U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: PERFORMANCE OF CANDIDATE MATERIALS

PRESENTER: DR. R. DANIEL MC CRIGHT

PRESENTER'S TITLE: METALLURGICAL ENGINEER
AND ORGANIZATION: LAWRENCE LIVERMORE NATIONAL LABORATORY
LIVERMORE, CALIFORNIA 94550

PRESENTER'S
TELEPHONE NUMBER: (415) 422-7051

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VI Candidate Material Performance

R. D. McCright

Plan of Presentation

- **(A) Background of Degradation Mode Surveys (Purpose and Methodology)**
- **(B) Highlights of Degradation Mode Surveys**
  - Phase Stability
  - Oxidation and Corrosion
  - Localized Corrosion
  - Stress Corrosion Cracking
  - Hydrogen Effects
  - Weldability
- **(C) Comparison and Analysis**

(A) Background of Degradation Mode Surveys (Purpose and Methodology)

10CFR60.135 Design Criteria for the Waste Package

The design shall include, but not be limited to consideration of the following factors:

- solubility
- oxidation/reduction reactions
- corrosion
- hydriding
- gas generation
- thermal effects
- mechanical strength
- mechanical stress
- radiolysis
- radiation damage
- radionuclide retardation
- leaching
- fire and explosion hazards
- thermal loads
- synergistic interactions

Background of Degradation Mode Surveys

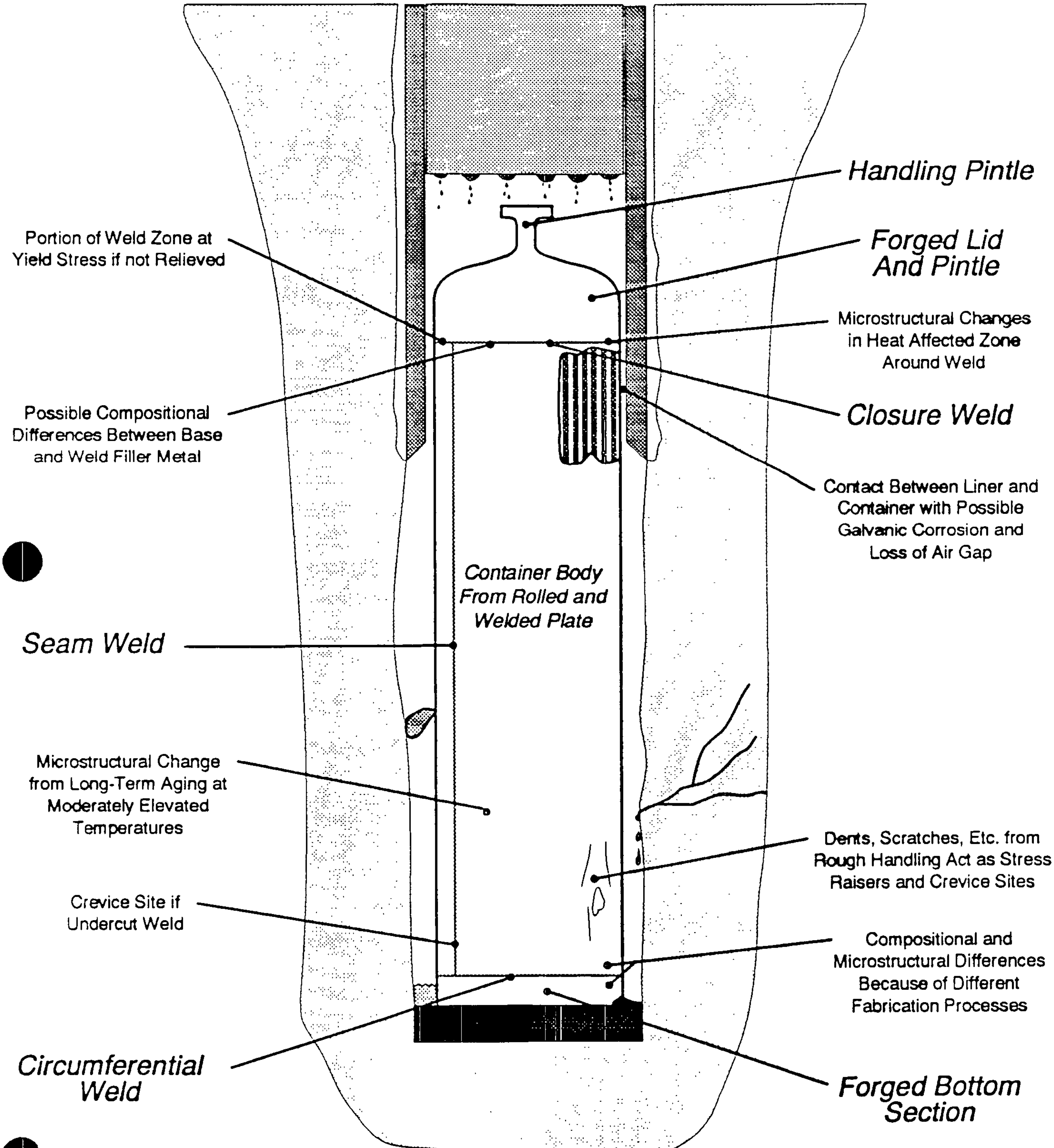
- **Purpose described in Information Need 1.4.2 (Material Properties of the Container) in YMP SCP.**
- **Development.**
  - First literature survey begun in early 1987.
  - Volumes on Phase Stability, Hydrogen Effects, Oxidation and General Corrosion drafted summer/fall1987.
  - Volumes on Localized Corrosion, Stress Corrosion begun in late 1987.
  - Because of performance concerns in welded regions, added volumes on weldability in spring 1988.
  - Draft of volumes completed in June 1988.
  - Overview written in June 1988.
  - Drafts available to Selection Criteria Peer Review Panel for perusal in September 1988.
- **Extensive review during rest of 1988 and 1989.**
  - Formal Project technical review.
  - Formal Project policy review.
  - Formal Project QA review.
  - Project approval of 8-volume set + overview in November 1989.

Next Viewgraphs Illustrate *Possible* Performance Concerns for Container

- **Schematic of vertically emplaced waste package.**
- **For purposes of illustration on the schematic.**
  - Assumptions made on container fabrication processes (other processes under consideration).
  - Assumptions made on configurations of shield plugs, borehole liners, etc. (other configurations possible).
  - Configurations not drawn to scale.
- **To the maximum practical extent, proper design of waste package and borehole, choice of container materials and container fabrication/closure processes will eliminate or mitigate some performance concerns.**

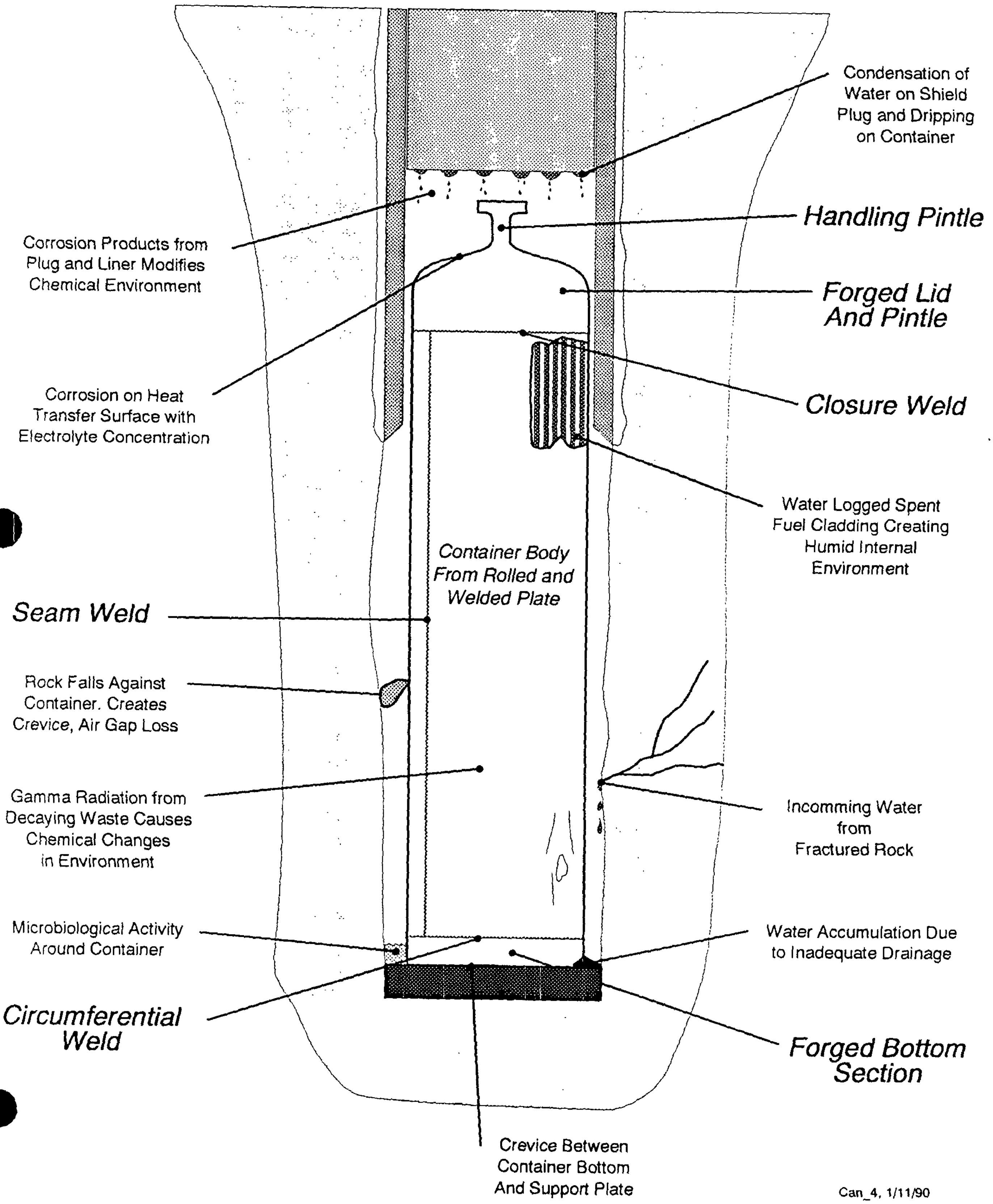
Container Performance Considerations

(Metallurgical / Mechanical)



Can_3, 1/11/90

Container Performance Considerations
(Chemical / Environmental)



Can_4, 1/11/90

Methodology Used in the Degradation Mode Literature Search

- **1. Computer searches of applicable data bases (esp.** *METADEX, NTIS, ENERGY, CHEM ABSTRACTS*).
- **2. Study of review articles for overview information.**
- **3. Obtaining references cited in review articles.**
- **4. Review of conference proceedings, e.g. NACE.**
- **5. Review of books on specific topics, e.g. ASTM STP series.**
- **6. Review of current literature for data/information not in current data bases, especially following journals:** *Corrosion, Materials Performance, Corrosion Reviews, Corrosion Science, British Corrosion Journal, Journal of Materials Science, Journal of Nuclear Materials*
- **7. Obtaining references identified in above (especially publications before 1960s that are not indexed in data bases). Manual search of selected journals.**
- **8. Use applicable NNWSI-published information.**

Accomplishments of the Degradation Mode Surveys

- Extensively reviewed the published technical literature
- Compiled existing data on candidate material degradation
- Interpreted data according to the situation of a container emplaced in Yucca Mountain
- Completed 8 volumes and an overview, more than 400 typeset pages and 1200 references
- Surveys will be used to assist in (1) materials selection, (2) performance model development, and (3) experimental design for parametric studies

Degradation Mode Survey Topics

Volume 1	Phase Stability
Volume 2	Oxidation and Corrosion
Volume 3	Stress Corrosion Cracking and Localized Corrosion of the Austenitic Candidates
Volume 4	Stress Corrosion of the Copper-Based Candidates
Volume 5	Localized Corrosion of the Copper Based Candidates
Volume 6	Hydrogen Effects
Volume 7	Welding Effects in the Austenitic Candidates
Volume 8	Welding Effects in the Copper-Based Candidates

(B) Highlights of Degradation Mode Surveys

Highlights of Degradation Mode Survey
Volume 1

Phase Stability

- Copper Base Alloys

- Austenitic Alloys

Phase Stability Affects Degradation When Brittle or More Corrosion Prone Phases Form

- Identify known phase transformations in alloy system
- Effects of phase transformation on mechanical properties of material
- Effects of phase transformation on corrosion behavior of material

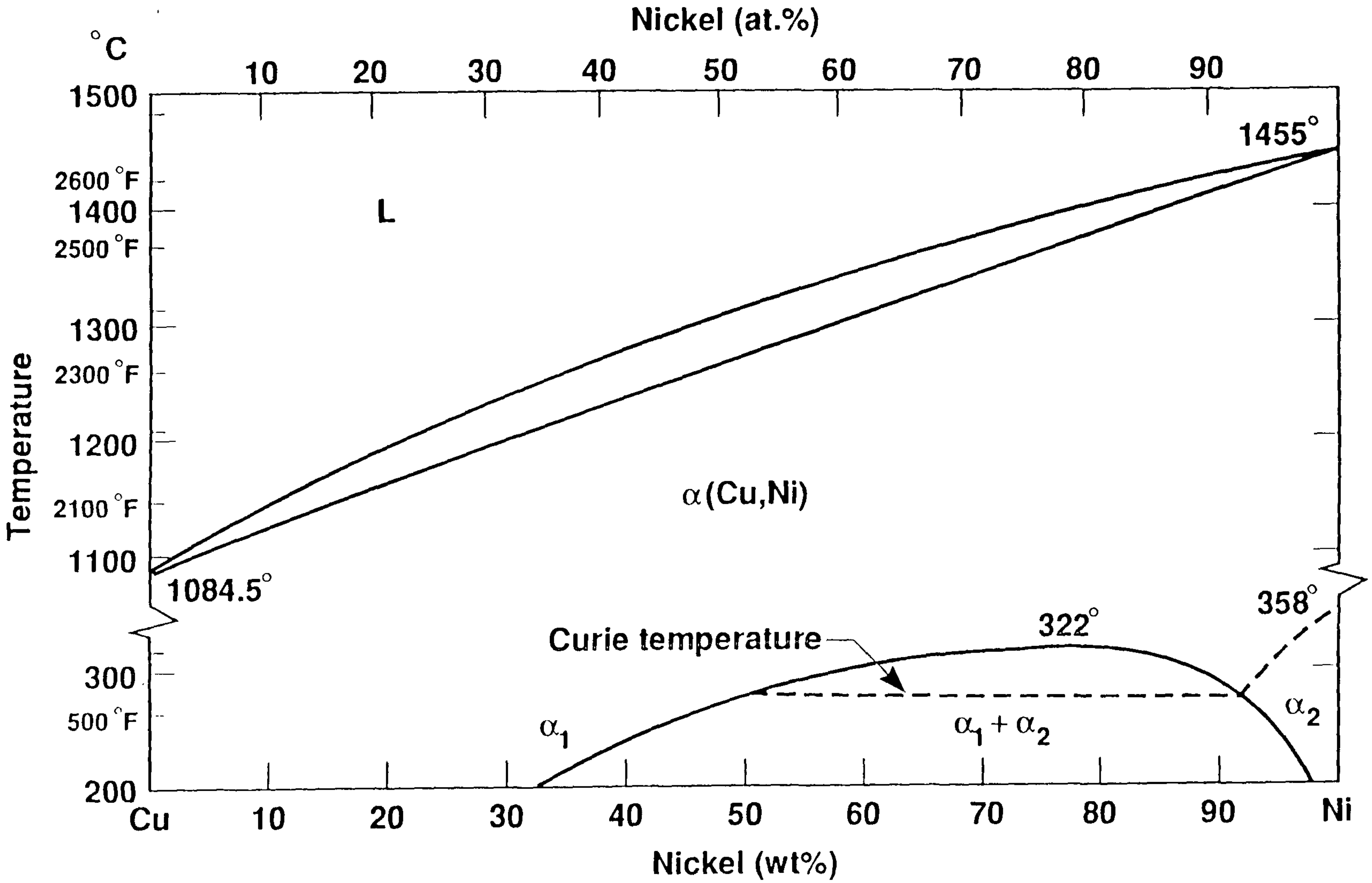
Copper-based candidates

- CDA 102
  - single phase, fcc metal
  - internal oxidation could be a problem
  - phosphorus-deoxidized alloy could be used

- CDA 613 (aluminum bronze)
  - single phase material with small Fe precipitates
  - precipitates harden the alloy
  - Sn enhances IGSCC resistance in steam
  - dealloying may be a concern

- CDA 715 (Cu-30Ni)
  - solid solution of Ni in Cu
  - low temperature miscibility gap predicted

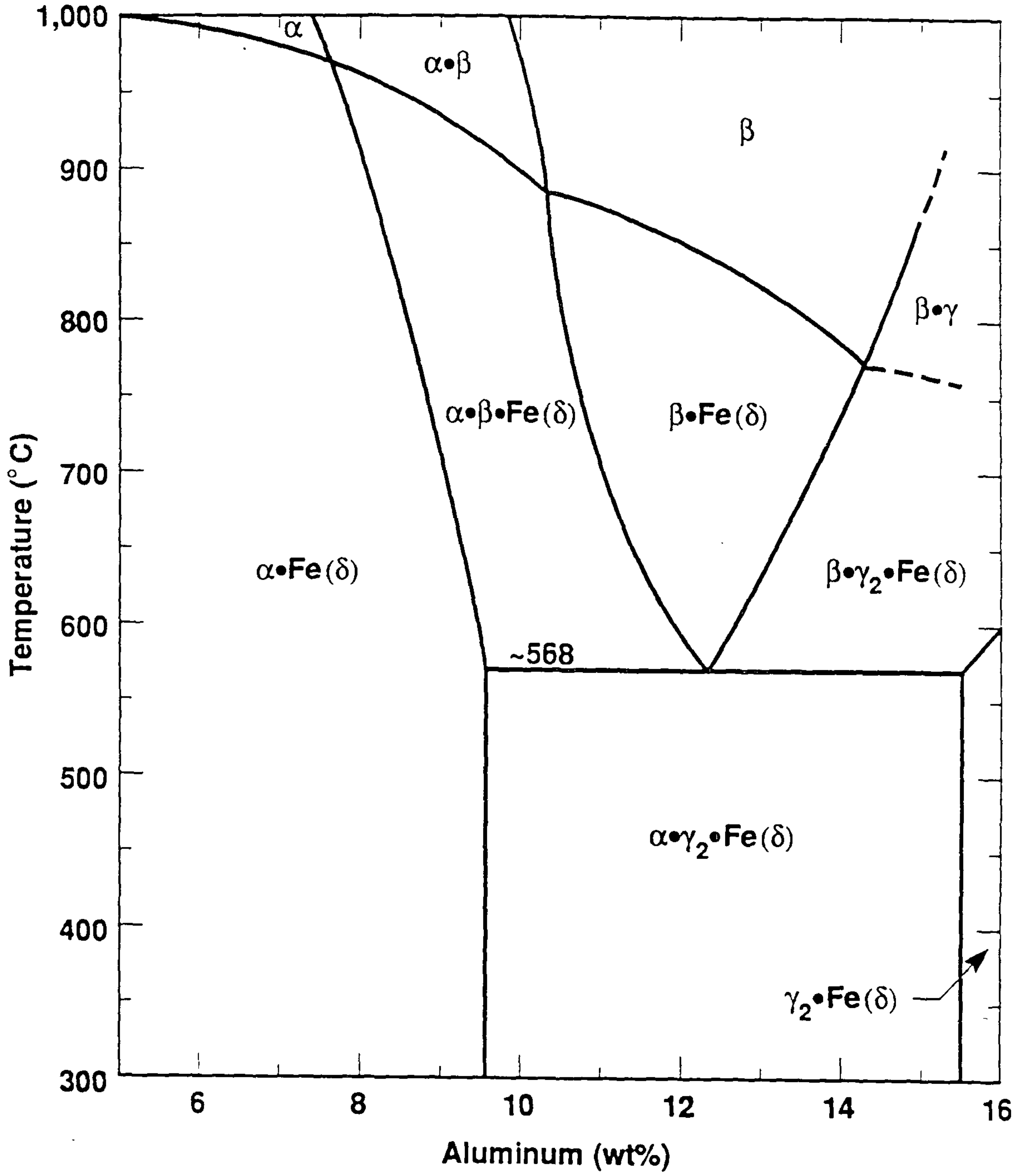
Copper–nickel equilibrium phase diagram



From ASM Metals Handbook, 8th Ed., Feest and Doherty, J. Inst. Metals, Vol. 99, 1971, p.102

LW-023-u-1131-3a

Copper–aluminum equilibrium phase diagram at 3% iron



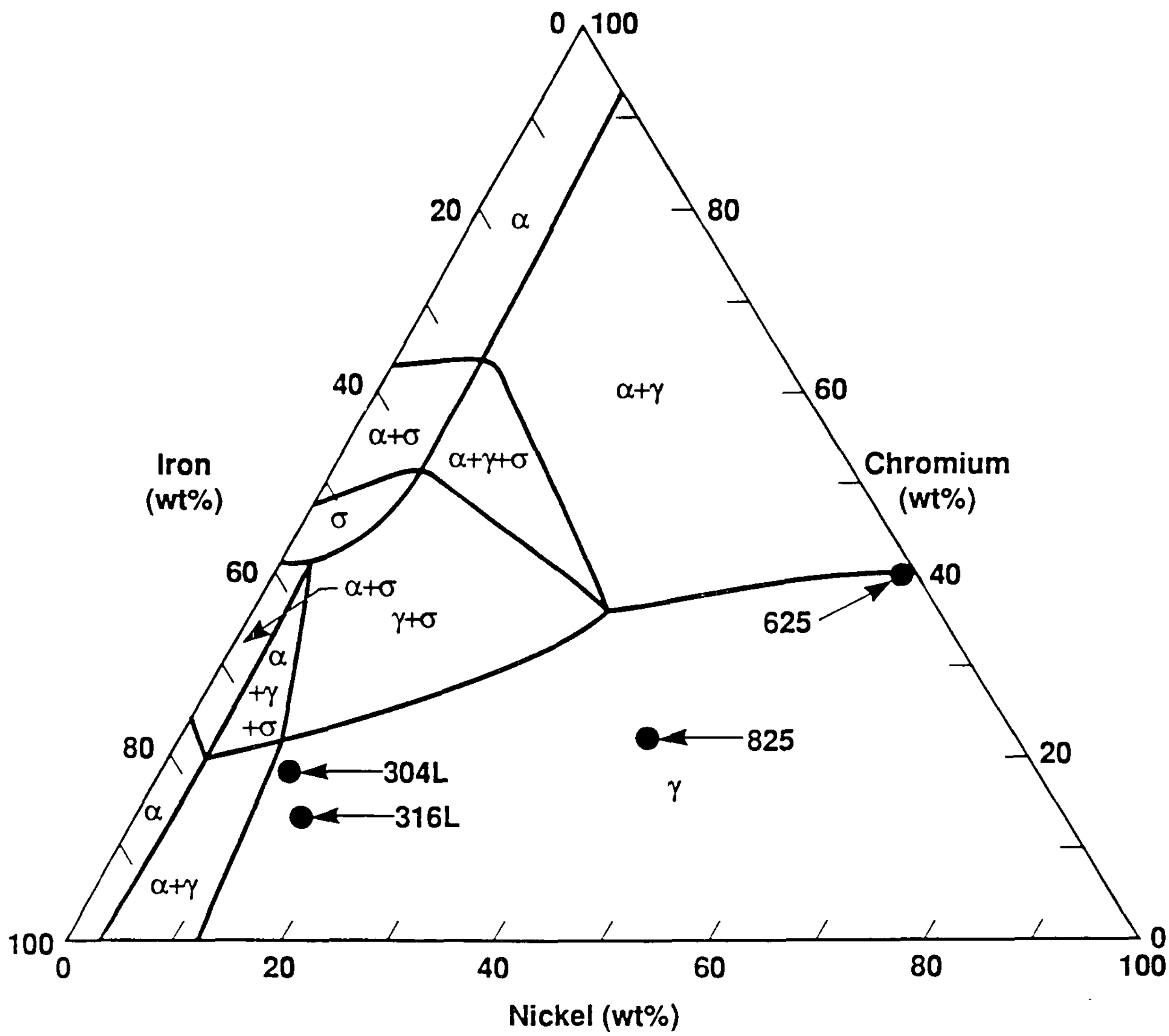
From West, Copper and Its Alloys, John–Wiley, 1982

LW-023-u-1131-2a

Austenite candidate materials

- Iron-nickel-chromium alloys
- Types 304L and 316L are metastable alloys
  - transform to ferrite and martensite at low temperatures
- Alloy 825 is austenite stable
- Carbide formation and subsequent sensitization are potential problems
  - can cause intergranular stress corrosion cracking (IGSCC)
  - thermal history is important
  - low temperature sensitization
  - low carbon grades are better
- Intermetallic phases can form in stainless steels
  - degrade mechanical and corrosion properties

Types 304L and 316L are close to two–phase regions and are believed to be metastable. Alloy 825 is thermodynamically stable.

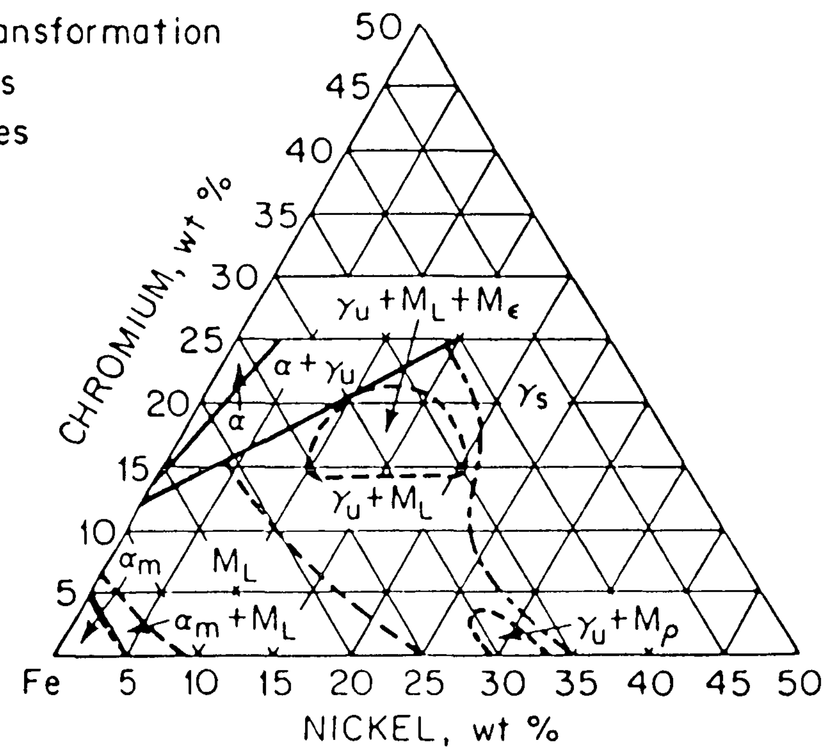


Iron–chromium–nickel equilibrium phase diagram at 650°C. From Bullen and Gdowski, UCID–21362, Vol. 1, June 1988.

LW-023-u-1131-1a

Fe-Cr-Ni system at room temperature

α_m = Ferrite formed by massive $\gamma \rightarrow \alpha$ transformation
M_L = Martensite in which units are small laths
M_ρ Martensite in which units are large plates
M_ϵ = Hexagonal close-packed martensite
γ_u = Unstable austenite (may transform if cold worked)
γ_s = Stable austenite



Intermetallic Phases in Austenitic Alloys

- Sigma (σ) , Chi (χ), and Laves (η) are thermodynamically stable in Fe-Ni alloys containing Cr, Mo, and other elements

- Sigma (σ) Phase
  - tetragonal structure (A_4B to B_4A) A: Fe, Ni and B: Cr, Mo
  - can result in fracture toughness reduction at $T < 600^{\circ}$ C
  - can cause intergranular corrosion
  - promoted by Si, V, Ti, Mo
  - Mo is constituent in Alloy 825 (~ 3 %) and 316L SS (~ 2.5%)
  - has been positively identified in 316L SS
  - presence speculated in some heats of Alloy 825

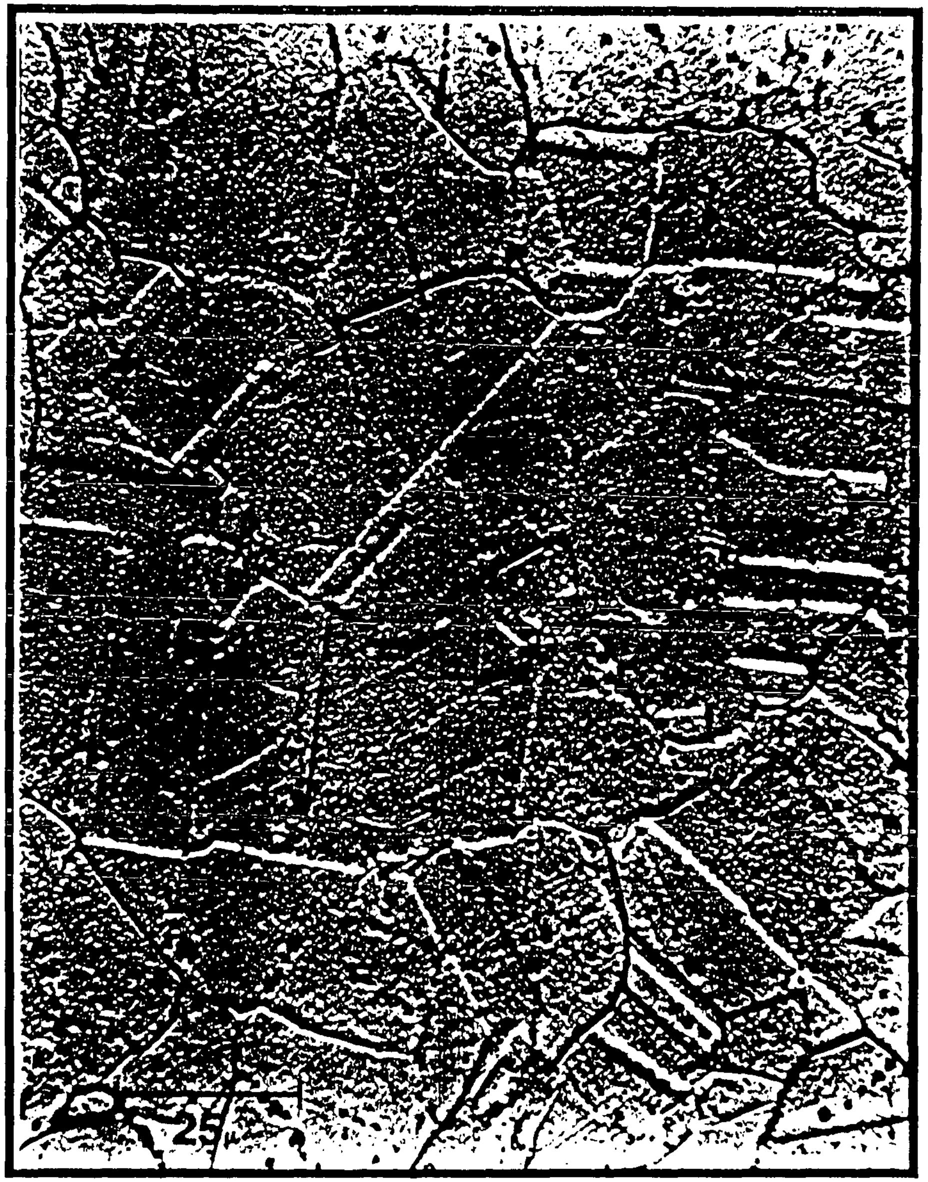
- Chi (χ) Phase -- $(Fe, Ni)_{36}Cr_{12}Mo_{10}$
  - can contribute to intergranular embrittlement

- Laves (η) Phase -- Fe_2Mo
  - can contribute to intergranular embrittlement

Carbide Formation in Austenitic Alloys

- Carbide formed is predominately $M_{23}C_6$ on grain boundaries
- Carbide formation can cause sensitization
  - Sensitization is due to chromium depletion (Cr < 13 wt. %)
  - Sensitized areas susceptible to intergranular attack (IGA) and stress corrosion cracking (SCC)
- Sensitization depends on thermal history and composition
  - Sensitization primarily occurs in $500 < T < 800°$ C range
  - Lower carbon grades are less susceptible
  - Grades containing other carbide forming elements (e.g. Ti, Ta, Nb) are less susceptible
  - IGA and SCC susceptibility (with normal processing):
    Alloy 825 < Type 316L SS < Type 304L SS
- Low temperature sensitization
  - Facilitated by carbide precipitation at higher temperatures
- Healing can occur at long times
  - Cr diffusion back into depleted regions

1000 X



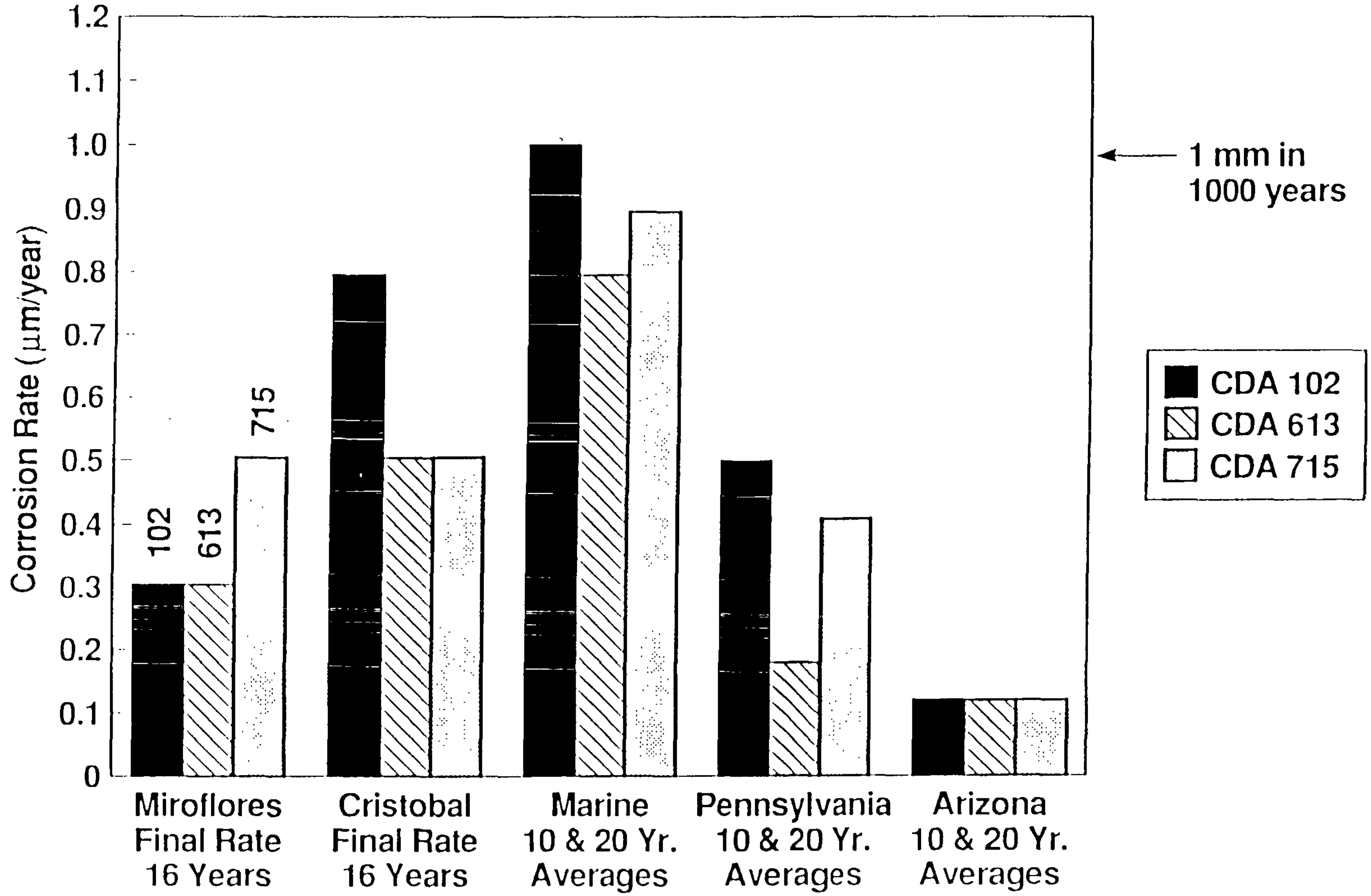
Optical Micrograph of Stabilized Structure of Incoloy 825 Showing $Cr_{23}C_6$ and TiC precipitates

Highlights of Degradation Mode Survey
Volume 2

Oxidation and Corrosion

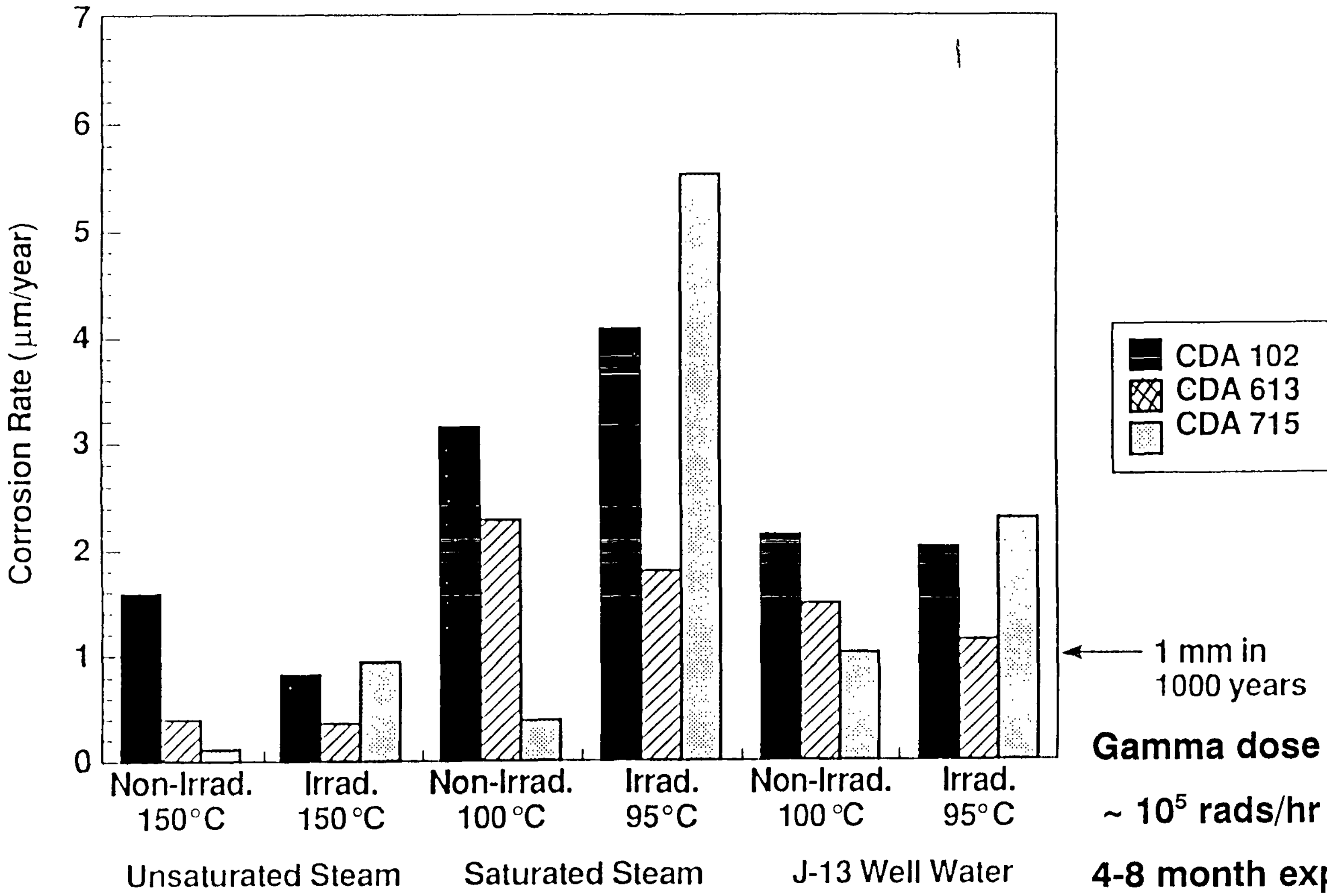
- Copper Base Alloys
- Austenitic Alloys

Container life will not be limited by uniform atmospheric corrosion of the copper-based alloys



From Gdowski and Bullen, UCID-21362, Vol. 2, September 1988 (Tables 6-9)

Gamma irradiation promotes uniform oxidation and corrosion of cupronickel alloys such as CDA 715



Gamma dose rate

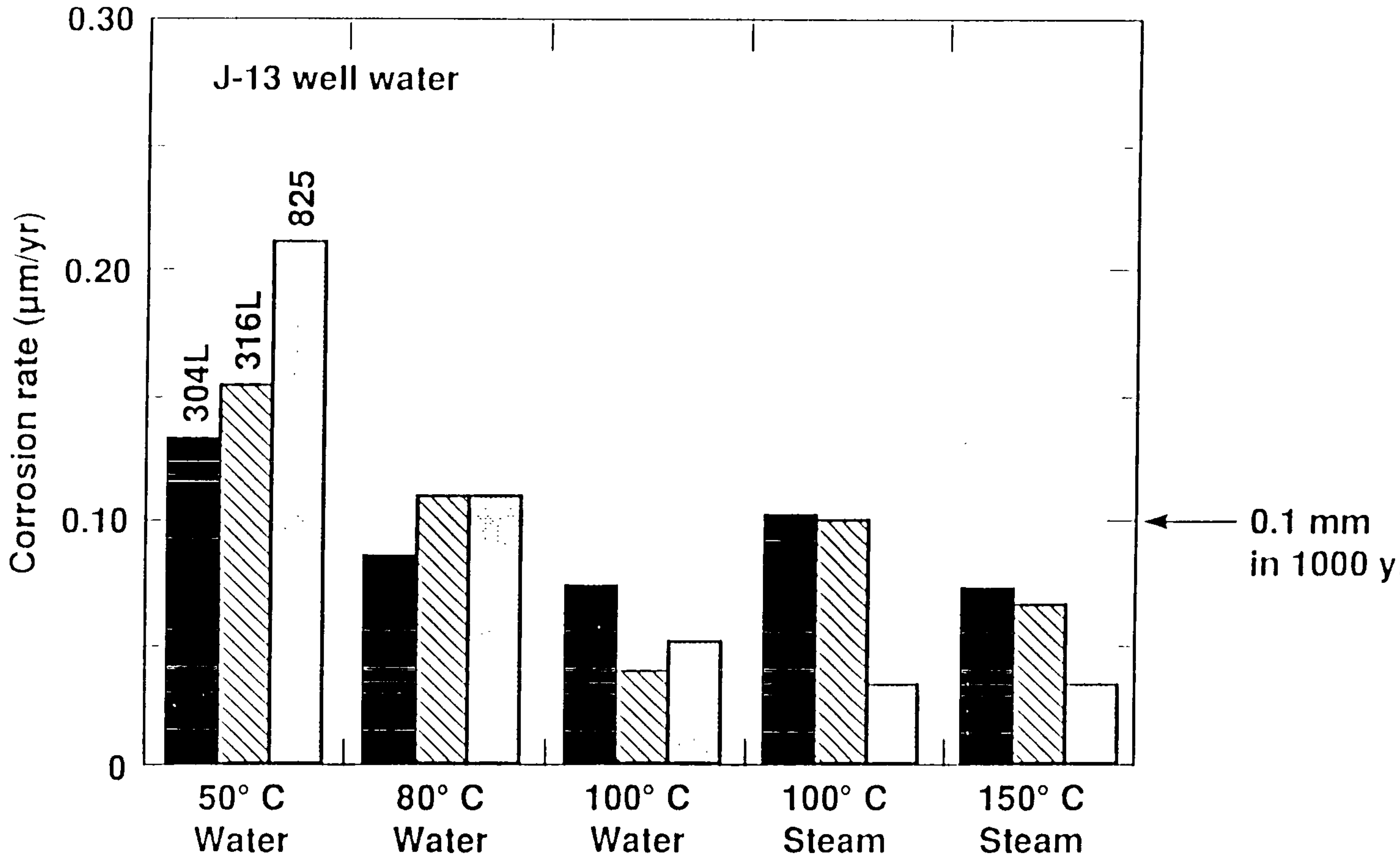
~ 10^5 rads/hr

4-8 month exposures

From McCright et al., UCID-21044, December 1987 (Table 16)

ZC-011-U 1131-006

Container life is not limited by uniform corrosion and oxidation of the austenitic alloys



From McCright et al., UCID–21044, December 1987 (Table 2)

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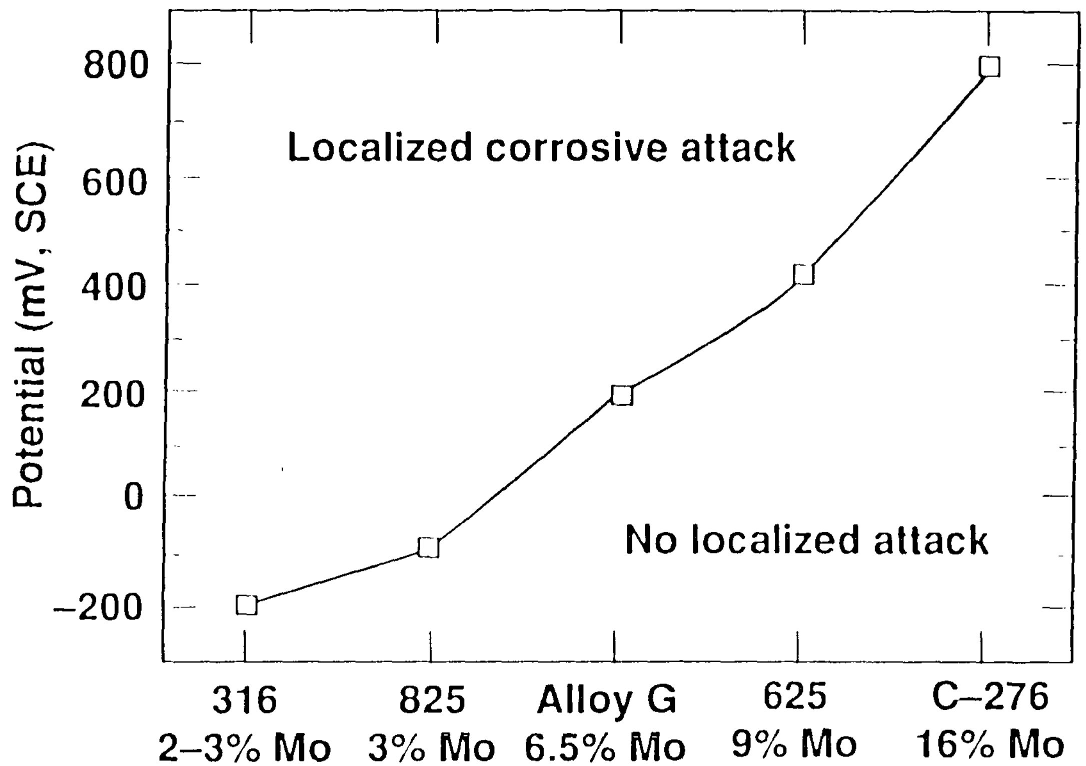
Highlights of Degradation Mode Survey
Volume 3

Localized Corrosion and Stress Corrosion Cracking

- Austenitic Alloys

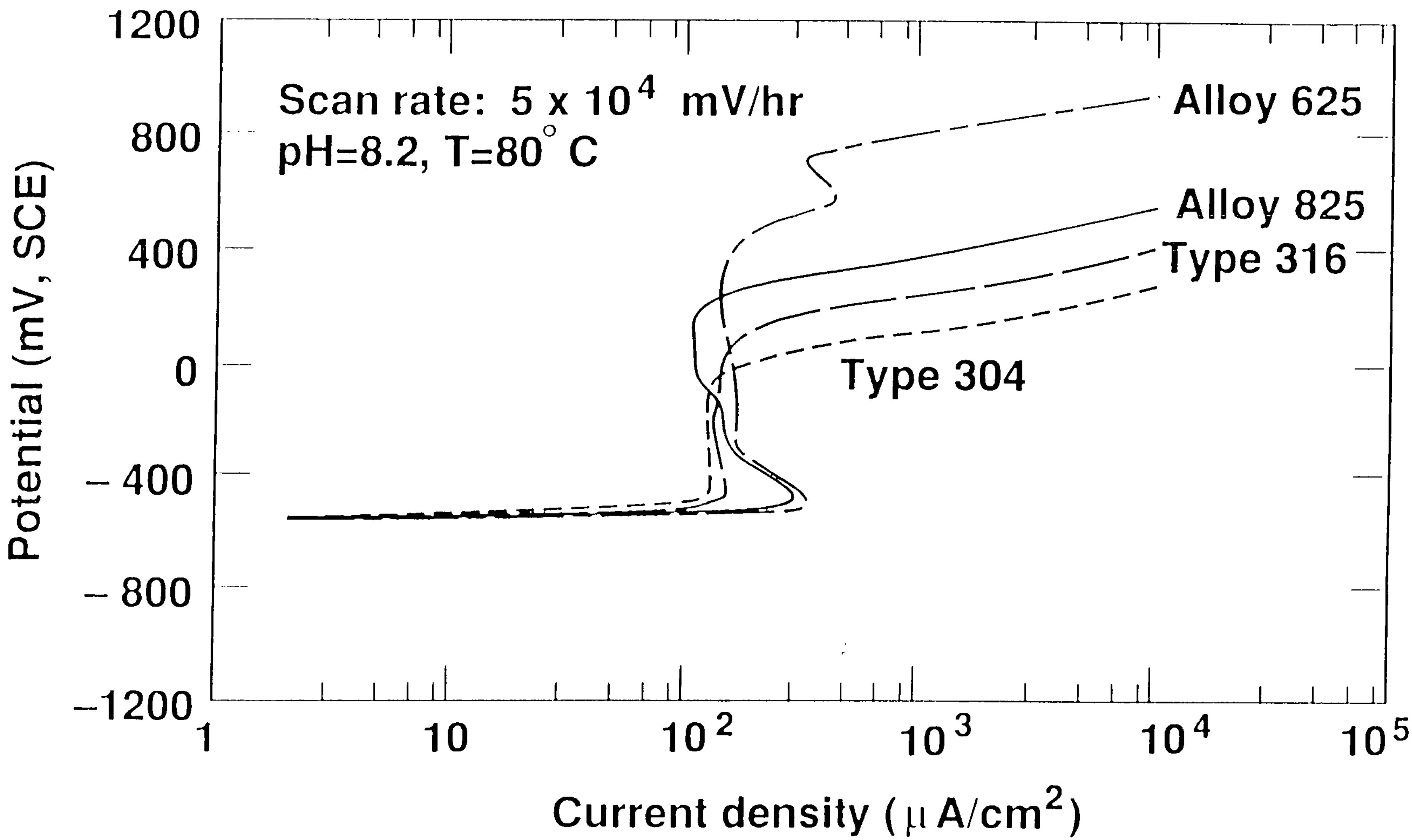
Molybdenum additions enhance resistance to localized corrosion



Exposure to 3.8% $FeCl_3$ at 70°C for 24 hours, constant applied potential.
From Asphahani, Matls. Perform. Vol.19, No.8, August 1980, p.9.

rs-u-001-8855-18a

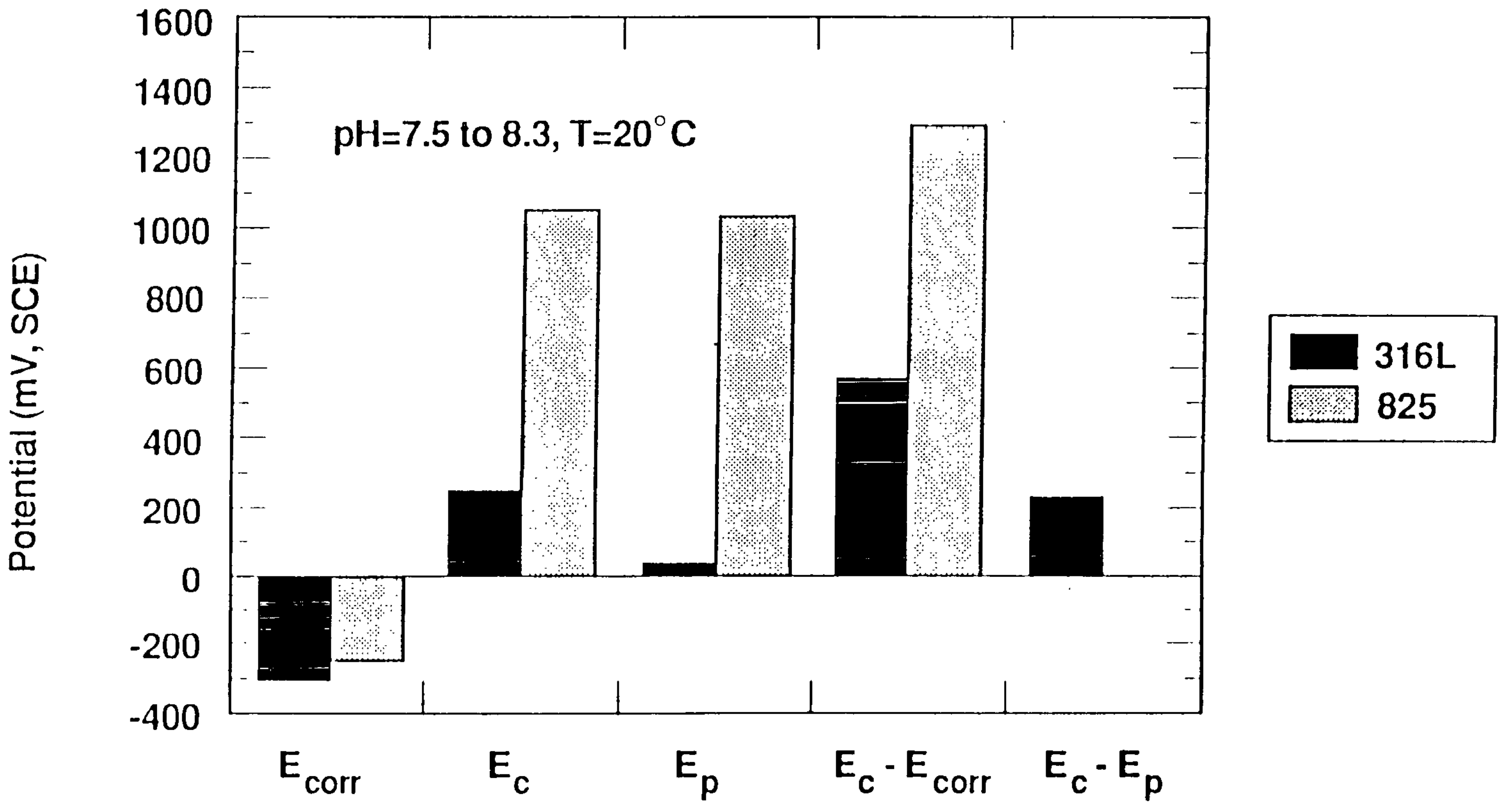
Pitting potentials were determined by linear sweep anodic polarization



Slow scan tests in deaerated sea water. From Scarberry et al., Paper No.. 245, Corrosion 79, Atlanta, Ga., March 12-16, 1979

CC U 005 7098 2 A

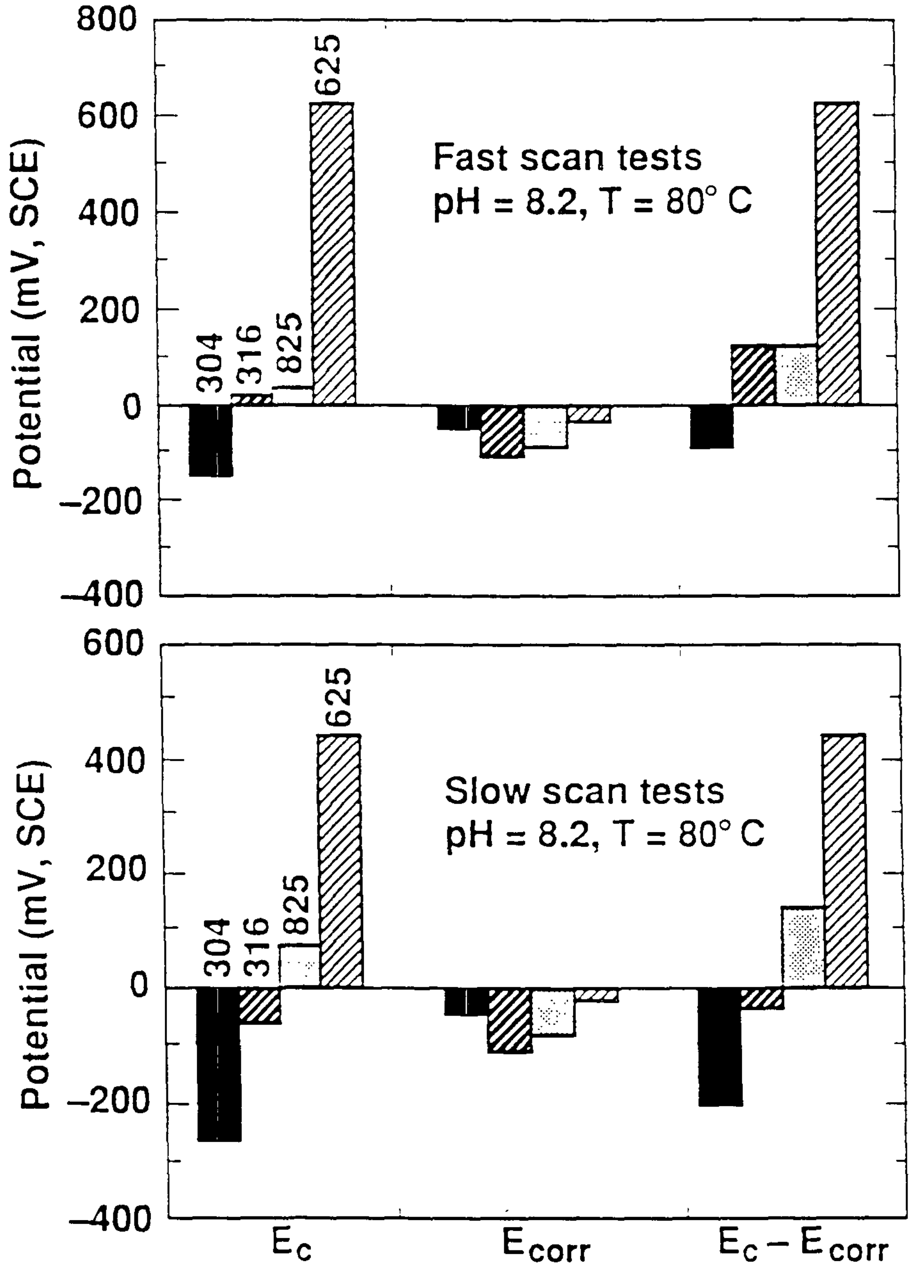
Alloy 825 has more resistance to both crevice and pitting corrosion than Type 316L stainless steel in aerated sea water at 20°C



From Hodgkiess and Rigas, Desalinsation, Vol. 44, 1983, p.283.

G.B. 008 U 1131 002

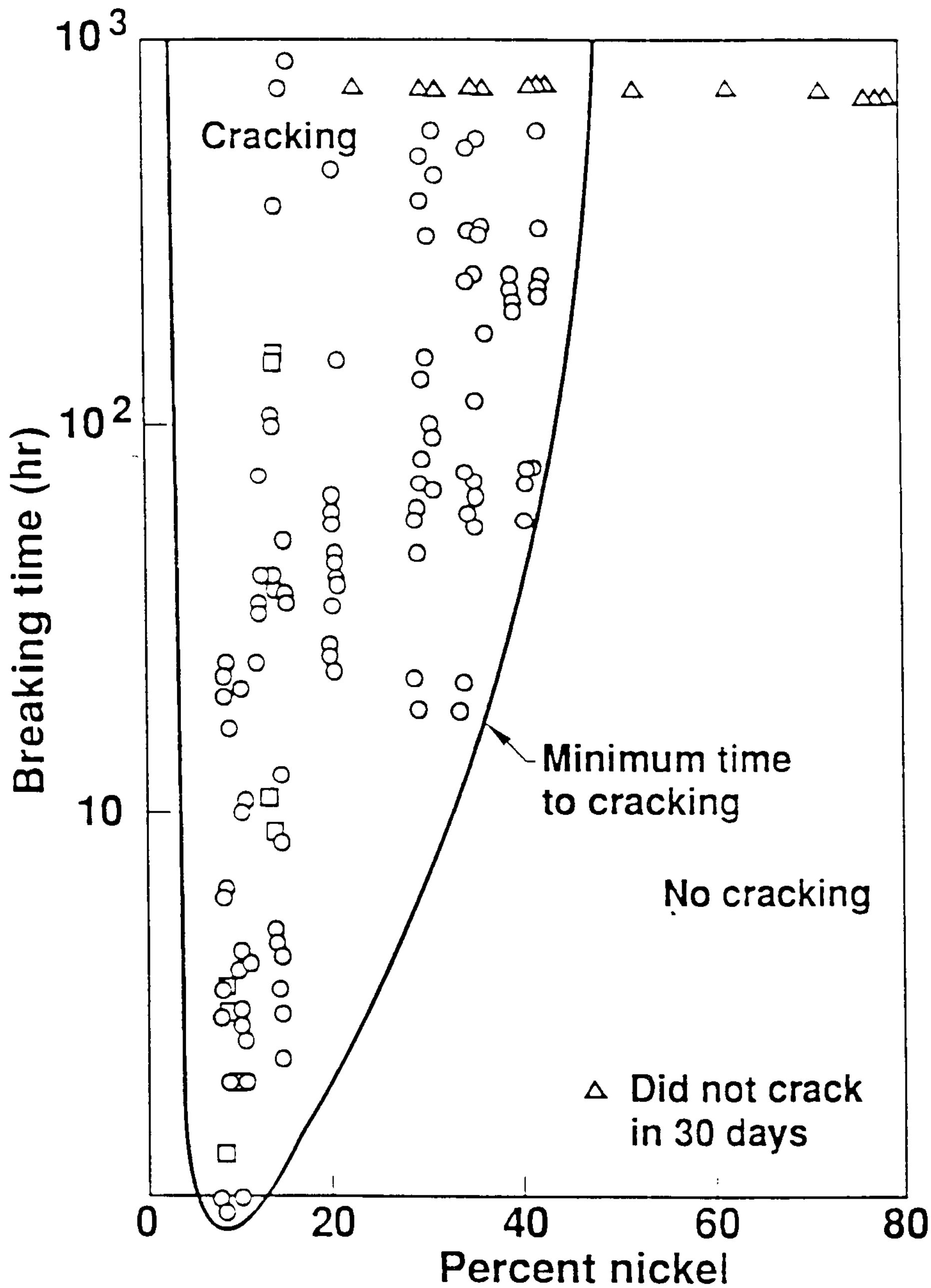
Of the candidate austenitic alloys, Alloy 825 has the greatest resistance to pitting in SO_2-saturated sea water



Alloy 625 is a possible weld filler metal for Alloy 825. From Scarberry et al., Paper No. 245, Corrosion 79, Atlanta, GA, March 12-16, 1979.

AH-004-U-1132-12

Nickel additions to austenitic alloys decrease susceptibility to stress corrosion cracking



Specimens exposed to boiling 42% $MgCl_2$. From Copson, Physical Metallurgy of Stress Corrosion Fracture, Interscience, 1959, p. 247

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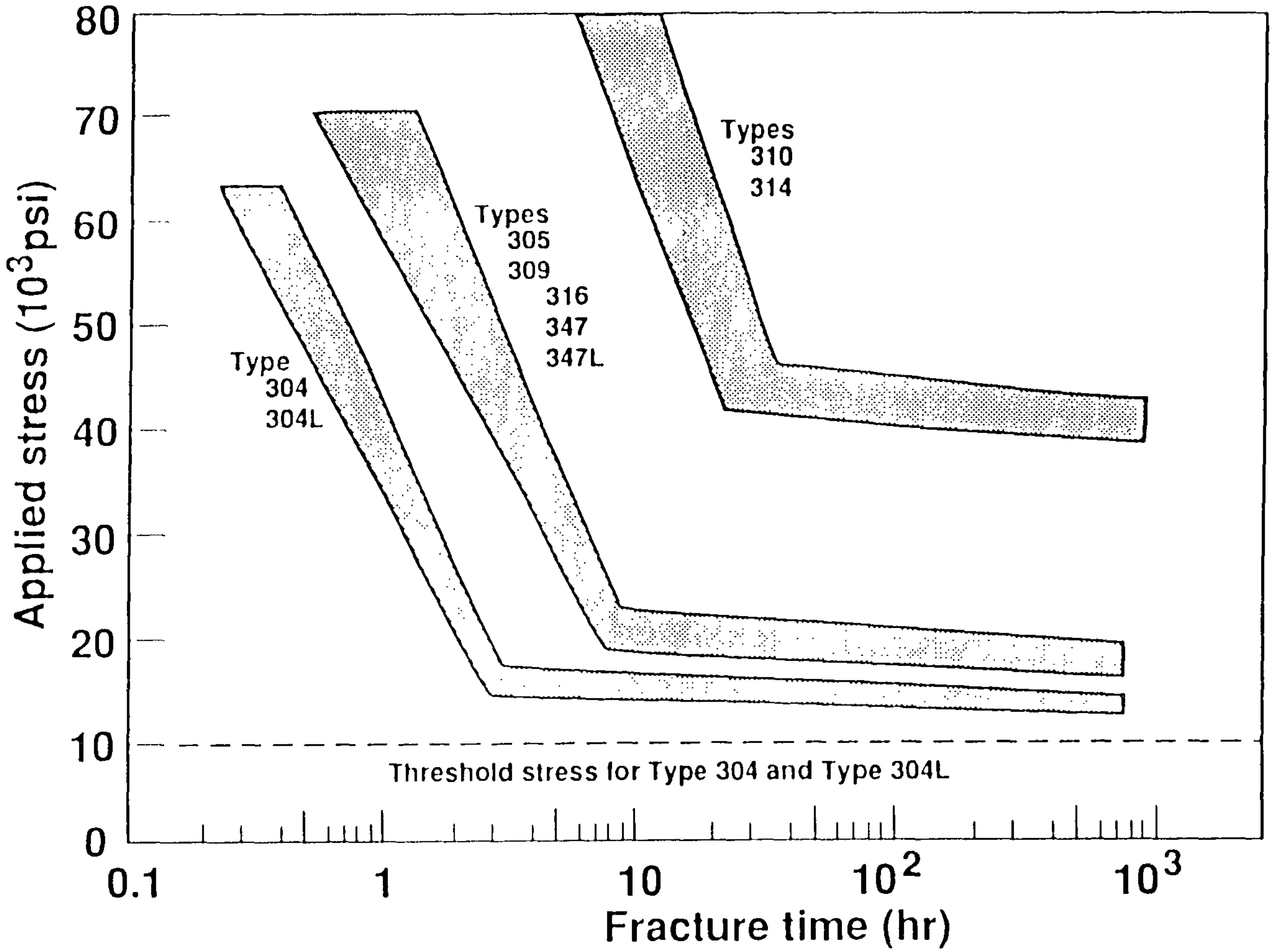
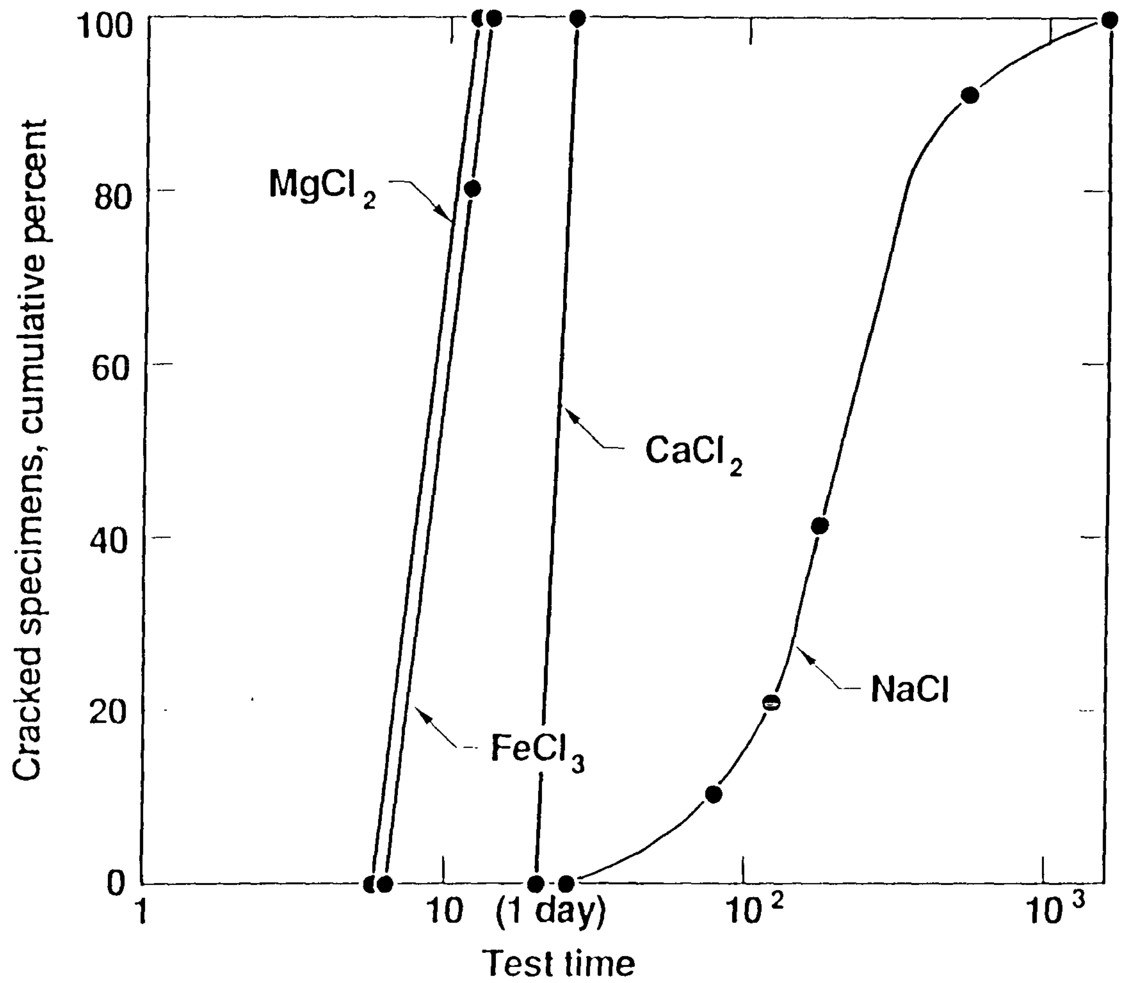
The threshold stress for Type 316L is higher than that for Type 304L



Specimens exposed to boiling 42% $MgCl_2$. From Copson, Physical Metallurgy of Stress Corrosion Fracture, Interscience, 1959, p 247

CC U 005 7098 28 A

Chloride salts containing magnesium are the most aggressive promoters of stress corrosion cracking



Effect of metallic cation on the time-for-cracking of Type 304 stainless steel specimens exposed at 100°C to water containing 100 ppm chloride. From Warren, Proc. 15th Ind. Waste Conf., May 3-5, 1960

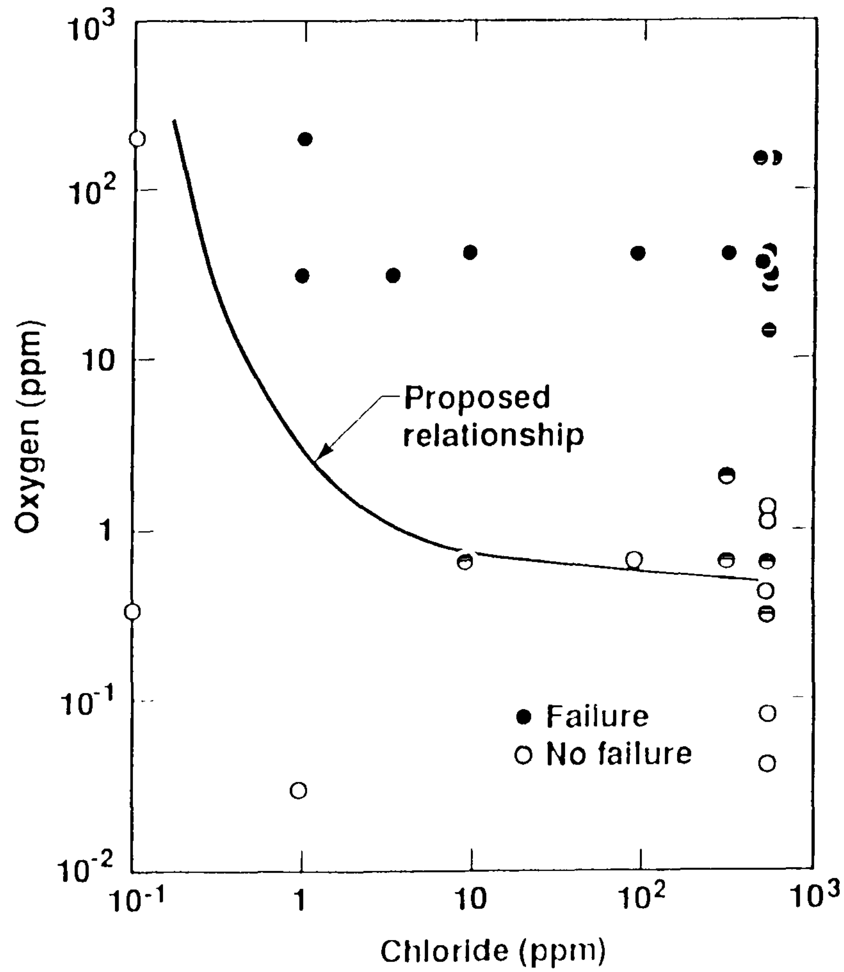
Alloy 825 is more resistant to stress corrosion cracking in strong acids with chloride than Types 304 L and 316 L stainless steels

U-bend specimens after 30 day exposure:
0.8% NaCl + HCl (pH ≈ 2.2) at 141°C (285°F)

Alloys	10 Day Exposure	30 Day Exposure
304	No cracking	Cracking
304 L	No cracking	Cracking
316	No cracking	Cracking
316 L	No cracking	Cracking
825	No cracking	No cracking

From Asphahani, Matls. Perform., November 1980, p. 9

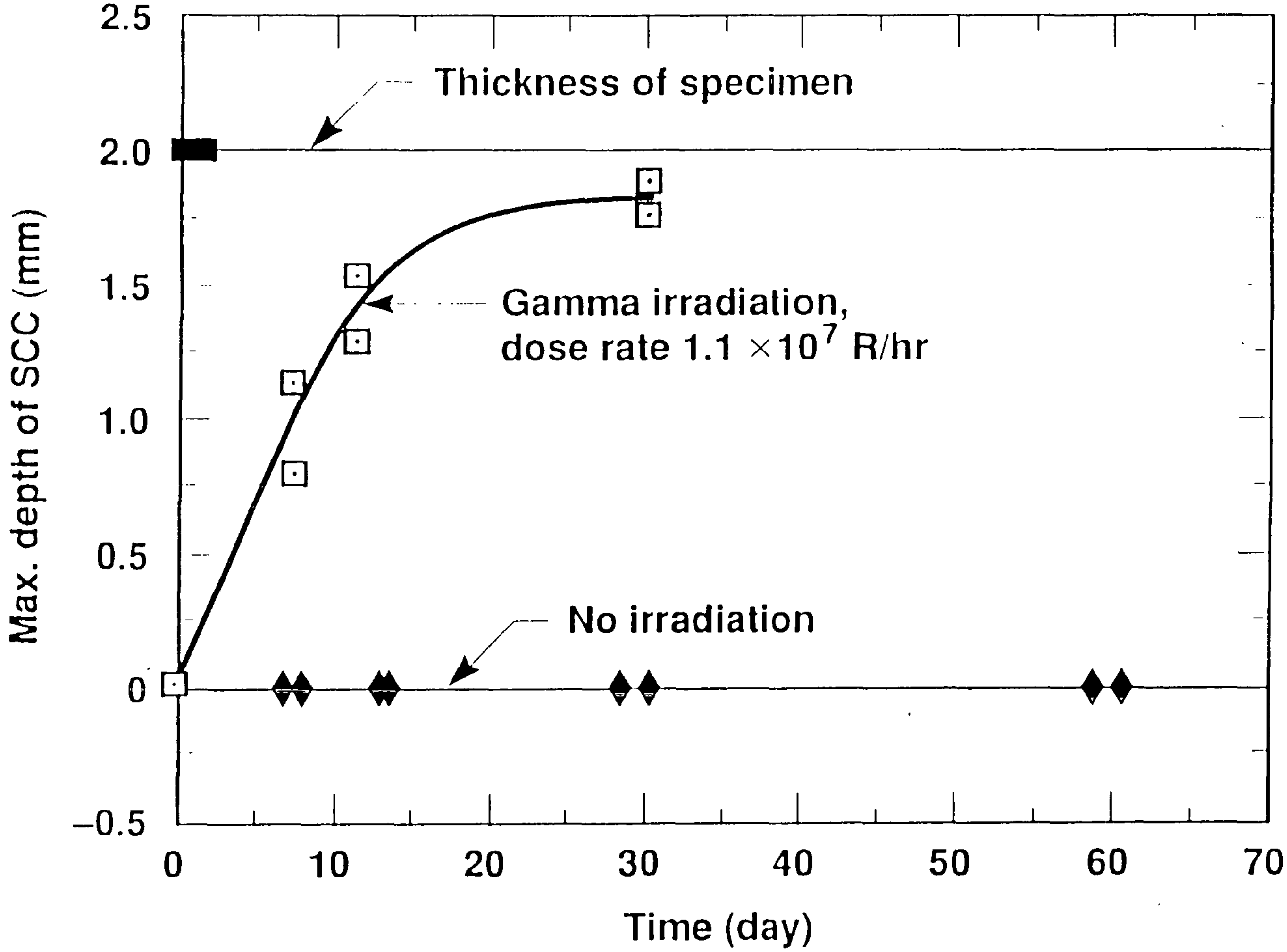
The chloride and oxygen concentrations in the ground water near the repository are probably sufficient to cause stress corrosion cracking in Type 304 stainless steel



Specimens exposed to the steam phase above alkaline-phosphate treated boiler water.
From Williams, Corrosion, Vol. 13, August 1957, p. 539t.

AH 004 U 1131 13

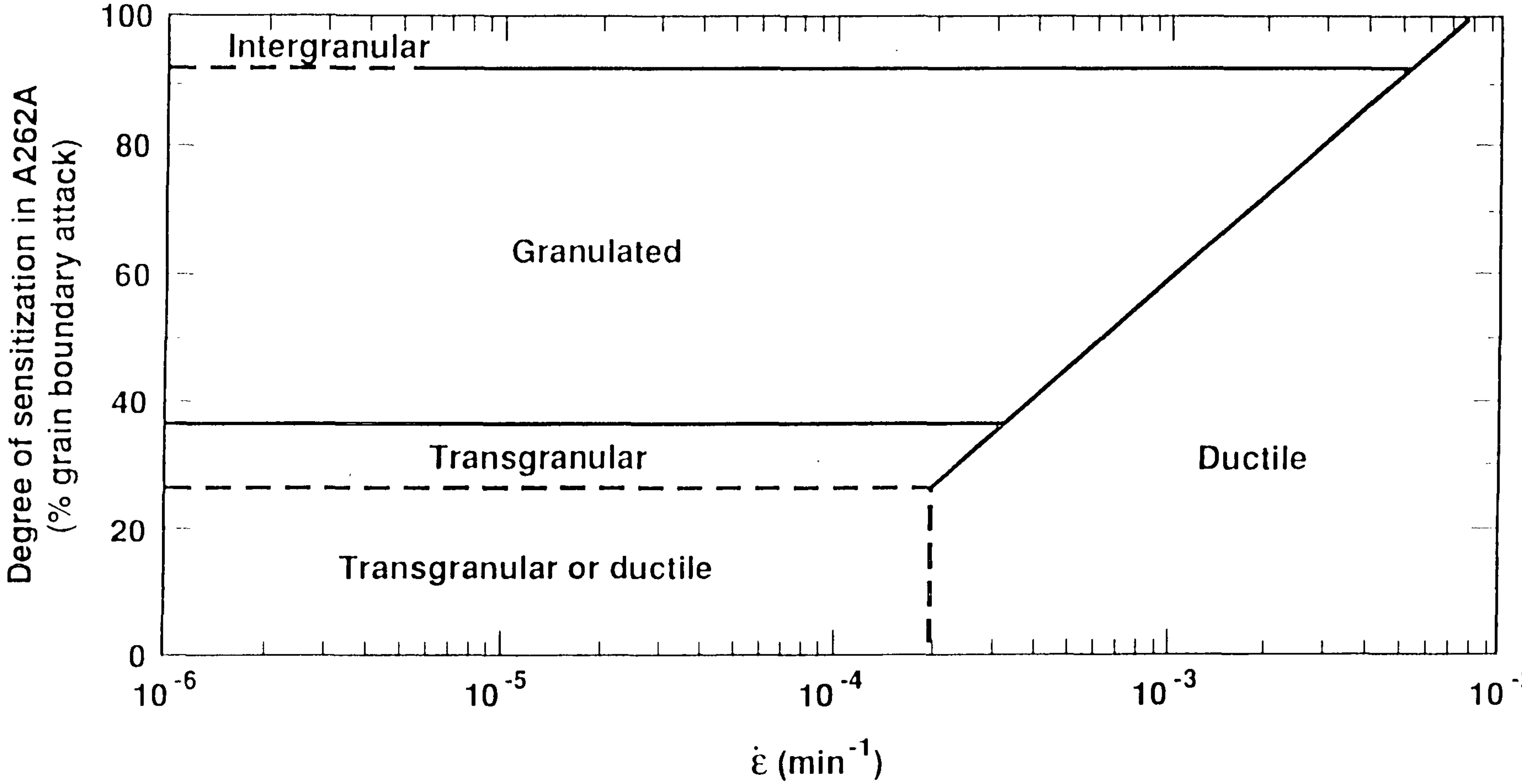
Gamma irradiation promotes IGSSC in sensitized microstructure



Effects of gamma irradiation on SCC failures of sensitized Type 304 stainless steel. From Fujita et al., Corrosion, Vol. 37, No. 6 June 1981, p.335

AH 173 U 8637 14

Stress corrosion cracking tests must be conducted at relatively low strain rates ($<10^{-4}$ min^{-1})



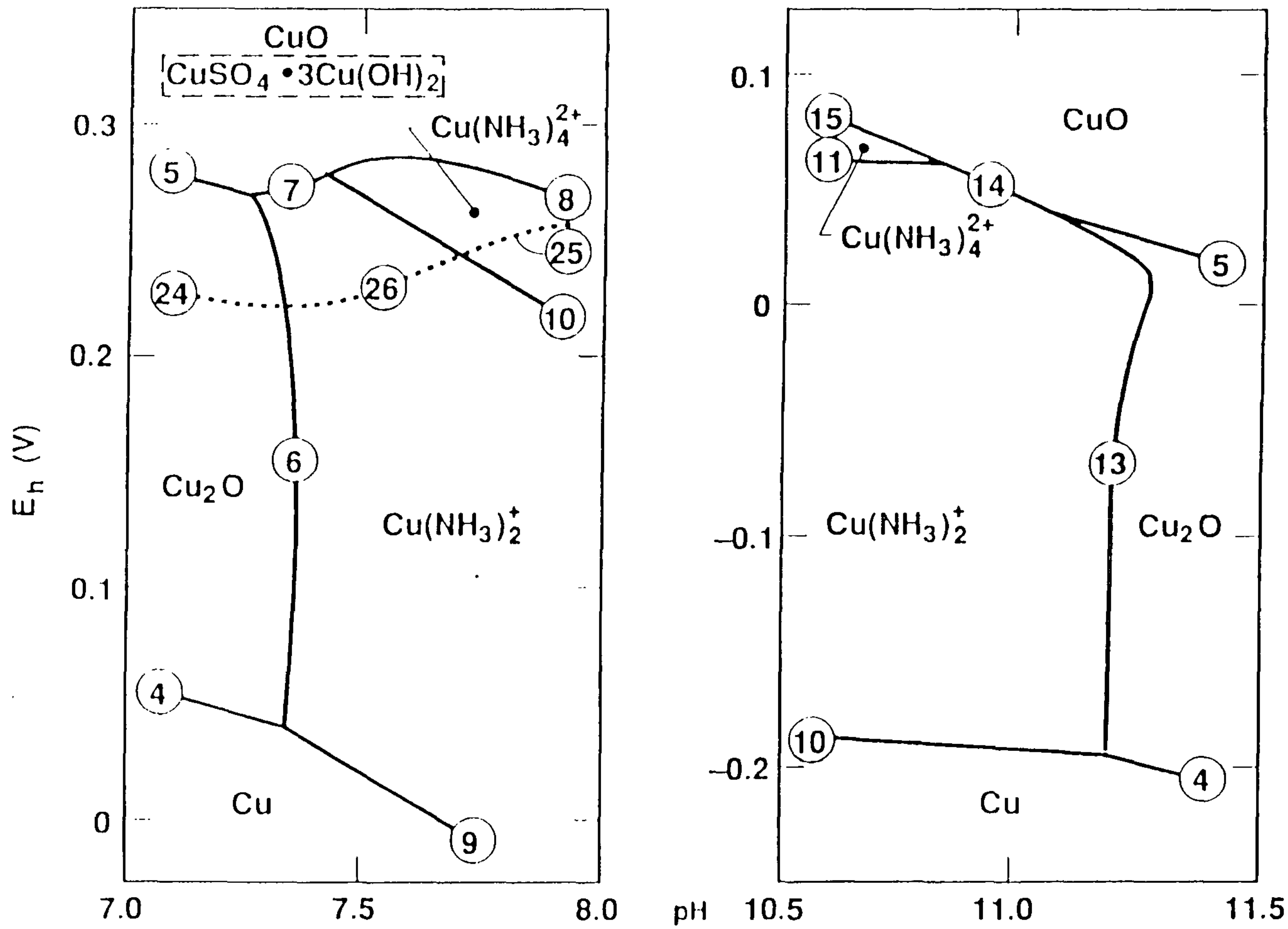
From Solomon, Corrosion, Vol. 40, No. 9, September 1984, p. 493

Highlights of Degradation Mode Survey
Volume 4

Stress Corrosion Cracking

- Copper Base Alloys

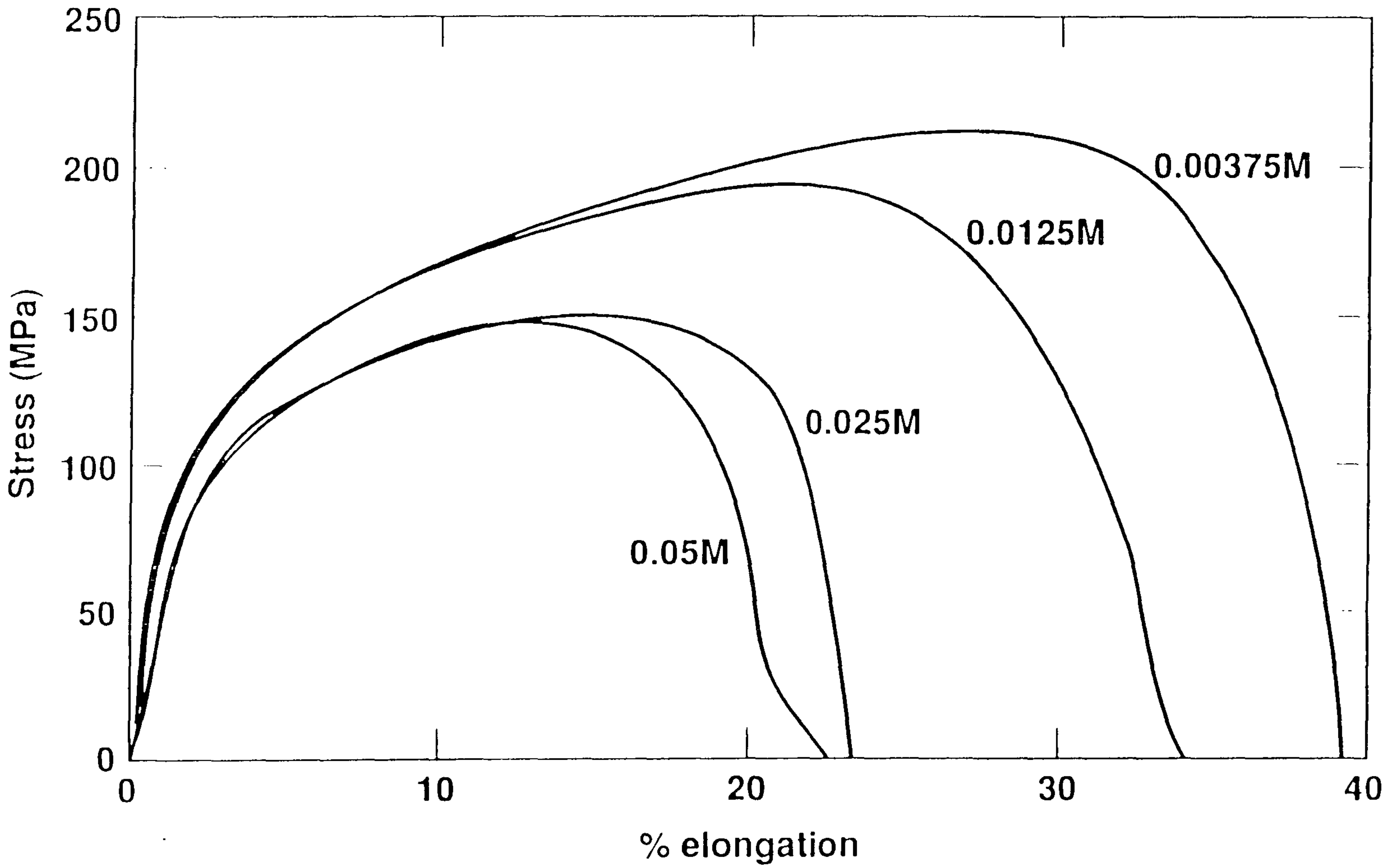
Stress corrosion cracking of copper in moist ammonical environments is known to occur at two pH levels, 7.3 and 11.3. The passive film is known to be unstable under these conditions.



From Hoar and Rothwell, Electrochimica Acta, Vol. 15, 1970, p. 1037.

AH 004 U 1131-16

Stress corrosion cracking of copper is very sensitive to the concentration of sodium nitrite



Specimens were maintained at 25°C and 100 mV, SCE. The strain rate was 2.6 × 10^{-6} s^{-1}. From Benjamin et al., KBS Technical Report No. 83-06, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 1983.

Highlights of Degradation Mode Surveys
Volume 5

Localized Corrosion

- Copper Base Alloys

Localized Corrosion Resistance of Copper Base Materials

- Few quantitative data found for comparing materials
- Most information from exposure performance in sea water
- General ratings by resistance to type of localized attack:
  - *Pitting Corrosion*
    - CDA 102 = CDA 715 (best) > CDA 613 (worst)
  - *Local Dealloying*
    - CDA 102 (best) > CDA 715> CDA 613 (worst)
  - *Crevice Corrosion*
    - CDA 715 = CDA 613 (best) > CDA 102 (worst)
  - *Biofouling*
    - CDA 102 (best) > CDA 715 = CDA 613 (worst)

Highlights of Degradation Mode Surveys
Volume 6

Effects of Hydrogen

- Copper Base Alloys
- Austenitic Alloys

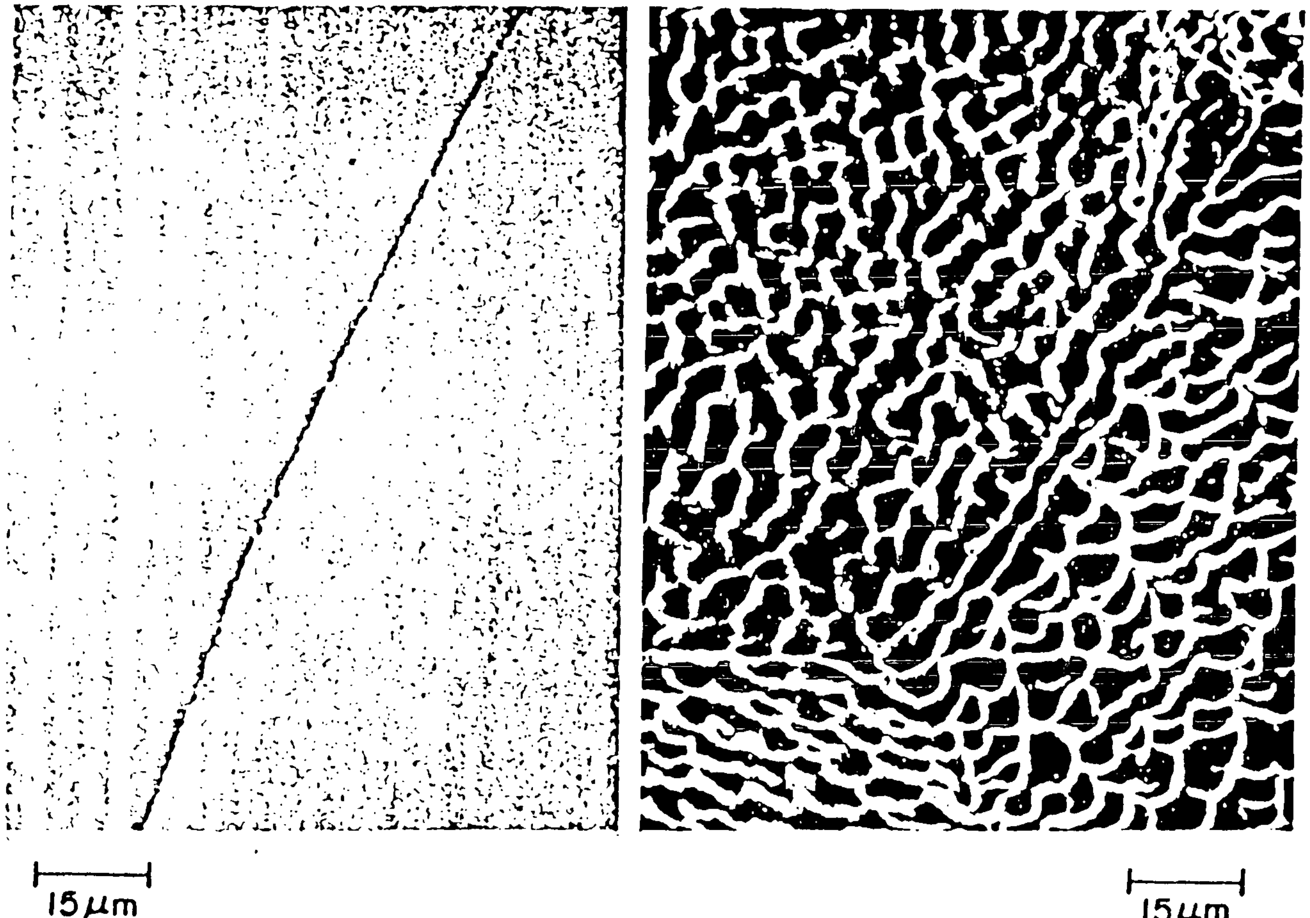
Hydrogen Effects in Copper Base Materials

- Most severe effect is formation of internal water in high purity copper containing as little as 22 ppm atomic oxygen ("hydrogen sicknesss")

- Some degradation of mechanical properties in copper and bronzes due to absorbed hydrogen

- Little information on detrimental hydrogen effects in cupronickel

"HYDROGEN SICKNESS" FRACTURE SURFACE



Water Vapor Bubble Microstructure and Fracture Surface for Copper Annealed in Hydrogen at 500 C for Approximately 25 Hours (From Nieh).

Hydrogen Effects in Austenitic Materials

- Absorbed hydrogen lowers mechanical properties
- Not especially bad degradation in fcc structures
- However, 304L stainless steel is more susceptible to hydrogen embrittlement than 316L
- Little information on hydrogen effects in alloy 825

Highlights of Degradation Mode Surveys Volumes 7 and 8

Weldability

- Austenitic Alloys
- Copper Base Alloys

Weldability Concerns Related to Material Performance

- Austenitic alloys:
  - Principal concerns:
    - Resistance to sensitization and SCC.
    - Weld cracking.
    - Brittle intermetallic formation.
  - 304L, 316L Stainless Steel - Balance composition to assure small amount of delta ferrite in weld. Maintain low carbon and other interstitial contents.
  - Alloy 825 - Choice of matching filler material of higher nickel alloy (Alloy 625). Alloy 625 filler less prone to weld cracking than matching filler is.

Weldability Concerns Related to Material Performance

- Copper-base alloys:
  - CDA 102 - Prone to hydrogen sickness or porosity formation because of reduction of entrapped cuprous oxide particles.
    - As an alternate, use a deoxidized copper, e.g. phosphorous deoxidized copper, CDA 122.
  - CDA 613 - Greatest difficulty in fusion weld process.
    - Aluminum oxide particles if inadequate inert gas shielding.
    - High aluminum fillers make alloy more subject to de-alloying and localized corrosion.
    - Loss of ductility in 400 - 600°C range during cooling.
  - CDA 715 - Fewest performance problems of copper-base candidates.
    - Any microsegregation effects can be readily overcome (control of impurities, grain size).

(C) Comparison and Analysis

Comparison of the Austenitic Candidate Materials from Information Presented and Analyzed in Degradation Mode Surveys

Phenomenon	Most Resistant	Least Resistant
Phase Stability	825	304L
Oxidation/General Corrosion	825, 316L	304L
Hydrogen Effects	825, 316L	304L
Pitting Corrosion	825	304L
Crevice Corrosion	825	304L
Stress Corrosion Cracking	825	304L
Welding Effects	825	316L
Radiation Enhanced Corrosion	825	304L
Microbial Enhanced Corrosion	825	304L

From Farmer, et al., UCID-21362, Overview, June 1988

Comparison of the Copper Base Candidate Materials from Information Presented and Analyzed in Degradation Mode Surveys

Phenomenon	Most Resistant	Least Resistant
Phase Stability	102	613
Oxidation/General Corrosion	613	102
Hydrogen Effects	715	102
Pitting Corrosion	715, 102	613
Crevice Corrosion	715, 613	102
Local Dealloying	102, 715	613
Stress Corrosion Cracking	715	613
Welding Effects	715	102, 613
Radiation Enhanced Corrosion	613, 102	715
Microbial Enhanced Corrosion	102	715, 613

From Farmer et al., UCID-21362, Overview, June 1988

Based on Analysis in Degradation Surveys

- Alloy 825 is most corrosion resistant material among the three austenitic alloys.

- Probably, CDA 715 is the copper-base material that is the most corrosion resistant. However, CDA 613 merits some consideration.

- Other important factors enter into selection criteria (parametric study results, fabrication and closure process evaluations, models of degradation behavior, etc.) and selection of material for advanced studies must consider these.

Comparison of Behaviors
Alloy 825 vs. Copper-Base Materials

- Few direct comparisons of these materials in published literature.

- Planned parametric study work aimed at making these comparisons under repository relevant conditions.

- Alloy 825 more sensitive to halide ions; copper-base materials more sensitive to nitrogen bearing species in the envirornment (localized and stress corrosion effects).

- Copper-base materials much more sensitive to radiation induced corrosion/oxidation. Need to establish if corrosion products are protective.

- CDA 715 is the simplest alloy under consideration; it appears to have fewest detrimental welding effects.