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ENVIRONMENTAL FACTORS INFLUENCING STRESS CORROSION
CRACKING IN BOILING WATER REACTORS*John R. Weeks
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ABSTRACT

The mechanisms of intergranular stress corrosion cracking (IGSCC) of sensitized stainless steels in boiling water reactor (BWR) primary coolant are reviewed, with emphasis on the role the environment plays on both the initiation and propagation processes. Environmental factors discussed include oxygen (corrosion potential), temperature, and dissolved ions in the water and the range of strain rates at which IGSCC occurs. Both crack propagation rates and the range of strain rates at which IGSCC occurs decrease rapidly as temperature is increased above approximately 200°C, in essentially the same manner as the solubility of magnetite decreases in acidic solutions. A mechanism of crack propagation is presented based on this observation.

To establish water chemistry guidelines for crack-free operation of BWR's containing sensitized stainless steel, more information is needed on the role of absorption of impurities in the surface and deposited oxides and on the interaction between the oxygen and impurity levels required to maintain an electrochemical potential in a range where IGSCC is unlikely to occur. The relative effects of short bursts of impurities and longer term lower concentrations of these same impurities also need to be evaluated.

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INTRODUCTION

Intergranular stress-corrosion cracking (IGSCC) has been occurring in BWR and PWR nuclear power plants for a number of years. The recent identification of the problem in the large diameter piping of a number of operating BWRs¹ has not indicated the occurrence of any new phenomenon, but rather that the phenomenon already known and previously discussed² is being found in a wider range of locations, probably because of longer operating times and improved inspection and detection techniques. In this paper the purpose is to summarize the current understanding of the problem with emphasis on its environmental causes and to indicate what information needs to be developed to evaluate environmentally-based remedial actions.

IGSCC in stainless steels arises from the synergistic effects of stress and the environment on a material that is susceptible to the phenomenon. Each of these aspects of the synergism can be examined separately.

A susceptible material: Types 304 or 316 SS, in a certain temperature range, will form grain boundary networks of Cr carbides, accompanied by adjacent areas depleted in Cr³. The production of the Cr carbides in these areas results in a network of narrow zones adjacent to the grain boundaries in which the Cr levels in solid solution are sufficiently lower than those in the bulk of the grains to enable electrochemical cells to be set up between the lower Cr grain boundary material and the higher Cr bulk grain material. Precipitation of the Cr carbides and formation of Cr-depleted zones are a function of

the composition of the steel and the time that the steel is heated in the temperature range at which the kinetics of the reaction are sufficiently rapid and thermodynamics favor production of the Cr carbides. While sensitization can be produced in stainless steels containing carbon levels as low as 0.02 wt.%, IGSCC has seldom if ever been seen in BWRs in stainless steels containing significantly less than 0.04 wt.% carbon; the probability of IGSCC occurring appears to increase rapidly with carbon⁴ concentrations above this level up to 0.055%, and thereafter to be constant up to the limit for Type 304 or Type 316 SS of 0.08 wt.%. All stainless steels in United States light water reactors (LWRs) are specified to be in the solution-annealed state prior to fabrication⁵. At the solution-annealing temperatures, the Cr and carbon in the steel are in solid solution. Rapid cooling following solution-annealing prevents carbide precipitation from occurring. However, the welding of stainless steel pipe produces a narrow band of material in an area adjacent to the weld which has been heated into the sensitization range by the heat of welding; the pipe cracks are occurring primarily in this area.

Although the general phenomenon of IGSCC has been mainly attributed to the formation and extent of the Cr-depleted zones in the grain boundaries, other minor constituents of the stainless steel can affect either the kinetics of formation of the Cr-depleted zones or the initiation and propagation of the stress-corrosion cracks. Steels containing alloying elements that form carbides more stable than Cr carbide (such as niobium carbide or Ti carbide) are less prone to sensitization. However, even with these steels there is a potential area immediately adjacent to the weld fusion line in which Cr-depleted zones can be produced if the carbon levels are high (knife-line attack). The

relative freedom of the Swedish and the newer German BWRs from IGSCC is thought to be related to the use of a 0.05% carbon limit in Sweden, and the use of a low-carbon, niobium-stabilized stainless steel (often referred to as Type 347NG) in West Germany⁵.

Stress: Austenitic stainless steels as a general rule do not deform elastically to a sharp yield stress and plastically at stresses above it. Rather, some plastic deformation can occur at stresses considerably below the nominal "design yield" (0.2% offset) strength. It is generally considered that straining or creep of the stainless steel under tension produces a rupture in the protective oxide films, followed by a relatively rapid bare metal corrosion until the film reheals. The lower Cr content in the sensitized grain boundaries results in locally greater metal loss prior to rehealing. Repeated rupture of the film, caused either by alternating the stresses or applying continuous stresses appreciably above the yield point, produces a crack along the grain boundary, since preferential attack occurs at the Cr-depleted grain boundaries. The primary source of tensile stress in the operating BWR piping is considered to be the residual stresses from welding². Added to this, however, are operational pressure stresses, vibrational stresses, and thermal stresses, particularly during heatup and cool-down. The combined effects of all these tensile stresses on the inner surface of the piping in the sensitized regions need to be considered in determining the susceptibility of a given welded area to IGSCC. Generally, sufficient stress to cause repeated rupture of the protective oxide film is believed to be necessary to initiate cracking. Although in terms of conventional engineering design, creep is negligible in austenitic stainless steels at BWR

operating temperatures, the strain rates associated with stresses at or above "yield" are sufficient to produce rupture of the oxide film. This may even be true for stresses below "design yield," particularly if they are applied intermittently, because of the tendency of the material to creep. Once a crack is initiated, a continued tensile stress intensity at the crack tip is believed to be required for crack propagation.

Environment: In the BWR primary coolant, the presence of residual oxygen from radiolysis puts the electrochemical potential of the stainless steel in a range in which the intergranular stress-corrosion cracks can initiate and propagate in sensitized material. The species responsible for conducting the electrochemical currents in IGSCC are assumed to come either from the environment (such as in-leakage of impurities from the condenser or resin bead break-up and decomposition) or from corrosion of the metal itself, particularly from bare-metal corrosion following film rupture, producing salts of sulfur, phosphorus, silicon, or other anions. These species can produce a current-carrying capability in the grain boundary cracks, so that IGSCC can occur in theoretically pure water at sufficiently high stresses in the presence of an oxidizing potential. Since the materials and stress patterns are fixed in plants already built, methods of mitigating the environmental factors causing IGSCC are of considerable interest both to industry and regulatory agencies.

MECHANISMS OF IGSCC

IGSCC can be described in terms of an initiation phase and a propagation phase, the mechanisms of which are reviewed briefly below.

Initiation Phase - The surface of stainless steels is protected from corrosion by a thin, adherent, passivating protective oxide. In addition to this passive layer, the surfaces of the austenitic stainless steel pipes in a BWR have a relatively thick layer of mass-transported oxides deposited on them in the form of crud, which contains some radioactivity. These crud deposits can also be highly specific absorbents for impurities entering the solution, such as sulfates or chlorides, and this property may have some influence on the crack-initiation process.

It is difficult to determine the precise point of crack initiation from laboratory data, and impossible from field experience. In slow strain rate stress-corrosion tests, if the protective passivating oxide layers are ruptured frequently enough, localized corrosion of sensitized grain boundary material at the root of these ruptures can produce an environment in a relatively short period of time that is capable of carrying the electrochemical corrosion current, and therefore bringing about IGSCC. The presence of the crud deposits and of materials or ions adsorbed in these deposits may also influence the initiation of IGSCC. Laboratory tests have shown that very small concentrations of anions⁶ can accelerate the initiation of IGSCC in a constant load test when the electrochemical potential is held in a range at which IGSCC is known to occur.

Crack initiation is assumed to have occurred at the point in time at which an electrolyte, capable of carrying the electrochemical currents required for crack propagation builds up in the crevice between the ruptured

protective and deposited oxides and the bare-metal surface. This electrolyte is usually considered to be acidic. This rather vaguely defined point of transition between initiation and propagation stages is difficult to measure experimentally. In terms of a mechanism for IGSCC, however, it is consistent with the experimental data.

Propagation - Once IGSCC has been initiated, the subsequent growth of these cracks depends upon several factors: the stress intensity (determined from the geometry of the crack and the applied tensile stress), the presence in the crevices of impurities that can stabilize a conducting (usually acidic) environment in the crevice, and the degree of sensitization of the material (which affects the potential of the electrochemical cells existing between the higher Cr and lower Cr areas). It also depends upon the continued presence in the bulk solution of an oxidizing species, controlling the overall chemical potential of the steel surface.

Experimental evidence on the role of impurities, electrochemical potential, sensitization, and stress intensity factors in crack propagation rates is much more abundant than are the data on crack initiation⁷. This evidence has shown that crack propagation can be terminated by a shift in the electrochemical potential (e.g., by removing oxygen from the system)⁸, by a change in the material (e.g., by the crack running into a duplex weld structure containing sufficient delta ferrite to control the chromium-depleted zones)⁹, or by a reduction in the stress intensity factor to a level below K_{SCC} (e.g.,

by the crack reaching an area of residual compressive stresses). Once a crack has been initiated, however, the environment within the crack is difficult to change, and will continue to favor propagation unless the chemical potential is changed by reducing the oxygen levels in the system. Thus, given sufficient stress intensity, a crack may continue to propagate into material normally considered resistant to IGSCC in a BWR environment.

Water Chemistry Controls in Operating BWRs - The water chemistry of each operating BWR is required by its operating license to remain within certain specified limits (Plant Technical Specifications). In most cases, these limits are identical to those spelled out in Regulatory Guide 1.56, "Maintenance of Water Purity in Boiling Water Reactors"¹¹. Table 1 lists the limits given in this guide. To date, it has been accepted that the oxygen concentration in BWRs was fixed by the radiolysis of water in the reactor core and the boiling process to 0.2 - 0.3 ppm at full power levels^{2, 11}.

ROLE OF IMPURITIES ON INITIATION AND PROPAGATION OF IGSCC

Recent research at General Electric¹² and at Argonne National Laboratory⁶ has shown that, within the water purity limitations spelled out in Regulatory Guide 1.56, there are significant effects of dissolved anionic impurities on both the initiation and the propagation of IGSCC. The three most common anions that can concentrate in films and produce electrolytes in the crack are chloride, which frequently enters a BWR coolant through condenser leakage, sulfate or sulfite, which can enter the coolant from condenser leakage or resin breakup, and carbonate, which can enter the coolant from air or water

leakage into the condenser. The material itself may also provide a sufficient source of impurities, by oxidation of sulfide, phosphorus, or carbide impurities. Further, crack-tip chemistry may differ significantly from bulk chemistry, through corrosion processes. Breakup of demineralizer resins can cause injection of the sulfonate cation resin beads, which decompose in the heat and radiation in the reactor to sulfites or sulfates, depending upon the oxidizing potential. If resin beds have been used for an extended period of time, particularly on a coastal plant, their breakup may inadvertently introduce chlorides that had been adsorbed in the resin beds, along with the sulfur species, to the coolant.

Although tightening the allowable limits on these species (or on conductivity) in the BWR coolants could have a beneficial effect on the occurrence of IGSCC, it may not always be easy for a utility to operate with significantly tighter controls over a long period of time. It is known from laboratory tests¹² that chloride ions, for example, once introduced into the coolant, will adsorb in the films near the growing cracks and are not easily removed following elimination of the chloride in-leakage into coolant. How much chloride, sulfate, and even carbonate are codeposited or adsorbed in the crud deposits is not known at the present time, nor is their role on subsequent cracking well understood. In a slightly different reactor Ondrejcin¹³ identified high concentrations of chloride in the crud deposits (which in that reactor were primarily hydrated aluminum oxides), despite maintenance of less than 0.2 ppm Cl^- in the reactor coolant. This work did not establish, however, that Cl^- was a major contributor to the observed IGSCC.

It is difficult to demonstrate a clear benefit from operation with low impurity levels from current plant operating data. Differences in materials and stress patterns may override differences in water chemistry between operating units. However, the laboratory data clearly indicate that for a given material and loading conditions, additions of sulfates, chlorides, or carbonates have a significant detrimental effect.

ROLE OF OXYGEN AND TEMPERATURE

The role of the oxygen in the BWR coolant appears to be to shift the electrochemical potential of the sensitized stainless steel from a passive region into one in which active IGSCC can occur. Maintaining the oxygen level to below 5 ppb by the use of hydrogen addition in PWR primary coolant has totally eliminated this problem in these units². The steady state oxygen level (.2-.3) ppm in BWRs has been shown in laboratory experiments to be sufficient to cause IGSCC and relatively little acceleration of crack propagation rates has been observed by increasing the oxygen level much above this point⁷. As a matter of laboratory convenience, researchers frequently study IGSCC in water saturated with oxygen at room temperature (8 ppm).

Using room temperature saturated water (Andresen and Ford¹⁴,) have shown that the rate of crack propagation appears to reach a maximum at approximately 200°C and become lower above this temperature. Unpublished work by Vyas and Isaacs in the author's laboratory¹⁵ showed some similar effects. In these experiments, samples machined from a single heat of stainless steel given an

identical sensitizing heat treatment, were pulled at different strain rates and temperatures in pure water containing 22 ppm oxygen. Figure 1 shows the results of this experiment as a plot of the crack propagation rates, estimated from these tests, as a function of strain rate and temperature. The maximum crack propagation was found at a different strain rate at each temperature investigated. Further, the range of strain rates at which IGSCC occurred was much wider at 200°C than at temperatures either higher or lower than this. In Figure 2 the maximum crack propagation rates at each temperature investigated are plotted as a function of reciprocal temperature. Clearly at 200°C there is a major change in the rate limiting step in the crack propagation. In acidic solutions, the solubility of iron from Fe_3O_4 decreases with increasing temperature above 100°C, as shown in Figure 3¹⁶. In Figure 4 are compared the temperature dependence of IGSCC shown previously in Figure 2 with the solubility of Fe in high temperature water containing 10^{-5}M HCl from Figure 3. The drop in Fe solubility and crack propagation rates above 200°C are very much of the same order of magnitude. While this particular agreement may be fortuitous, it does suggest that an electrochemical crack propagation mechanism is in fact operative.

The maximum in crack propagation rates at approximately 200°C has suggested that deaeration of a BWR coolant during startup, when the temperature passes through this region of maximum propagation rates and strain rate susceptibility, might be beneficial as a mitigating action for IGSCC in BWRs, and attempts to perform startup deaeration have been made in several

countries⁷. However, the relative period of time in which the reactor is under these conditions and the relatively small benefit in decreasing the oxygen from 8 ppm down to the steady state 0.3 ppm suggest that startup deaeration would not by itself produce a significant reduction in the occurrence of IGSCC and indeed service experience has confirmed this conclusion.

Controls of Oxygen in BWR Coolant

Since IGSCC of sensitized stainless steel can occur in high purity water containing oxygen, chemical controls for prevention of IGSCC in a BWR require a reduction in the levels of both the ionic species and the oxygen in the primary coolant. If sufficiently low levels of oxygen are achieved, the electrochemical potential of the stainless steel will be shifted to a region at which IGSCC will neither initiate nor propagate. The oxygen levels required to prevent IGSCC depend strongly on the level of ionic impurities present. Current data suggest maintaining the electrochemical potential to less than -350 mV on the standard hydrogen scale and the conductivity of the coolant to less than 0.2 $\mu\text{S}/\text{cm}$ will suffice to prevent IGSCC⁶. Such shifts in potential can be achieved by the injection of hydrogen into the BWR coolant⁷. Demonstrations of this technique have been made in Sweden at Oskarshamn and Ringhals and in the U. S. at Dresden-2⁷ in which a corrosion test loop is deliberately tapped into one of the recirculation lines to monitor the corrosion potential of sensitized stainless steel and the behavior of stress-corrosion cracks in this environment.

Both in Sweden and at Dresden-2, short-term tests have shown that the SCC can be stopped: in the Dresden corrosion test loops, cracks already initiated stopped propagating when the hydrogen was injected^{7,17} and the electrochemical potential dropped below -350 mV. The same levels of hydrogen concentration in the feedwater appear to have a different effect on the corrosion potential at Dresden than they do at Ringhals. An argument has been made that these differences may be traced back to the fact that the Swedish BWRs do not have jet pumps. There are also possible differences due to other chemical impurities in the water, since a number of ionic species in the coolant are known to affect the ability of hydrogen at a given concentration to suppress production of radiolytic oxygen¹⁸.

Role of Other Impurity Intrusions: Decontamination

From the above discussions, it is apparent that any action which disturbs chemically the protective layers of oxides on the surface of the stainless steel can have an effect on IGSCC. Although research has shown that relatively mild decontamination solutions, such as those used in the CANDECON process¹⁹, do not increase the propagation rates of IGSCC in sensitized stainless steel in the laboratory²⁰, the effects of decontamination (removing the crud deposits and activating any ionic species that might be adsorbed in them) on initiation of SCC following return to service of the cleaned unit are not known. Many utilities faced with high radiation fields and frequent in-service inspections have felt it prudent to reduce personnel exposures by decontaminating the piping before the inspections. The long-term effects of this practice need to be investigated.

DISCUSSION

Remedial actions for IGSCC in BWRs that have been proposed include replacement of the piping with a less susceptible material, heat treatment techniques for the piping that reduce the tensile residual stresses in the heat affected zones of welds. These were discussed at considerable length at a recent EPRI workshop⁷. However, it is not always convenient to replace all the piping and sometimes not possible to use stress improvement heat treatments on all welds in the circuit. Therefore, for many operating units or those already constructed, improved water chemistry controls maybe the only practical method to minimize IGSCC. To achieve this, we need a much clearer understanding of the mechanisms of crack initiation. In particular, the role of the mass transported crud in producing surface crevices, in adsorbing anionic impurities either from corrosion products in the solution or demineralizer breakthrough or breakup, as well as in producing crevices on the surface that can act when the protective film is ruptured as a location for concentrating these impurities is not well understood. The experimental results that show chlorides remaining in the oxide films for an extended period of time suggest that a brief incursion of acid chlorides such as has occurred at several operating units, may have a long range effect. At the same time, however, if they are tightly chemisorbed in the crud deposits, this chemisorption could render them innocuous unless the chemistry of the system is disturbed (such as by a resin intrusion) to reactivate them.

Decontamination processes such as have been proposed remove the crud deposits and the protective oxides completely for a brief period of time, followed by repassivation efforts. By removing the crud deposits and therefore any crevices in them, the decontamination may in fact reduce the probability of IGSCC formation. At the same time, however, if any grain boundary etching occurs during this decontamination or is present from prior pickling of the pipe underneath the crud deposits and if these crud deposits contained adsorbed sulfite, sulfates, chlorides, etc. activating these species during decontamination could be detrimental. A research program under EPRI sponsorship is now underway to investigate these variables.

Much of the above discussion is related to the information needed to improve our understanding of the initiation phase. However, the mechanistic aspects of the propagation stage are also not clear. Vyas and Isaacs¹⁵ have suggested the model shown in Figure 5. Their results (Figure 2), suggests that a normal, chemically-activated propagation mechanism appears to be occurring from room temperature up to approximately 200°C. The low apparent activation energy, estimated from the data in Figure 2 to be approximately 3.4 to 4 Kcal/mole, suggests that the rate controlling step is migration of some ionic species (presumably Fe^{++}) through the solution in the grain boundary crevice. Since the inverse temperature dependence above 200°C is roughly parallel to the inverse temperature dependence of the solubility of Fe or magnetite in acid solutions, such as are anticipated to be present in a crevice, the reduced solubility of Fe^{++} reduces the concentration of iron available for migration in the crevices, and therefore, the rate of crack propagation at higher temperatures. While the Fe_3O_4 solubility data were

obtained in solutions containing H_2 and the BWR environment contains residual O_2 , corrosion-produced H_2 is present at the root of an actively — growing crack.

By far the best water chemistry mitigating action would be adding sufficient hydrogen to shift the corrosion potential of the sensitized stainless steel into a passive region. However, the hydrogen levels needed to achieve this effect may differ from plant to plant, due (among other things) to differences in ionic species present in the coolant or in the oxide films which can influence the effectiveness of the hydrogen to suppress radiolysis of the water. Addition of H_2 alone, then, may not be sufficient to prevent IGSCC in a given operating unit. Startup deaeration and strict controls on impurity ingress would also be required. Many questions remain to be answered in order to set specifications for such an approach that ensure its effectiveness.

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TABLE 1
ACCEPTABLE REACTOR WATER CHEMISTRY LIMITS

PARAMETER	LIMIT	MAXIMUM LIMIT
<i>Specific Conductance at 77°F (25°C)</i>		
1. Power Operation Steaming rates greater than 1% of rated steamflow	1 $\mu\text{mho/cm}^a$	10 $\mu\text{mho/cm}^b$
2. Startup/Hot Standby and Power Operation Steaming rates less than 1% of rated steamflow	2 $\mu\text{mho/cm}^c$	—
3. Cold Shutdown Reactor is not pressurized [i.e., at or below 212°F (100°C)]		10 $\mu\text{mho/cm}$
<i>Chloride</i>		
1. Power Operation Steaming rates greater than 1% of rated steamflow	0.2 ppm ^a	0.5 ppm ^b
2. Startup/Hot Standby and Power Operation Steaming rates less than 1% of rated steamflow	0.1 ppm	—
3. Cold Shutdown Reactor is not pressurized [i.e., at or below 212°F (100°C)]		0.5 ppm
<i>pH at 77°F (25°C)</i>		
1. Steaming rates greater than 1% of rated steamflow	pH not less than 5.6 nor greater than 8.6 ^d	—
2. Reactor is not pressurized [i.e., at or below 212°F (100°C)]	pH not less than 5.3 nor greater than 8.6	

^a Time above 1 $\mu\text{mho/cm}$ at 77°F (25°C) and 0.2 ppm chloride not to exceed 72 hours for any single incident, but the total time for all incidents should not exceed 2 weeks per year. When the time limits are exceeded, an orderly shutdown should be initiated within 4 hours.

^b When the maximum conductivity or chloride concentration limits are exceeded, an orderly shutdown should be initiated immediately, and the reactor should be brought to the cold standby condition as rapidly as cooldown rate permits.

^c Time above 2 $\mu\text{mho/cm}$ at 77°F (25°C) and 0.1 ppm chloride not to exceed 48 hours for any single occurrence. When the time limits are exceeded, the reactor should be brought to the hot shutdown condition until the limits are restored.

^d The reactor should be shut down if pH is <5.6 or >8.6 for a period of 72 hours.

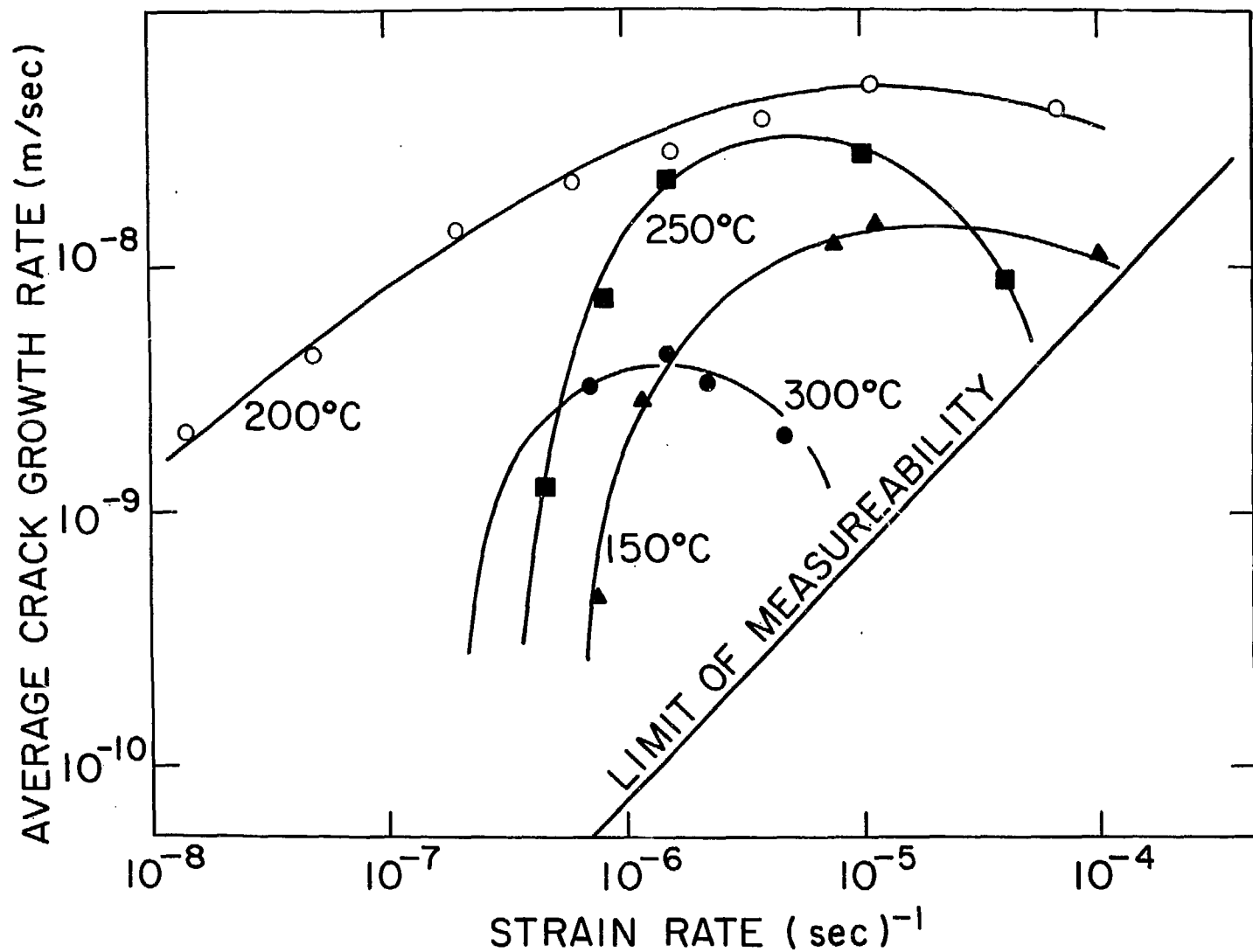


Figure 1 Crack propagation rates in furnace-sensitized Type 304 stainless steel, estimated from slow strain rate tests (from 15)

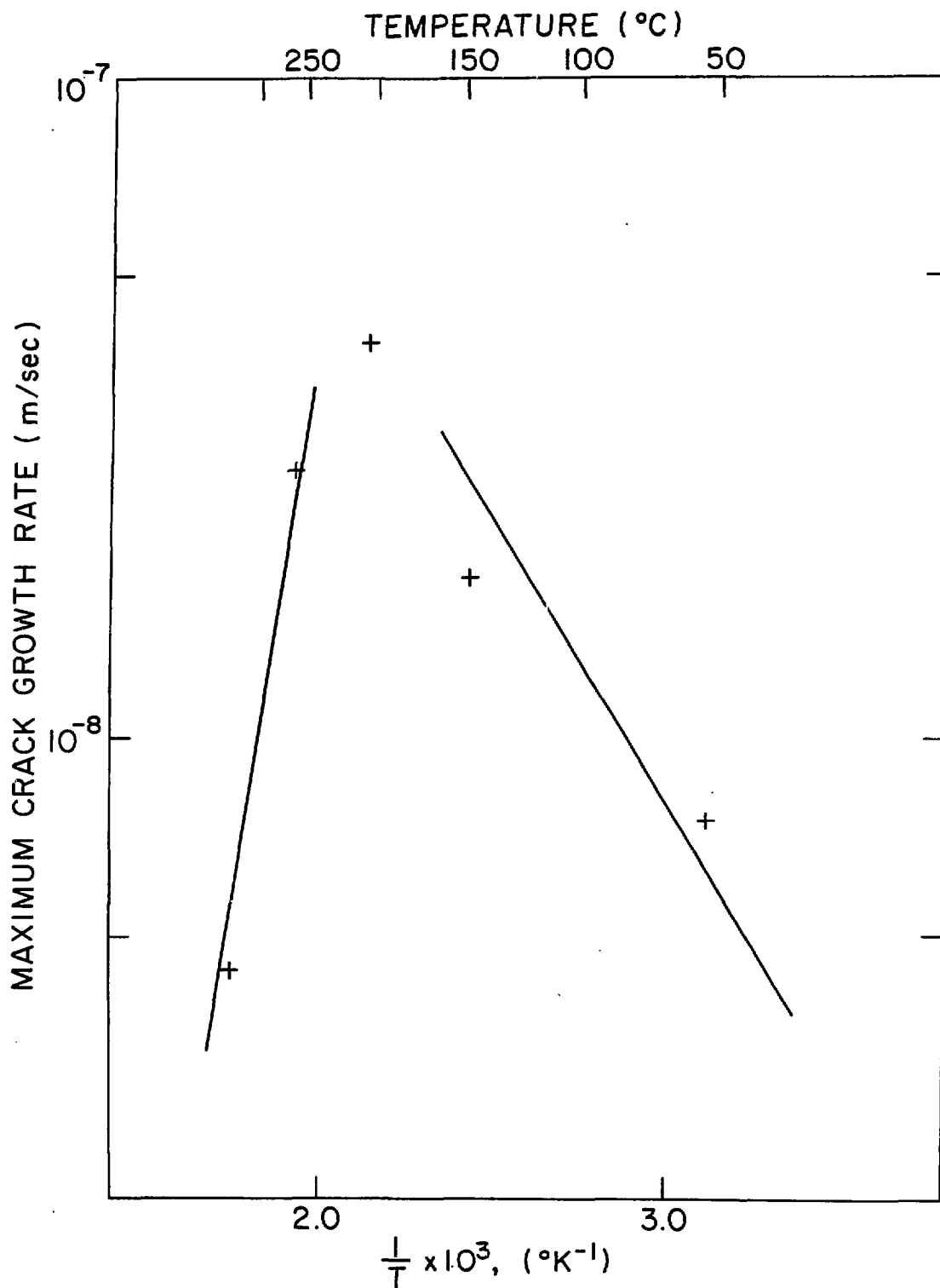


Figure 2 Effect of temperature on maximum crack propagation rates, taken from data in Figure 1 (from 15).

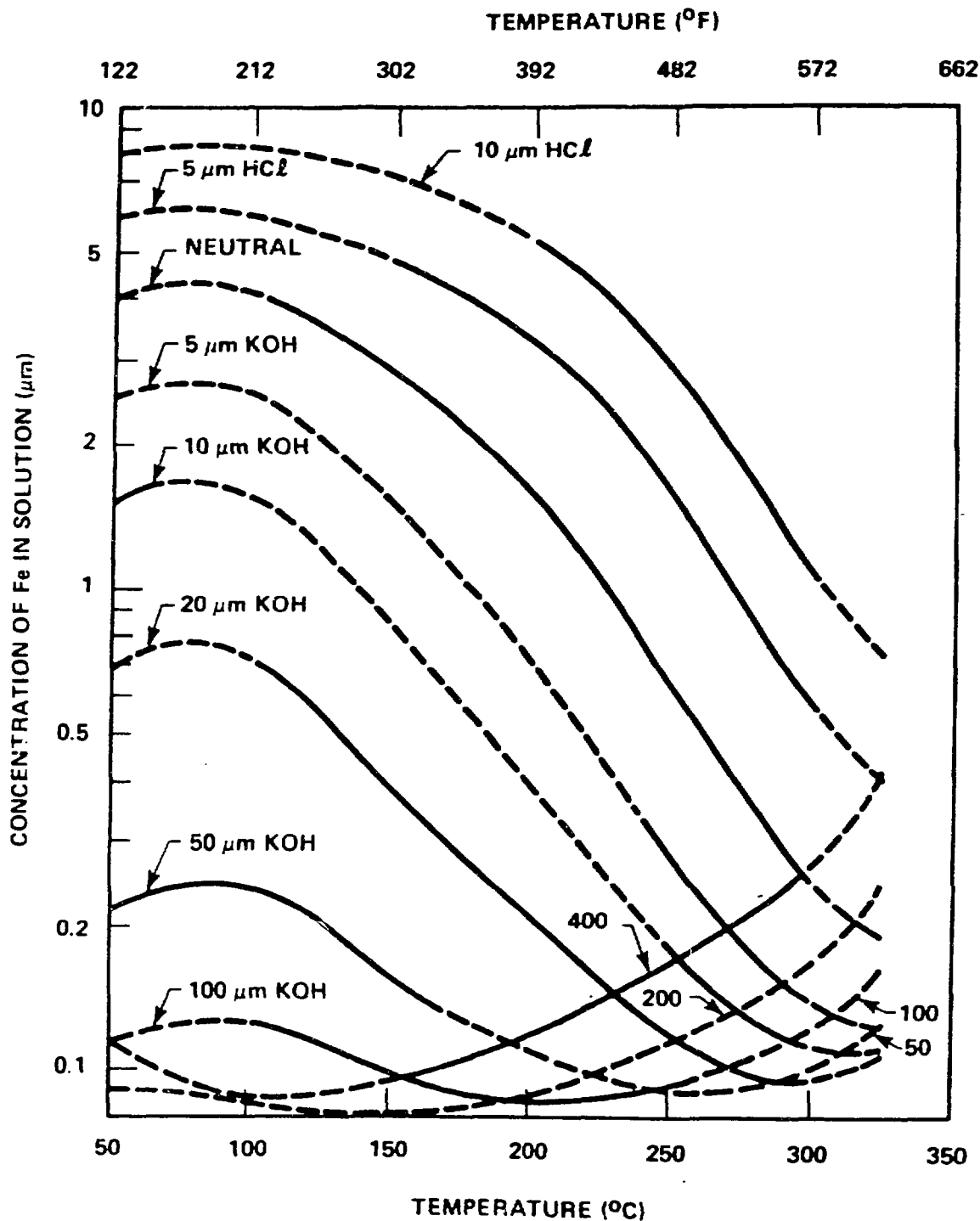


Figure 3 Solubility of Fe_3O_4 in solutions saturated with H_2 at 1 atm at 25°C (from 16).

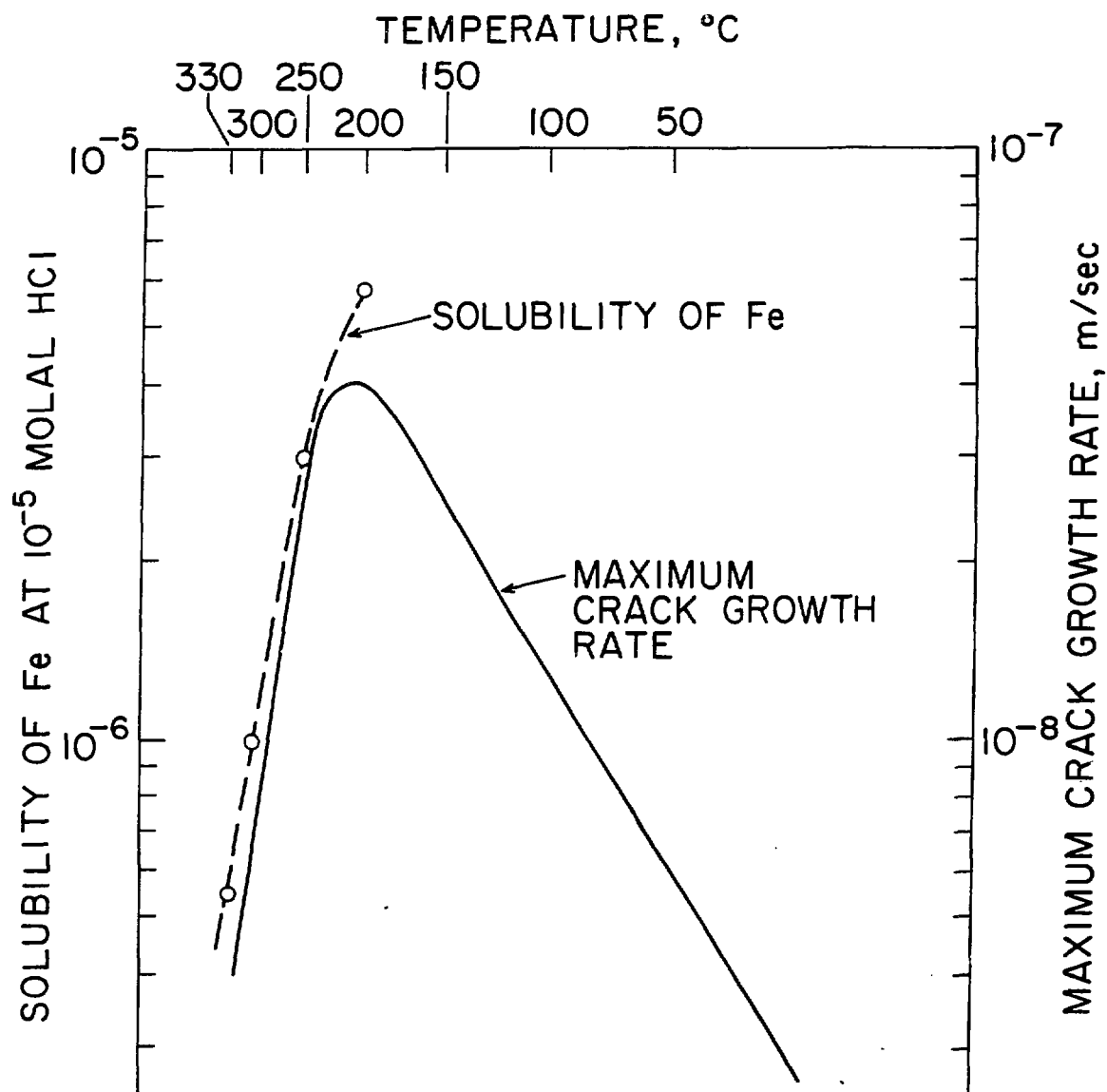


Figure 4 Comparison of curves from Figure 2 with solubility of Fe in 10⁻⁵ m HCl, from Figure 3.

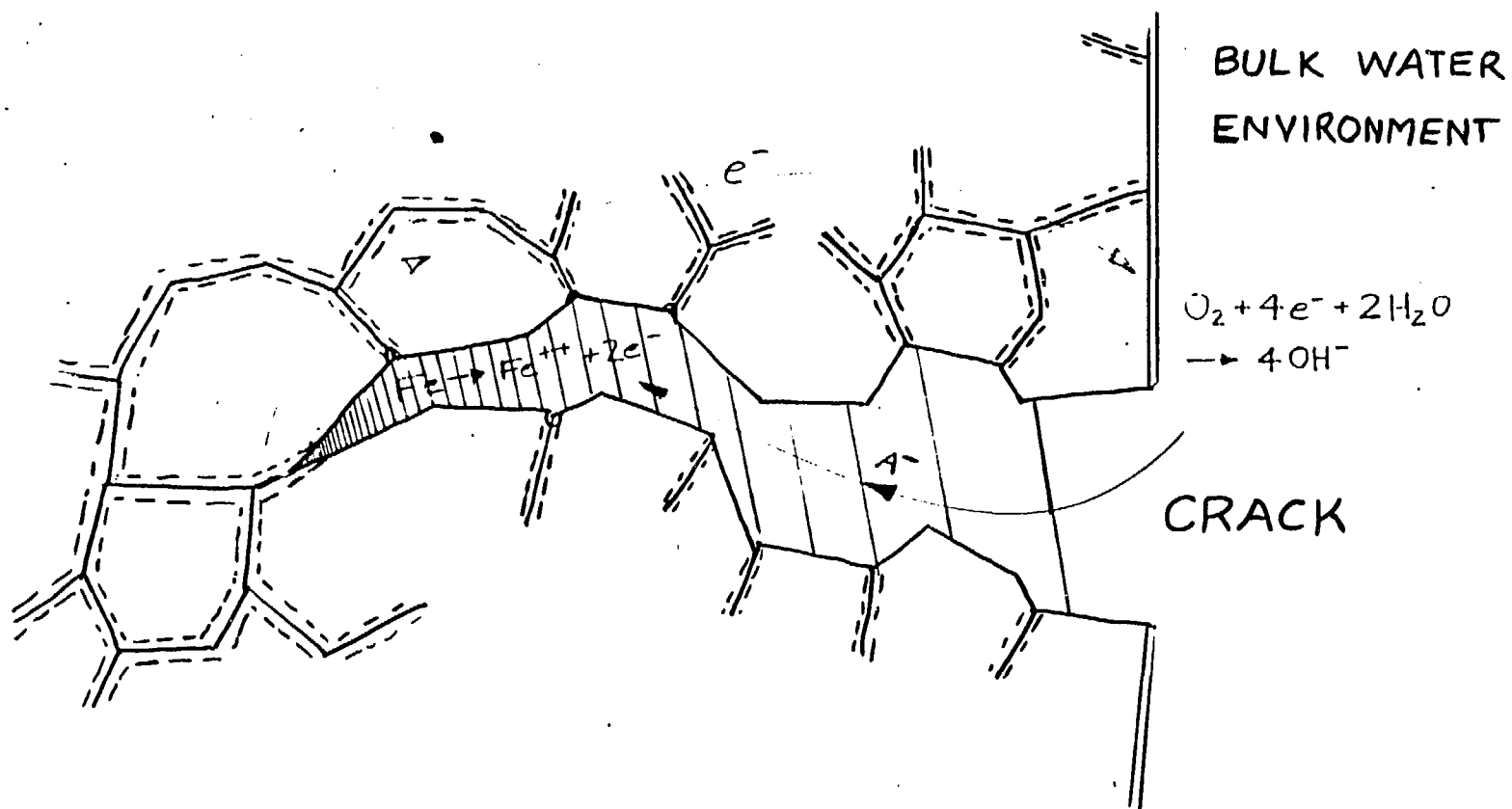


Figure 5 Schematic model of crack propagation mechanisms (from 15).