approach that needs additional study to deal with the problems of SCC in BWRs. The most promising candidates in replacing hydrogen at the moment seem to be alcohols (e.g., methanol or ethanol) and hydrazine. Both alcohol and hydrazine can act as reducing agents in the PCC of a BWR, and preliminary experimental results have demonstrated that these chemicals could effectively scavenge dissolved oxygen and they do not form significant amounts of radioactive, volatile species after reacting with water. Although the main goal of zinc addition (preferably prior to the adoption of HWC/NMCA) is to reduce the shutdown dose rate in a BWR, it is possible that the structural components may actually benefit from the surface composition modification after zinc addition in terms of deterred SCC, probably resulted from less conducting property of the treated component surfaces. In each of these cases, quantitative examinations of SCC response are needed along with proper characterizations of water chemistry effect on corrosion product films.

Task B: PWR Issues

There have been concerns over that the currently adopted hydrogen injection rate in PWR primary water may not be appropriate to minimize IGSCC in Ni-base alloy components. Further study is needed including quantitative crack-growth-rate testing to better quantify the relationships among hydrogen level, electrochemical potential (versus the Ni/NiO line) and cracking. It is critically important to establish this response for the lower-Cr alloys (e.g., alloy 600 and weld metals) and higher-Cr replacement alloys (alloy 690 and weld metals). Although the main goal of Zn addition is to reduce the shutdown dose rate in a PWR, it is possible that the structural components may actually benefit from the surface composition modification. Once again, quantitative examinations of SCC response are needed along with proper characterizations of water chemistry effect on corrosion product films.

Chemistry modifications can be much more aggressive on the PWR secondary-side environment. Recent observations of high Pb levels in surface films, IG attack and IGSCC cracks may suggest that it may be beneficial to add species that can remove Pb from solution. It becomes extremely important to better understand the solution chemistry in the secondary-side water and in crevices. Thermodynamics and kinetics of reactions between primary impurities of concern (e.g., Pb and S) with possible mitigation species need to be determined and critical tests performed.

Mitigation, Repair and Replacement Subgroup

Topic Area #4

Welding Optimization for Microstructural Control and Stress/Strain Modification to Improve Hot Cracking and SCC Resistance

Background and Overall Objective

Weldments continue to be a primary location of stress-corrosion cracking (SCC) in LWR systems. While problems related to heat-affected-zone (HAZ) sensitization and intergranular (IG) SCC of austenitic stainless steels in BWRs have been significantly reduced, SCC has now been observed in HAZs of non-sensitized and often L-grade materials. A key aspect of this SCC susceptibility results from welding-induced local strains and the final residual stresses. In addition, cracking has been observed in dissimilar welds where Ni-base alloy weld metals are used. Interdendritic (ID) or IGSCC has been observed in both BWRs and PWRs with recent examples for PWR pressure vessel penetrations (upper and lower head) producing the most concern. By comparison to the Ni-base alloy welds, stainless steel welds have shown much greater resistance to SCC although a few cases of cracking have been identified in BWR components. This brief overview demonstrates the critical need for an improved understanding of welding materials and the welding process itself.

The research objective of this topic area is broad-based and encompasses existing LWR weldments and materials, replacement materials, repair considerations and new welding approaches for next generation LWRs. A combination of experimentation and modeling is proposed to develop fundamental understanding of weld metal and HAZ metallurgy then quantitatively link these characteristics to SCC and hot cracking in some cases. The emphasis is expected to be on Ni-base alloy dissimilar-metal welds, but is not limited to these materials. A key aspect will be establishing microstructural/microchemical and stress/strain evolution in the weld metal and HAZ as a function of welding procedures and component aspects. The ability to effectively model these relationships may allow welding approaches to be tailored on a pass-by-pass basis to optimize final weldment resistance to service failure.

Several brief descriptions of possible research tasks are given below. These are provided to illustrate a few more specific areas where fundamental understanding is needed and are not intended to restrict proposed ideas within this general topic.

Task A: Improved Understanding of Microstructural/Microchemical Evolution and Hot Cracking in Nickel-Base Alloys Weld Metals

Scope

The understanding of the metallurgy in Ni-base alloy welds is not sufficient to effectively assess performance. It is highly desirable to expand our knowledge base through detailed characterizations of LWR-qualified weldments. Examinations should be performed at moderate-to-high resolutions of weldments removed from LWR service, mock-ups welds and various test welds made with alloy 182/82 and alloy 152/52. Measurements should be made spanning macroscopic to microscopic techniques and in some case will require characterizations at nanometer resolutions. The intent will be to greatly expand our understanding of weld metal structures in actual and simulated LWR service components with a focus on solidification segregation and second-phase precipitation particularly at interdendritic grain boundaries. The second key aspect will be relate these same microstructural and microchemical features to the susceptibility to hot cracking for both the low-Cr alloy 182/82 welds and the high-Cr, alloy 152/52 welds.

Task B: Influence of Weld Metal Microstructure/Microchemistry and Pre-Existing Hot Cracks on Stress-Corrosion Cracking of Nickel-Base Alloys

Scope
An important disconnect between the technical community who believe cracking in Ni-base alloy weld metal (alloy 182 or 82) can occur solely due to SCC and utility perception that susceptibility primary results from pre-existing hot cracks due to poor manufacturing. Key tests are needed to critically assess the influence of not only pre-existing hot cracks, but solidification segregation or precipitation on SCC. An improved understanding of dendritic and grain boundary compositions in weld metals must be established and used to systematically create realistic material conditions for quantitative SCC crack-growth tests. Gleeble experiments should be conducted to document controlled heating and cooling on interfacial structure and composition. Finally, the influence of pre-existing hot cracks on SCC initiation and propagation must be explored. Initial experiments can be run on samples removed from laboratory welds where hot cracking has been investigated.

Task C: Assessment and Modeling of Stain and Stress States in Weld Metal and Heat-Affected-Zone Regions for Optimized Welding

Scope
SCC susceptibility in both weld metal and HAZ regions is typically driven by welding-induced local strains and the final residual stresses. Prior work related to BWR pipe cracking has examined welding procedures and component issues such as pipe diameter and constraint on the plastic strains developed in the HAZ on a pass-by-pass basis. Modern finite element modeling (FEM) approaches can effectively evaluate temperature, stress and strains that evolve dynamically during welding. Additional experimental work will be needed to assess key FEM predictions on a pass-by-pass basis to quantify the predictive capability. Once established, FEM would be used to systematically evaluate welding procedures on the stress/strain evolution and even microstructural changes (through the temperature/strain history) for specific weld-metal and HAZ regions. Controlled experiments will be run to test model parameters and help validate predictions. The intent will be to tailor weld parameters for the optimization of material microstructure and final stress/strain condition.

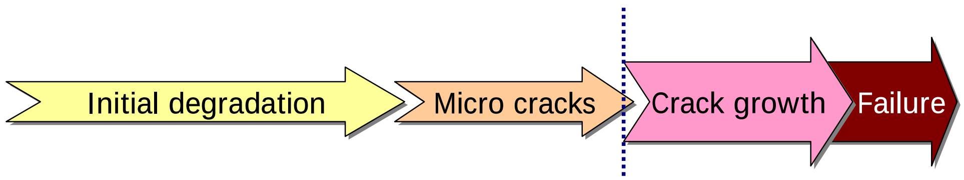
Inservice Inspection & Continuous Monitoring Subgroup

Topic Area #1

Detection and Evaluation of Micro/macro Cracks

Background, technical issues

In nuclear power plants micro cracks are initiated and their growth is driven by the surface degradation caused by environmental factors such as pressure, vibrations, high temperature, etc. The growth of micro cracks into larger cracks (see figure below) is a crucial problem and a contributor to the failure of major components in nuclear power plants. Thus detection and evaluation of micro cracks is a major issue in the proactive management of materials degradation.



However, using conventional nondestructive testing methods such as bulk wave ultrasonic testing, eddy current testing, etc, it may not be possible to quantitatively detect and evaluate micro cracks since these conventional methods have been developed primarily for detection and evaluation of defects with relatively large size.

Therefore, new nondestructive testing techniques are necessary for improving the detection and evaluation of micro cracks.

Current Status

Conventional NDE techniques have not shown the capability to detect and characterize micro cracks however laboratory research techniques indicate the potential for detecting and evaluating micro cracks.

Some of the research under development includes the following

- The detection of material degradation caused by corrosion-fatigue has been demonstrated using a computer controlled backscattered surface wave system.
- Very high-frequency surface wave acoustics (in GHz range) have demonstrated the

detection of micro-scale stress corrosion cracks based on velocity variation.

- Time reversal techniques for improving probability of detection (POD) of small flaws such as hard alpha inclusions, stress corrosion cracks, circular cracks, etc have been adopted.

Objectives

1. Development and evaluation of NDE techniques for reliable detection and accurate characterization of micro cracks in LWR components.
2. Determine characteristics of micro cracks parameters (size, number, distribution, etc.) and their influence on materials degradation status.

New research to be conducted, scope, variables topic

- Investigation of performance and limitations of conventional NDE methods for detection and evaluation of micro cracks
- Develop theoretical models for predicting responses from micro cracks that describe the underlying physics related to generation and acquisition process
- Development of new signal processing and interpretation methods for quantitative micro crack evaluation.
- Develop new/advanced NDE techniques for detection and evaluation of micro cracks located on the surface and/or embedded in the subsurface
- Establish relationships between micro crack parameters and materials degradation status.

Inservice Inspection & Continuous Monitoring Subgroup

Topic Area #2

Detection and Characterization of Material Degradation Precursors

Background and Technical Issues

Presently NDE is used to identify defects (cracks, fabrication flaws, wall thinning) that have already developed and may challenge component integrity. The capability to detect and characterize the precursors to degradation initiation enables materials degradation management.

Materials degradation management may be accomplished by inspection alone or by a combination of inspection and mitigation. The earlier degradation can be detected the greater the potential for efficient management and cost reduction.

The precursor stage of degradation may exhibit physical characteristics substantially different than the macro-defect that ultimately manifests. The ability to predict degradation by detecting and characterizing precursor state(s) may require an inspection capability that is:

a. evolutionary (i.e., higher spatial resolution ultrasound)
b. revolutionary (i.e., entirely new application of physics/engineering to this NDE problem).

The technical issues for development of new NDE approaches to precursor characterization range from advanced engineering concepts to more fundamental understanding of how physical states and material features (or properties) are exhibited and hence, measurable.

Current Status

Presently precursor states are not well understood with respect to degradation mechanism. Fundamental work associated with understanding precursors of defects in nuclear reactor materials is part of the PMDM program and will provide guidance to NDE and monitoring research activities.[1]

Conventional NDE methods do not currently measure precursor states.

We don't know what to measure and we don't know how… yet!

Objectives

1. Establish collaborative efforts with materials researchers developing theories on precursors to establish the measurable physical properties.

2. Design, develop and evaluate advanced laboratory NDE techniques to quantify precursor state, validate theories on precursors and demonstrate potential for field deployment.

3. Develop a physical basis for NDE measurements of precursors - theory and modeling.

4. Design and develop advanced in situ measurement techniques for precursor inspection.

5. Validate the techniques by inspecting/monitoring in situ reactor components

New Research to be Conducted, Scope, Variables

NDE technology for identifying and quantifying precursors to degradation is a new field. Research is needed to develop a sound technical foundation for advances in measurement science related to precursors. Development of new/advanced NDE theory and systems needs to occur in parallel with precursor materials research.

Research activities include:

1. Establish or identify measurable precursors to degradation
    a. Localized surface chemistry changes
    b. Surface phenomena (bubbles, micro cracks, voids, etc.)
    c. Material properties changes
        i. Stress
        ii. Fracture toughness
    d. Corrosion
2. Develop theoretical models that provide the physical basis for direct and indirect relationships between material degradation precursors and NDE measurement(s).
3. Develop new/advanced NDE inspection measurements and sensors with sufficient spatial and contrast resolution, signal-to-noise ratio, etc. for precursor assessment.
4. Demonstrate developed NDE systems on reactor components.

Reference

1. Topic #1 “Initiation and Propagation of SCC in cold worked stainless steel and Alloys 600 and 690: Fundamental assessments of crack tips” and other papers/publications (PMDA App. B?) associated with precursors.

Inservice Inspection & Continuous Monitoring Subgroup

Topic Area #3

Continuous Monitoring for Detecting LWR Materials Degradation

Background and Technical Issues

Degradation has been occurring in light water reactors (LWRs) since reactors started operation. NDE is one layer of the defense-in-depth for safe operation by detecting degradation before it challenges the structural integrity of nuclear reactor components.

There are significant limitations to the required NDE that is performed on a periodic basis as part of the inservice inspection (ISI) program. Improvements can be made to ISI programs to overcome some of the limitations through improvements in how frequently inspections are performed (reduction from a 10 year interval to every refueling outage), the effectiveness of the NDE method (employing SAFT or phased arrays versus conventional amplitude based UT), etc. Other limitations are not solvable with simplistic improvements in the ISI program. For example, there are a number of locations where access to the areas requiring inspection are limited because the surface of the component is in an as welded condition or surface geometries (tapers) limit inspection. There are also limitations because of other components or structures preventing delivery of the NDE energies to the zones requiring inspection. In addition there are classes of problems such as the coarse grained materials which are found in cast stainless steels, dissimilar metal welds, corrosion resistant cladding and the far side inspection of austenitic stainless steels for which reliable and effective inspections have not been developed.

Where there are limitations dealing with periodic ISI, there needs to be alternative approaches to managing degradation through the use of technologies such as continuous on-line monitoring.

Current Status

Degradation is continuing to occur on the aging fleet of nuclear power plants. Degradation must be managed and a key element is the NDE/ISI program to insure continued safe operation and continued public confidence in this form of electricity production. Continuous on-line monitoring of reactor systems and components is one means to overcome some of the important limitations of periodic ISI.

Continuous on-line monitoring technology has been developed and demonstrated for fatigue and IGSCC through extensive laboratory studies and on plant monitoring for several fuel cycles. This technology is in the ASME Code for monitoring ISI detected cracks. The technology in the ASME Code is based on the use of acoustic emission (AE). This technology has not yet been employed on a nuclear power plant to detect the initiation of degradation. There no technical reason why it will not work to detect initiation, it just has not been demonstrated other than in the laboratory. Furthermore, any degradation process that results in the release of acoustic energy during initiation and growth should produce detectable AE events. The use of AE is a passive way to monitor components and structures.

The use of alternative technologies such as guided waves is an active method to monitor large areas and these technologies can be employed on-line to provide monitoring capability.

Objectives

Develop and demonstrate continuous on-line methods to monitor all forms of LWR materials degradation as it initiates and grows.

Include in the evaluation other methods besides AE that can be used to provide more information about degradation precursors on a continuous on-line basis

Validate continuous on-line technology on operating plants to demonstrate the viability for performing this type of monitoring without false alarms and to provide an accurate reflection of degradation status.

New Research to be Conducted, Scope, Variables

Although AE has been demonstrated and extensively tested for a number of degradation processes including fatigue and IGSCC, it must be demonstrated for a wide range of expected degradation such as PWSCC, SCC, etc. in order for this technology to establish the case that all degradation occurring or expected to occur will be detectable.

The AE demonstrations that have been conducted in the past on operating plants occurred over 10 years ago and advances in computers, electronics and sensors need to be integrated into a new state-of-the-art system for validation on nuclear power plants.

Review degradation precursors and processes and assess other monitoring technologies such as guided waves to support, compliment, replace and/or enhance AE continuous monitoring.

Conduct demonstrations of technology to address engineering issues of cabling and full plant monitoring needs.

Assess all forms of nuclear power plant emissive energies to determine viability for passive monitoring of materials degradation.

Inservice Inspection & Continuous Monitoring Subgroup

Things Missed

- Crack growth rate monitoring for predicting remaining life
- What more can be learned from conventional NDE
- NDE can lead the way to managing degradation
- Screening method for large areas so that very sensitive measurements in localized areas can be performed
- Generic assessment of NDE methods for measuring stages of degradation – survey other technologies in other fields for use
- Diagnostics and prognostics for managing degradation
- Laser acoustics using fiber optics
- Guided waves
- Absorption spectroscopy
- Stand off remote systems
- Acoustic microscopy for surface studies
- Field deployment Issues
- Coordination activities with materials and degradation as well as repair, replacement and mitigation research activities

Topics for Proactive Materials Degradation Assessment

May 2006

Allen Baum

Suggested Algorithm for Ranking Level of Concern

- $[f \bullet (s - \alpha c - \beta k) - \gamma i - \delta m]p$

- f = consequence of failure
- s = susceptibility
- c = confidence
- k = knowledge
- i = inspectability
- m = ease of mitigation
- p = relative population (i.e. 600 vs 690; PWR vs. BWR; NWC vs. NMC)

- α, β, γ, and δ are weighting factors

- $\alpha \approx 0.2$, $\beta \approx 0.3$, $\gamma \approx 0.1$, $\delta \approx 0.1$

SG Tubing SCC

- Pb + NaOH
  - Determine stress dependence for reference chemistries and tubing materials
    - Is there a threshold stress for no SCC?
    - Is there a threshold degree of cold work for SCC at hydraulically expanded tubesheet joints?
      - If so, can NDE identify these locations?
  - Quantify Pb transport process between bulk and crack face (ppt to % concentrations)
    - Does chemical cleaning promote or prevent further transport?
  - Quantify extent of buffering in SG crevices compared to tests

SG Tubing SCC (continued)

- **Sulfur-species SCC**
  - Quantify cold work required for SCC at tubesheet joints
    - A600SR (OTSG) tubes (mechanically rolled?)
    - A600TT and A690TT tubes (hydraulically expanded)
- **PWSCC (or LPSCC)**
  - Quantify cold work required for SCC at hydraulically expanded tubesheet joints

May 25, 2006

MEMORANDUM TO: Jennifer L. Uhle, Deputy Director
Materials Engineering
Division of Fuel, Engineering and Radiological Research, RES

FROM: Joseph Muscara, Senior Technical Advisor ***/RA/***
Materials Engineering
Division of Fuel, Engineering and Radiological Research, RES

SUBJECT: MEETING SUMMARY FOR THE CHARLESTON, SC MEETING TO CONTINUE PLANNING AN INTERNATIONAL COOPERATIVE GROUP AND RESEARCH PROGRAM FOR PROACTIVE MATERIALS DEGRADATION MANAGEMENT

On May 11 to 13, 2006, staff from the Office of Nuclear Regulatory Research and contractors from Pacific Northwest National Laboratory, held a third meeting in Charleston, South Carolina to plan an international cooperative group and research program focused on conducting research and sharing results for implementing Proactive Materials Degradation Management (PMDM) programs. Participants (see enclosed attendance list) were from a range of countries and organizations including the United States, Canada, Belgium, Korea, Japan, Czech Republic, and Taiwan. Participants represent utilities, regulators, manufacturers, universities, and research laboratories. This activity is supported by the Commission's SRMs M041108AB and M060206A.

The purpose of the meeting was to continue to plan and organize an international cooperative research program and group whose function would be to develop and conduct a broad-based research program that can provide the technical basis for any organization to develop and implement proactive materials degradation management (PMDM) programs, or provide regulatory guidance for same. In particular, the main focus was to continue the development (initiated during the previous meeting) by the international community of a broad-based research program plan and overview that would identify the research needed for PMDM that would potentially become part of the cooperation. The meeting was opened (agenda enclosed) by Dr. Joseph Muscara of the Office of Nuclear Regulatory Research at the Nuclear Regulatory Commission (NRC) who provided welcoming remarks, meeting objectives and initiated introductions of meeting participants. He then made a presentation (handout enclosed) to introduce some of the proactive materials degradation assessment (PMDA) work that has been sponsored by the NRC. In particular, his presentation gave an overview of the NRC's PMDA program that assembled a panel of experts which used a Phenomena Identification Ranking Table (PIRT) technique to evaluate degradation phenomena for thousands of PWR

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and BWR components. He discussed the motivation, scope, approach, and some of the findings of this study, including the expert panel's assessment of research needs. Dr. Muscara continued with a discussion of the need and benefits for international research cooperation, and provided a summary of the activities and progress made in the previous planning meeting related to development of a broad-based research program plan. Dr. Muscara indicated that the main focus of this meeting is to continue development of the plan including short write-ups of key research issues and needs. Dr. Allen Baum (NRC consultant) followed and provided a discussion and detailed list of research needs as identified in the NRC's expert panel report from the PMDA study. Following these presentations, five meeting attendees made short presentations related to activities within their organizations, their interests and research needs, and potential research that some of them might provide to the cooperation. The above presentations and discussions were completed by mid-afternoon on May 11, 2006.

Following the above presentations and continuing to the end of the meeting at Noon on Saturday May 13, 2006, the meeting attendees separated into three focus groups to discuss specific research issues, define research needs, and write summaries to further the development of an international broad plan for PMDM research. The three focus groups addressed the areas of 1) mechanisms and materials, 2) inservice inspection techniques and continuous monitoring, and 3) mitigation/repair/replacement. The mechanisms and materials focus group discussed an extensive number of issues that make-up about twenty research topics. It was decided that the key major areas relate to crack initiation, crack growth, and aging effects. Thus three overview papers will be prepared for these areas. Many of the specific issues will fall under one of these areas, and summaries for the specific issues will be written and incorporated under these main areas. Other issues span a number of areas, and in these cases, stand-alone summaries will be prepared. Assignments were made for different meeting participants to write, and for others to review, the various papers over the next several weeks and before the next planning meeting. The inservice inspection and continuous monitoring focus group discussed a number of research issues and needs, and wrote draft summary papers on 1) detection and evaluation methods for micro/macro cracks, 2) detection and characterization of materials degradation precursors, and 3) continuous monitoring for detecting LWR materials degradation. The focus group on mitigation/repair/replacement prepared draft summary papers on 1) surface modification techniques to improve the stress corrosion cracking (SCC) and fatigue resistance, 2) surface coatings for corrosion and SCC mitigation, 3) modification of water chemistry, and 4) welding optimization for microstructural control and stress/strain modification to improve hot cracking and SCC resistance.

The meeting was successful because it continued to raise interest in the international community for participating in an international cooperative research program for PMDM; one additional group indicated its intent to participate. The meeting was also successful because considerable progress was made towards the development of the broad-based research plan overview for the cooperative PMDM research program and group. The next working meeting for the international cooperative group and research program for PMDM is tentatively planned for September 2006 in Europe.

Enclosures:
1. List of Attendees for May 11 to 13, 2006 Public Meeting Agenda
2. Agenda
3. Copy of handout for Dr. Joseph Muscara's Presentation

The meeting was successful because it continued to raise interest in the international community for participating in an international cooperative research program for PMDM; one additional group indicated its intent to participate. The meeting was also successful because considerable progress was made towards the development of the broad-based research plan overview for the cooperative PMDM research program and group. The next working meeting for the international cooperative group and research program for PMDM is tentatively planned for September 2006 in Europe.

Enclosures:
1. List of Attendees for May 11 to 13, 2006 Public Meeting Agenda
2. Agenda
3. Copy of handout for Dr. Joseph Muscara's Presentation

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