ANL/ET/CP--89183
CONF-960426--2

ENVIRONMENTALLY ASSISTED CRACKING OF LIGHT-WATER REACTOR MATERIALS

O. K. CHOPRA, H. M. CHUNG, T. F. KASSNER, and W. J. SHACK
Argonne National Laboratory
Argonne, Illinois

Energy Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439 USA

February 1996

For publication in the Proceedings of American Power Conference, Vol. 58, April 9–11, 1996.

*Work supported by the U.S. Nuclear Regulatory Commission, Office of Nuclear Regulatory Research.

ENVIRONMENTALLY ASSISTED CRACKING OF LIGHT-WATER REACTOR MATERIALS

O. K. CHOPRA, H. M. CHUNG, T. F. KASSNER, and W. J. SHACK
Argonne National Laboratory
Argonne, Illinois

Introduction

Environmentally assisted cracking (EAC) of light-water reactor (LWR) materials has affected nuclear reactors from the very introduction of the technology. Corrosion problems have afflicted steam generators from the very introduction of pressurized water reactor (PWR) technology. Shippingport, the first commercial PWR operated in the United States, developed leaking cracks in two Type 304 stainless steel (SS) steam generator tubes as early as 1957, after only 150 h of operation.[1] Stress corrosion cracks were observed in the heat-affected zones of welds in austenitic SS piping and associated components in boiling-water reactors (BWRs) as early as 1965.[2] The degradation of steam generator tubing in PWRs and the stress corrosion cracking (SCC) of austenitic SS piping in BWRs have been the most visible and most expensive examples of EAC in LWRs, and the repair and replacement of steam generators and recirculation piping has cost hundreds of millions of dollars. However, other problems associated with the effects of the environment on reactor structures and components are important concerns in operating plants and for extended reactor lifetimes.

Cast duplex austenitic-ferritic SSs are used extensively in the nuclear industry to fabricate pump casings and valve bodies for LWRs and primary coolant piping in many PWRs. Embrittlement of the ferrite phase in cast duplex SS may occur after 10 to 20 years at reactor operating temperatures,[3] which could influence the mechanical response and integrity of pressure boundary components during high strain-rate loading (e.g., seismic events). The problem is of most concern in PWRs where slightly higher temperatures are typical and cast SS piping is widely used.

Low-cycle fatigue is potentially a significant degradation mechanism in LWR piping.[4] Current fatigue design for this piping is based on the ASME Section III Fatigue Design Curves. Environmental effects were not explicitly considered by the Code in the development of these curves. The design curves include design margins intended to account for a variety of effects not explicitly considered in the experimental data upon which the curves are based. However, only a fraction of this design margin can be considered as reflecting the effect of the environment, because the margin must also account for differences in behavior between specimens and real components due to size effects, differences in surface finish, and data scatter. Under some conditions the effect of the standard BWR environment can completely erode the entire design margin in the Code curves for carbon and low alloy steels.

In addition to its widespread use for steam generator tubing, Alloy 600 is used for a variety of structural elements in reactor systems. Cracking has been observed in a number of these components, e.g., instrument nozzles and heater thermal sleeves in the pressurizer, penetrations for control-rod-drive mechanisms in reactor vessel closure heads in the primary system of PWRs,[5] and in shroud-support-access-hole covers in BWRs.[6]

Another concern is failure of reactor-core internal components after accumulation of relatively high fluence. The general pattern of the observed failures indicates that, as nuclear plants age and neutron fluence increases, many apparently nonsensitized austenitic materials become susceptible to intergranular failure[7] by a degradation process that has become known as irradiation-assisted stress corrosion cracking (IASCC). Failures have been reported for components subjected to relatively low or negligible stress levels, e.g., control-blade sheaths and handles and instrument dry tubes of BWRs. Although most failed components can be replaced, some safety-significant structural components, such as the BWR top guide, core plate, and shroud, would be very difficult or impractical to replace.[8,9]

Impact of USNRC Sponsored Research

Although the primary responsibility for the assessment of the impact of environmentally assisted cracking on reactor structural integrity and the development of remedies which can mitigate or eliminate the problems lies with the nuclear power industry, the U.S. Nuclear Regulatory Commission (USNRC) has sponsored research to provide an independent capability for the assessment of environmentally assisted degradation in light water reactor (LWR) systems in several programs at the Argonne National Laboratory (ANL) since 1980.

Historically the program was initiated to study SCC of austenitic stainless and ferritic steels. Later additional work focused on the embrittlement of cast SSs. The current emphasis of the work is on IASCC of reactor core internal structures, the effects of reactor environments on fatigue life of reactor piping materials, and EAC of high nickel alloy structural components.

There have been a number of important technical results achieved in these programs. Perhaps that with the most significant impact on the operation of nuclear power plants was the demonstration of the large impact of very low levels of impurities in reactor coolant water on susceptibility to SCC. The work at ANL identified sulfates as particularly deleterious species, and conversely demonstrated that even sensitized SSs can show resistance to SCC in very high purity water. These results have been incorporated into the reactor water chemistry guidelines developed by the BWR Owners Group.[10] These guidelines require lower impurity levels and explicit monitoring of sulfate levels. The development of the guidelines and the realization of the importance of water chemistry have led to remarkable improvements in plant water purity. Table 1 shows one measure of this progress, the number of licensee event reports (LERs) of violations of the plant technical specifications for reactor coolant purity. Water conductivity records maintained by General Electric show similar striking improvements.[11]

Table 1. LERs for Violations of Plant Technical Specifications for Reactor Coolant Purity

Up to 1979	2.6–3.4 /reactor year
1979–1987	0.2/reactor year
1986–1987	0.05/reactor year

The work on the embrittlement of cast duplex SSs by thermal aging led to the development of a procedure for assessing thermal embrittlement of cast SS components during reactor service from known material information. Charpy–impact energy, fracture toughness J–R curves, and tensile properties of aged cast SSs can be predicted from known material information. The correlations successfully predict the mechanical properties of service–aged cast SSs from the Shippingport, Ringhals 2, and KRB reactor components.[12] The estimated and measured impact energies for materials from these reactors are plotted in Fig. 1 as a function of aging time at different temperatures. The estimated impact energies show very good agreement with the experimental data. Although initially developed to provide a independent means for the USNRC to assess the fracture toughness of aged cast SSs, the analysis is now also widely used in industry.

Current Research Activities

The program is currently focused on four tasks: fatigue initiation in pressure vessel and piping steels, fatigue and environmentally assisted crack growth in cast duplex and austenitic SS, IASCC of austenitic SSs, and environmentally assisted crack growth in high–nickel alloys. Some recent progress in the work on IASCC, fatigue, and environmentally assisted crack growth is outlined in the following sections.

Irradiation Assisted Stress Corrosion Cracking

Failures of reactor–core internal components in both BWRs and PWRs have occurred after accumulation of relatively high fluence (>5 x 10^{20} $n{\cdot}cm^{-2}$, E >1 MeV). Although most failed components can be replaced, some components would be very difficult or impractical to replace. There is wide heat-to-heat variation in susceptibility to IASCC, even among high–purity (HP) materials containing virtually identical chemical compositions. Although radiation–induced grain-boundary Cr depletion is widely believed to play an important role in IASCC, additional deleterious processes may be associated with trace impurities that are not usually identified in material specifications. Such trace elements could be introduced during steelmaking processes or during fabrication and welding. Since the actual mechanisms that produce cracking are not well understood, there is currently no reliable method to predict the IASCC susceptibility of a given type or heat of material. The objective of the present research program is to characterize the behavior of materials currently in reactors in terms of crack growth rates and fracture toughness and to better understand the mechanisms of cracking so that eventually susceptibility to IASCC can be characterized and resistant materials identified.

As shown in Fig. 2, recent test suggest that a higher level of fluorine on grain boundaries may be associated with higher susceptibility to IASCC.[13] Inadvertent contamination of reactor components by fluorine could occur during an iron– and steelmaking process (utilizing a neutral flux fluorspar, ≈75% CaF_2), pickling (in a solution containing HF) in the case of tubular components such as neutron–absorber–rod tubes, or by an F–containing weld flux in the case of large welded components such as BWR core shrouds and some older top guides. A synergistic effect of a lower concentration of Cr and a higher concentration of fluorine on grain boundaries on susceptibility to IGSCC is consistent with IGSCC results by Ward et al.[14] Halide impurities can play a catalytic role in accelerating aqueous corrosion of Fe and Fe–base alloys.[15] While it is too early to make a conclusive statement regarding the importance of the effects of halides (most likely fluorine) to cracking of LWR core–internal components, irradiation–induced grain–boundary depletion of Cr and contamination during iron– and steelmaking process or subsequent component fabrication appear to be the two key processes that may produce synergistic effects leading to increased susceptibility to IASCC.[16]

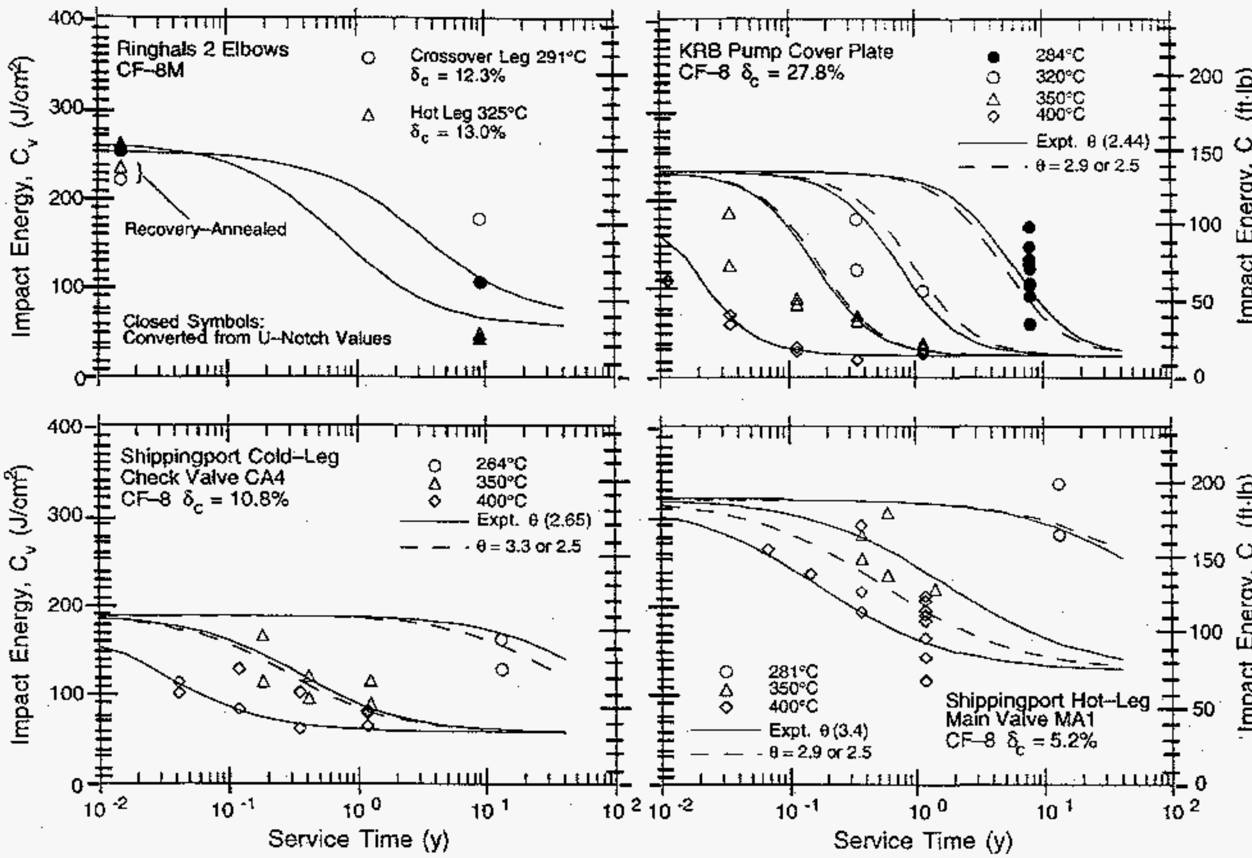

Figure 1.
Variations of estimated and measured room–temperature Charpy–impact energy with service time for cast SS from the Ringhals, KRB, and Shippingport reactors

Fatigue of LWR Structural Materials

Appendix I to Section III of the ASME Boiler and Pressure Vessel Code specifies fatigue design curves for structural materials used for the reactor–coolant pressure boundary. However, as noted previously, the effects of reactor coolant environments are not explicitly addressed by these design curves. Data show that environmental effects on fatigue life are significant when five conditions are satisfied simultaneously, viz., the applied strain range is above a minimum threshold level that may vary with material and loading conditions, but is ≈0.36% for the materials and conditions used in our tests, the strain rate <1%/s, the temperature ≥150°C, the DO ≥0.05 ppm, and the sulfur content in steel >0.003 wt.%.[4,17–19] Under adverse loading and environmental conditions, fatigue lives in reactor–coolant environments can be a factor of 100 shorter than those in air. Interim fatigue design curves that account for environmental effects were developed as part of the USNRC research program at ANL and presented in NUREG/CR–5999. A more rigorous statistical analysis of the available data was presented in NUREG/CR–6335.

Although the correlations in NUREG/CR–5999 and NUREG/CR–6335 are in excellent agreement with available laboratory data for loading histories with constant strain amplitudes and constant strain rates during the tensile portion of the loading cycle, actual reactor loading histories are far more complex. Exploratory fatigue tests are being conducted with waveforms where the slow strain rate is applied during only a fraction of the tensile loading cycle. The results of such tests will be used to develop a "damage rule" that can be used to predict life under complex loading histories.

The variation in fatigue life of A106–Gr B and A533–Gr B steels as a function of the fraction of loading strain at slow strain rate is shown in Fig. 3; results from tests conducted at Ishikawajima–Harima Heavy Industries Co. (IHI) on the same heat of A106–Gr B steel are also included in the figure. Open symbols indicate tests where the slow portions occurred near the maximum tensile strain. Closed symbols indicate tests where the slow portions occurred near the maximum compressive strain.

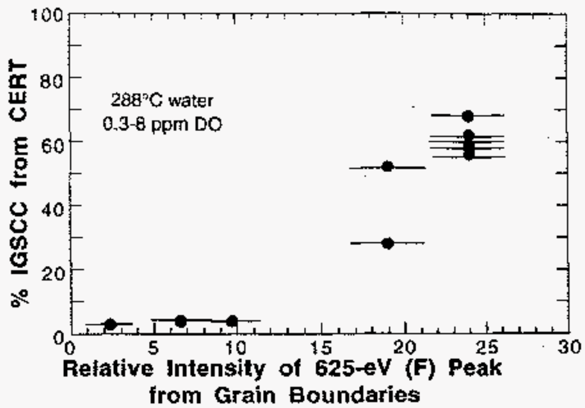

Figure 2.
Percent IGSCC vs. average intensity of fluorine signal from grain boundaries of HP and CP Type 304 SS BWR components

These results suggest that a slow strain rate applied during any portion of the loading cycle above the threshold strain is equally effective in decreasing fatigue life, i.e., the relative damage due to the slow strain rate is independent of the strain amplitude, once the amplitude exceeds a threshold value.[17–19] This can be illustrated using the results shown in Fig. 3. If the relative damage were totally independent of strain amplitude, the life should decrease linearly from A to C along the chain–dot line in Fig. 3. Instead, loading histories where the slow strain rate occurs near the maximum compressive strain (waveforms F, H, or K) produce little damage (i.e., they follow the horizontal line AD in Fig. 3, until the fraction of the strain history is sufficiently large that slow strain rates are occurring for strain amplitudes greater than the threshold. In contrast, for loading histories where the slow strain rate occurs near the maximum tensile strain (waveforms E, G, or H), life decreases continuously with the fraction of strain applied at the slow strain rate (line AB in Fig. 3), and then saturates as the fraction increases so that a portion of the slow strain rate now occurs at amplitudes less than the threshold value (line BC in Fig. 5). Thus, the hypothesis that each portion of the loading cycle above the threshold strain is equally damaging implies the decrease in fatigue life should follow line ABC when a slow rate occurs near the maximum tensile strain, and line ADC when it occurs near the maximum compressive strain.

SCC and Corrosion Fatigue of Austenitic and Aged Cast SSs

Because Section XI of the ASME Code currently provides only an in–air design curve, corrosion fatigue data from the literature were analyzed to develop corrosion fatigue curves for SSs in aqueous environments. The results of this review were published in NUREG/CR–6176. At that time, few data were available on crack growth rates (CGRs) in deaerated water at CGRs of 10^{-10} m·s^{-1} or less, which are of most interest in actual applications. Therefore, it was recommended that the correlations based on data obtained in water that contained ≈0.2 ppm DO should also be applied to low–oxygen environments characteristic of PWRs. This was recognized as a conservative assumption and additional CGR tests on cast duplex and austenitic SSs have been performed to provide a technical basis for updating the correlations given in NUREG/CR–6176 to explicitly include the effect of low DO levels and to ensure that the results are adequate to describe the behavior of thermally aged cast SSs.

These tests indicated that CGRs in thermally aged cast SSs are similar to those in wrought SSs. In Fig. 4, measured CGRs for aged and nonaged cast SSs are compared with the predictions based on correlations for wrought SSs in NUREG/CR–6176. Tests in low–DO water show lower CGRs than in water with 0.2 ppm DO. Ford et al.[20] developed a detailed CGR model that includes the effects of DO (through changes in ECP). Based on SSRT tests, Kassner et al.[21] suggested that CGRs exhibit an $\approx[O_2]^{1/4}$ dependence on DO concentration. Predictions of both models are in reasonable agreement with the observed decreases in CGR corresponding to a decrease from 8 ppm to 200 ppb, but the model of Ford et al. predicts a significantly larger decrease in CGR than that of Kassner et al. when the DO decreases to ≈ 1 ppb. Revised correlations based on the latter model are in good agreement with observed CGRs.

Tests were also performed on Types 316NG and 304 SS and as–received and thermally aged CF–3 cast SS to investigate threshold stress intensity factors ΔK_{th}^{EAC} for EAC. Threshold behavior was clearly observed, and the dependence of ΔK_{th}^{EAC} on load ratio for Types 347, 316NG, and sensitized 304 SS, and for thermally aged CF–3 and CF–8 grades of cast SS, was determined. A simple linear relationship was obtained:

$$\Delta K_{th}^{EAC} = 25.0(1 - R).$$

The correlations in NUREG/CR–6176 are being revised to include some "credit" for low DO in PWR environments. The data are being reviewed to determine whether thresholds can be included in the revised correlations.

References

1. I. H. Welinsky, W. F. Brindley, W. E. Berry, and S. F. Whirl, *Final Evaluation of Shippingport Power Station's Stainless Steel Generator after Five Years*, pp. 1-13 in Proc. Symp. on High Purity Water

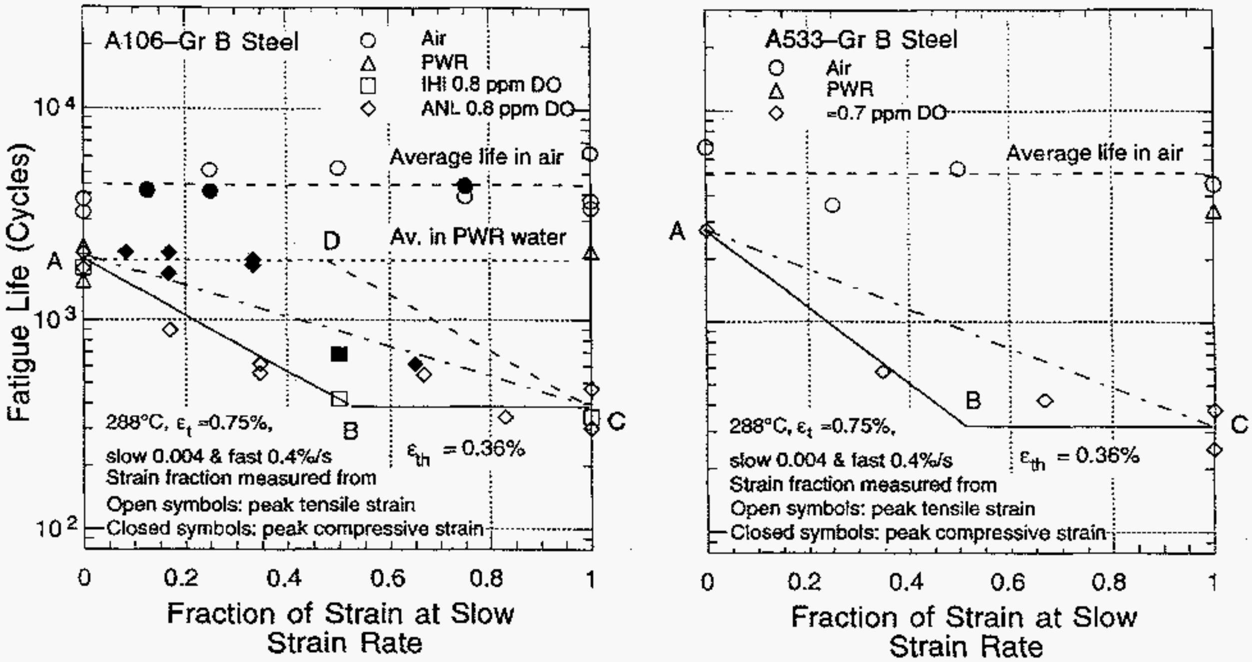

Figure 3.
Fatigue life of A106–Gr B and A533–Gr B steels tested with loading waveforms where slow strain rate is applied during a fraction of tensile loading cycle

Corrosion of Metals, 23rd NACE Conf., National Association of Corrosion Engineers (1968).

2. R. W. Weeks, "Stress Corrosion Cracking in BWR and PWR Piping," Proceedings of the International Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors - Myrtle Beach, SC, August 1983, NACE (1984).

3. Chopra, O. K., "Thermal Aging of Cast Stainless Steels in LWR Systems: Estimation of Mechanical Properties," in Nuclear Plant Systems/Components Aging Management and Life Extension, I. T. Kisisel, J. Sinnappan, R. W. Carlson, and W. H. Lake, eds., PVP Vol. 228, ASME, New York,, pp. 79–92 (1992).

4. M. Higuchi and K. Iida, *Fatigue Strength Correction Factors for Carbon and Low–Alloy Steels in Oxygen–Containing High–Temperature Water,* Nucl. Eng. Des. **129**, pp. 293–306 (1991).

5. USNRC Information Notice No. 90–10, "Primary Water Stress Corrosion Cracking (PWSCC) of Inconel 600" (Feb. 1990).

6. USNRC Information Notice No. 92–57, "Radial Cracking of Shroud Support Access Hole Cover Welds" (Aug. 1992).

7. P. O. Andresen, F. P. Ford, "State of Knowledge of Radiation Effects on Environmental Cracking in Light Water Reactor Core Materials," Proceedings of the Fourth International Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors - Jekyll Island, GA, August 1989, NACE (1990).

8. USNRC Information Notice No. 95–17, "Reactor Vessel Top Guide and Core Plate Cracking" (March 1995).

9. USNRC Information Notice No. 94–42, "Cracking in the Lower Region of the Core in Boiling–Water Reactors," June 1994; Notice No. 93–79, "Core Shroud Cracking at Beltline Region Welds in Boiling–Water Reactors" (September 1993).

10. BWR Hydrogen Water Chemistry Guidelines: 1987 Revision EPRI NP-4947-SR, Special Report, , 132 pages. Electric Power Research Institute, Palo Alto (December, 1988).

11. B. M. Gordon, and G. M. Gordon, Materials Aspects of BWR Plant Life Extension, Nucl. Eng. Des. **98**, pp. 109-121 (1987).

12. Chopra, O. K., Estimation of Fracture Toughness of Cast Stainless Steels during Thermal Aging in LWR

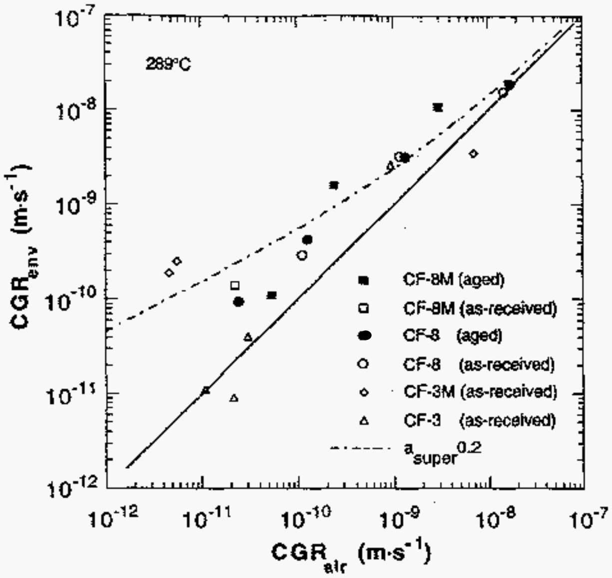

Figure 4.
Corrosion fatigue data for as–received CF–3, –3M, and –8M and aged CF–8M and –8 cast SS in water containing 0.2 ppm DO at 289°C. Diagonal lines correspond to crack growth in air in Section XI of the ASME Code. Dashed lines indicate predictions from correlations in NUREG/CR–6176.

Systems – Revision 1, NUREG/CR–4513 Rev. 1, ANL–93/22, August 1994.

13. H. M. Chung, W. E. Ruther, and J. E. Sanecki, in *Environmentally Assisted Cracking in Light Water Reactors: Semiannual Report, October 1993–March 1994,* NUREG/CR–4667 Vol. 18, ANL–95/2, pp. 27–35 (March 1995).

14. C. T. Ward, D. L. Mathis, and R. W. Staehle, *Intergranular Attack of Sensitized Austenitic SS by Water Containing Fluoride Ions,* Corrosion **25**, 394–396 (1969).

15. N. C. Huang and Z. Nagy, *Kinetics of the Ferrous/Ferric Electrode Reaction in the Absence of Chloride Catalysis,* J. Electrochem. Soc. **134**, 2215–2220 (1987).

16. H. M. Chung, W. E. Ruther, J. E. Sanecki, A. Hins, and T. F. Kassner, *Effect of Water Chemistry on Intergranular Cracking of Irradiated Austenitic Stainless Steels,* in Proc. 7th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, National Association of Corrosion Engineers International, Houston, TX, pp. 1133–1144 (1995).

17. O. K. Chopra, W. F. Michaud, and W. J. Shack, in *Environmentally Assisted Cracking in Light Water Reactors, Semiannual Report, April–September 1994,* NUREG/CR–4667 Vol. 19, ANL–95/25, pp. 3–18 (Sept. 1995).

18. O. K. Chopra and W. J. Shack, *Effects of LWR Environments on Fatigue Life of Carbon and Low–Alloy Steels,* in Fatigue and Crack Growth: Environmental Effects, Modeling Studies, and Design Considerations, PVP Vol. 306, S. Yukawa, ed., American Society of Mechanical Engineers, New York, pp. 95–109 (1995).

19. O. K. Chopra and W. J. Shack, *Effects of Material and Loading Variables on Fatigue Life of Carbon and Low–Alloy Steels in LWR Environments,* in Transactions of the 13th Int. Conf. on Structural Mechanics in Reactor Technology (SMiRT 13), Vol. II, M. M. Rocha and J. D. Riera, eds., Escola de Engenharia – Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil, pp. 551–562 (1995).

20. F. P. Ford, D. F. Taylor, P. L. Andresen, and R. Ballinger, *Corrosion-Assisted Cracking of Stainless and Low-alloy Steels,* EPRI NP-5064s, Electric Power Research Institute, Palo Alto, CA (February 1987).

21. T. F. Kassner, W. E. Ruther, and W. K. Soppet, *Mitigation of Stress Corrosion Cracking of AISI 304 SS by Organic Species at Low Concentrations in Oxygenated Water,* Corrosion 90, Paper No. 489, Las Vegas, NV (April 1990).