ROLE OF HYDROGEN IN STRESS CORROSION CRACKING

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ABSTRACT

Hydrogen embrittlement has been postulated as a cause of stress corrosion cracking in numerous alloy systems. Such an interrelationship is useful in design considerations because it permits the designer and working engineer to relate the literature from both fields to a potential environmental compatibility problem. This review emphasizes the role of hydrogen in stress corrosion of high strength steels and illustrates several techniques for minimizing the susceptibility to hydrogen stress cracking.

ROLE OF HYDROGEN IN STRESS CORROSION CRACKING

INTRODUCTION

The Typpi Oy ammonia plant in Finland was temporarily closed on Thursday, March 19, 1970, because of a catastrophic failure of forged and welded high-pressure, gaseous-effluent water-coolers. The head chambers of two coolers failed in a brittle manner; the 1.09-m-diameter chambers were thrown a distance about equal to their length (1.10-m), and fragments of the head chambers traveled up to 250 m. Investigations of the failure indicated that a pre-existing flaw or crack extended slowly under the influence of a stress corrosion mechanism. After a period of time, it reached a critical size where catastrophic failure occurred because of a reduction in fracture toughness by hydrogen embrittlement.[1] In this case, the investigation attempted to separate the effects of stress corrosion cracking and hydrogen embrittlement. Similar distinctions have been made in studies to develop "valid methods for detecting and recognizing stress corrosion and hydrogen embrittlement in line-pipe steels" in underground environments.[2]

The distinction between stress corrosion and hydrogen embrittlement is often a matter of semantics. Stress corrosion is defined by some investigators as metal failure resulting from the combined action of stress and chemical attack; because hydrogen embrittlement is not a corrosion process in the classical sense, it is excluded from the term *stress corrosion cracking.*[3] Other investigators define stress corrosion as a brittle-type delayed failure and exclude situations where cracking develops because of corrosion accelerated by stress.[4] Thus, the apparent role of hydrogen in stress corrosion processes may be significantly altered by definition. However, a review of the current literature clearly indicates that many investigators believe that hydrogen evolution and absorption are important processes in stress corrosion phenomena. Hydrogen embrittlement has been postulated as a cause of stress corrosion cracking in aluminum alloys,[5] high strength steels,[6] austenitic stainless steels,[7] titanium alloys,[8] 400 series stainless steels,[9] a nickel-copper alloy,[4] zirconium alloys,[10] and "with only a few possible exceptions, virtually all (examples of) stress corrosion cracking."[11]

Interrelationships, including the possibility of equivalency, between hydrogen embrittlement and stress corrosion cracking are useful in design considerations because they allow the designer and working engineer to relate the literature from both fields to a potential environmental compatibility problem. Emphasis in

this review is placed on the role of hydrogen in stress corrosion of high strength steels. This alloy-environment system was selected partially because the role of hydrogen has been rather well defined and partially because of the continued need for high strength, environmentally compatible materials in the transportation, space, chemical, energy, and petrochemical industries.

BACKGROUND

Stress corrosion cracking of high strength steels has been studied for at least six decades, and several comprehensive reviews are available.[12-14] Although, numerous causes of stress corrosion in high strength steels have been postulated, by the early 1960s there was general acceptance for two types of mechanisms (Figure 1):[15]

● Active path corrosion (APC) where cracks grew because of anodic dissolution along a susceptible path

● Hydrogen embrittlement cracking (HEC) where crack growth is controlled by absorption of atomic hydrogen

Irrespective of the mechanism, high strength steels have been observed to crack in a wide variety of environments including[6] chloride solutions, marine environments, and solutions containing H_2S, SO_4^-, PO_4^-, NO_3^-, and acetic acid.

Laboratory environments (Table 1) not generally considered as stress corrosion causing atmospheres have induced failures of notched samples in very short times.[16] Environmental exposure has been shown to cause failures at K values as low as 20 ksi $\sqrt{in}$. in steels with K_{IC} values approaching 100 ksi $\sqrt{in}$.[14] However, in addition to environmental effects, the mechanical properties of high strength steels are highly sensitive to processing variables such as melting practice (Figure 2).[14] Because of such effects, comparisons of environmental compatibility studies by various investigators is often difficult, and considerable data scatter is observed, even when fracture mechanics specimens have been used (Figure 3).[14] Such observations coupled with the apparent fact that in some cases distilled water may be more aggressive than 3% NaCl solutions in causing crack growth have presented considerable difficulty in specifying design parameters.

The susceptibility of a specific alloy to stress corrosion in a specific environment is affected by grain size, dislocation substructure, yield strength or hardness level, and other metallurgical variables.[17] In alloy-environment systems where hydrogen stress cracking is probable, correlations between alloy hardness and minimum stress for failure are often well established (Figure 4)[13] and tend to indicate that these factors are more important than the other metallurgical variables.

TABLE 1

Partial List of Environments Causing
Stress Corrosion Cracking of 300 M Steel[a]

Environment	Exposure Period to Failure, minutes
Recording ink	0.5
Distilled water	6.5
Butyl acetate	18
Butyl alcohol	28
Amyl alcohol	35.8
Acetone	120
Lubricating oil	150
Benzene	2,247
Air	none in 6,000

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a. Specimens were center notched and
   stressed to 75,000 psi.[16]

The need for evaluation of the alloy in the specific environment of potential application is also important. For example, recent studies with HSLA (high strength low alloy) steels have shown that there was no correlation between the corrosion resistance of steels exposed beneath test vehicles and steels exposed at the same time to the atmosphere through which the vehicles drove.[18] This result is typical of general corrosion studies and is unfortunate because it means that the information developed in one environment may not be useful in the selection of materials for structural application in related but not identical environments.

Results of many experiments indicate that at least three factors must be included in any investigation of stress corrosion cracking. These factors are:

● Severity of the environment

● Susceptibility of the material

● Stress level to which the material is subjected

The following sections of this paper provide several guidelines for selection of steels for applications where hydrogen stress cracking is of concern and summarize portions of the literature which indicate that absorption of hydrogen is a common factor in the environmental cracking of steels.[6]

- 4 -

THE CASE FOR HYDROGEN

The distinction between APC and HEC was based on the effect of a polarization current on the time to fracture (Figure 5). An APC mechanism was assumed in systems where application of anodic and cathodic currents decreased and increased, respectively, the time to failure (Figure 5a). The HEC mechanism was assumed in systems where the reverse was true (Figure 5b). Implicit in this type of analysis is the assumption that at bulk potentials noble to the reversible hydrogen potential, no hydrogen reduction from protons may occur at the crack tip; thus, hydrogen cannot be participating in the crack propagation mechanism.[6] Microanalytical techniques[19] and potential measurements,[20] however, have shown that bulk surface conditions do not reflect the prevalent conditions at crack tips, pits, and crevices. Such observations were discussed in detail in an earlier paper;[21] it is emphasized here that hydrogen is evolved from pits and crevices over a wide range of polarization potentials, including bulk potentials that would seem to preclude such evolution (Figure 6).[14] Thus, hydrogen absorption may occur under all the conditions shown in Figure 5a, and an exclusive anodic dissolution mechanism is not needed. However, under many of the conditions studied, anodic dissolution is necessary for hydrogen evolution, so an exclusive HEC mechanism cannot be justified.

Measurements of crack growth kinetics in a modified 12% Cr steel exposed in 3% NaCl solution[6] indicate that the rate-controlling mechanism for crack growth is hydrogen embrittlement. These measurements (Figure 7) show that the temperature dependences of crack growth in freely corroding, anodically polarized, and cathodically polarized specimens are nearly identical and in agreement with the ∿9 K cal/mol activation energy established for hydrogen embrittlement of high strength steels. Furthermore, the fractographic features of steel embrittled by hydrogen gas and those of a stress corrosion cracked steel are similar.[22] The above observations, and other studies with similar results, indicate that hydrogen embrittlement and stress corrosion cracking (SCC) of high strength steels are equivalent. An excellent review leading to this conclusion is given in Reference 14. This reference is also an excellent source of information on the behavior of numerous iron and steel alloys in many environments.

AVOIDING HYDROGEN STRESS CRACKING

"Clearly, the best solution to the SCC or hydrogen embrittlement problem is to avoid using a metal or alloy susceptible to embrittlement by the particular working environment whenever possible."[23] This solution is not as obvious or as practical as it may sound. For example in January 1975, it was reported that

"a number of corrosion fatigue failures of sucker rods and un-
anchored tubing strings occurred ..."[24] in an oil field environ-
ment which was known to require an inhibitor to minimize such
failures. However, "the inhibitor being used in the unit at the
time the failures occurred had been shown 8 years earlier to be
ineffective against corrosion fatigue in simulated oil field
environments in a limited number of laboratory tests."[24] Labor-
tory evaluation had been subsequently discontinued because of the
lack of correlation between test results and field experience.
Furthermore, hydrogen stress cracking continues to plague the oil
industry. The strength requirements for piping in deep, high
pressure wells require the use of alloys at hardness levels known
to be susceptibile to stress corrosion failure.[25] Chloride
leaching from thermal insulation continues to cause cracking of
steel piping in the chemical industry,[26] even though this effect
has been known for years. A one million dollar loss was reported
in 1973 and attributed to chloride stress corrosion of 304 stain-
less steel, an alloy which is well known for its stress corrosion
susceptibility.[26] It is apparent from a survey of the current
literature that stress corrosion cracking, in general, and hydrogen
stress cracking, in particular, are continuing problems that are
not being solved by avoiding the use of a material in an environ-
ment where it is known to be susceptible. However, investigations
have shown that hydrogen stress cracking failures can be minimized
by carefully considering material and environmental variables.

EFFECT OF HARDNESS

The National Association of Corrosion Engineers lists a
variety of materials that resist hydrogen stress cracking, in-
cluding 4130, 4140, and 4145 steels tempered at 621°C to a
hardness of R_c 22 or below.[27] Justification for this type of
recommendation was presented in Figure 4. Alloys heat treated
to higher hardness levels can be used if the flaw size is known
and the maximum stress intensity can be shown to be below the
threshold stress intensity for hydrogen stress cracking. For
example, studies of the effect of initial stress intensity on the
time to fracture 4340 steel have shown that $K_{ISCC} \simeq 50$ ksi $\sqrt{in.}$
in parts heat treated to about 200-ksi yield strengths (Figure 8);[28]
thus, this alloy could be used at hardnesses above R_c 22 if
$K < 50$ ksi $\sqrt{in.}$

EFFECT OF COMPOSITION AND MICROSTRUCTURE

Vacuum remelting of Type 410 martensitic stainless steel has
been shown to improve its resistance to hydrogen stress cracking
in various heat-treated conditions.[29] This observation corre-
sponds to the effects of melting practice on the fracture toughness

of high strength steels (Figure 2) and agrees with the conclusion that hydrogen stress cracking resistance correlates with notch sensitivity.[30] Grain refinement (of prior austenitic grains) is also beneficial in minimizing the susceptibility to hydrogen stress cracking.[31] TRIP (transformation induced plasticity) steels, characterized by high strength, good fracture toughness, and good ductility, have been shown to be resistant to cracking, even when loaded to a K value of 145 ksi $\sqrt{in}$. (80% of K_c).[32] TRIP steels have duplex structures (austenite and martensite), and as discussed earlier in this conference,[17] such structures typically have reasonable resistance to stress corrosion. In the TRIP steels, the cracking resistance has been attributed to a lack of hydrogen embrittlement in the austenite surrounding the martensite.[32]

Hydrogen cracking of steel weldments has been extensively studied (see Reference 13, Chapter 8, for example). A review of the effect of weld microstructure indicates that carbon segregation enhances hydrogen induced crack formation and that for both acicular and fine carbide microstructures, cracking tendency decreases with decreasing carbon content. Twinned martensite has a detrimental effect on cracking susceptibility, and the lack of soft phases at the columnar grain boundaries is beneficial in a cast structure. A summary of the effects of composition on hydrogen cracking of welds indicates that molybdenum, chromium, and vanadium additions typically reduce cracking, nickel has little effect, and manganese increases cracking tendencies.[13]

Detrimental effects of additions of carbon and manganese have also been demonstrated for base metal and are summarized in Figures 9 and 10. However, the beneficial effects of molybdenum and chromium observed for weld deposits were not found in studies with unwelded Type 4340 steels.[14] Furthermore, nickel, which had little effect on welded structures, was shown to decrease K_{ISCC} in quenched and tempered 0.3% C steels having approximately 195-ksi yield strengths (Figure 11). Thus, it is apparent that generalizations about the effect of alloying elements on stress cracking of high strength steels is difficult. This difficulty was discussed in a review[33] which emphasized that "trace elements may play an important part in promoting cracking susceptibility by acting as cathode poisons and thereby accelerating hydrogen absorption." Heat treatment may have significant effects on the distribution of trace elements;[34] thus, the observed effects of tempering temperature on time to failure (Figure 12)[33] are compatible with an alteration in the extent to which hydrogen is absorbed.

USE OF COATINGS OR PLATINGS

The fact that many of the high strength steels are susceptible to hydrogen stress cracking in water would preclude their use except for successful applications of various coatings or platings. Cadmium coatings are frequently used on high strength steel parts in the aircraft industry,[14] and problems encountered with this type of coating are perhaps typical. The coatings must be applied to a finished part, must provide a surface which is impermeable to moisture, and must withstand rather severe service conditions. To ensure that the coating meets these requirements, various plating, cleaning, deoxidizing, and stripping operations have been developed. Each of these operations may introduce hydrogen to the part and thus promote the very form of cracking that the coating itself is applied to prevent. Extensive effort has been placed on developing techniques which do not introduce hydrogen. Test specimens are typically cycled through the plating operations; for example, Douglas Aircraft uses stressed 4340 O-ring samples to ensure that application of cadmium coatings to aircraft components does not cause hydrogen embrittlement.[35] Other sites have developed other quality assurance tests,[36] developed mechanical plating techniques,[37] and used spray metallizing and vacuum deposition to avoid hydrogen embrittlement.[13] Actual plating techniques are described in Reference 13, Chapter 16.

SUMMARY

The objective of this presentation was to show that hydrogen absorption is an important phenomenon in the mechanism of stress corrosion cracking of metals. Although most of the references were to high strength steels, similar cases could have been developed for other alloy systems. This emphasis on the role of hydrogen in environmental embrittlement processes will continue in tommorow's session.

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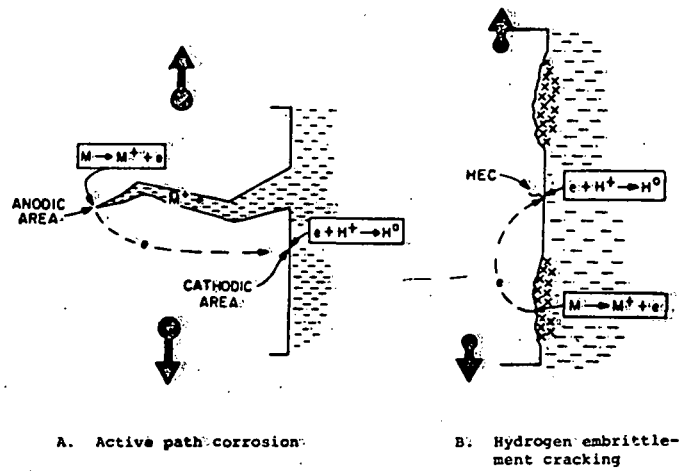
A. Active path corrosion   B. Hydrogen embrittlement cracking

FIGURE 1   Schematic Representation of Active Path Corrosion and Hydrogen Embrittlement Mechanisms *(From Reference 15)*
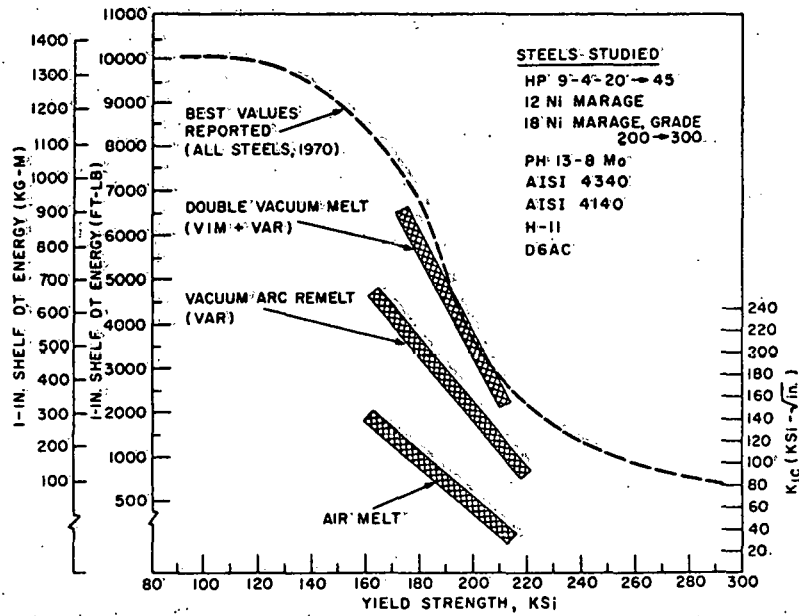

FIGURE 2   Effects of Melting Practice and Yield Strength on the Fracture Toughness of Some High Strength Steels *(From Reference 14)*
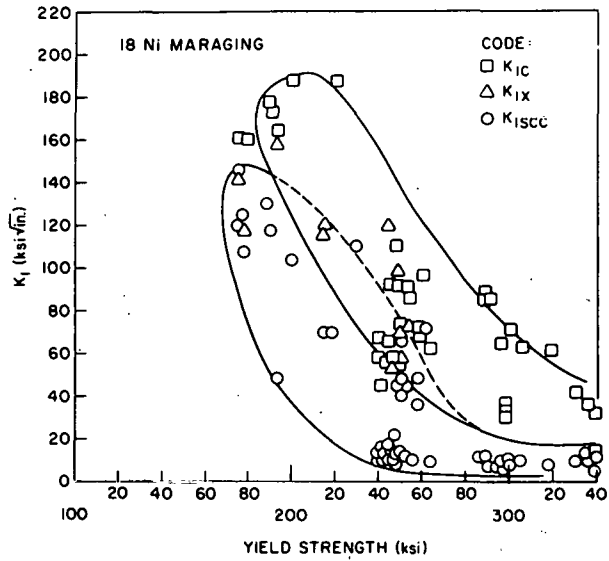
FIGURE 3. Stress Corrosion Resistance and Fracture Toughness of
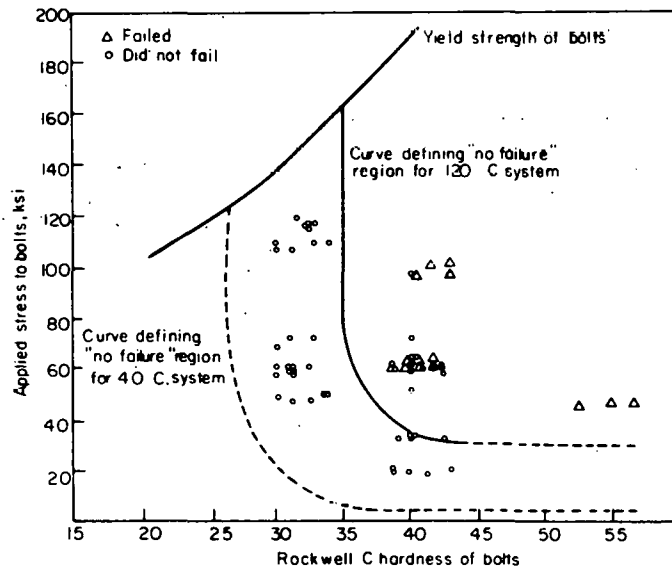18Ni Maraging Steel. K_{IX} is an approximation of K_{IC}
(From Reference 14)

FIGURE 4 Cracking Susceptibility of AISI 4140 Bolts of Different
Hardnesses Exposed up to 1 Year in a Pressurized H_2S-H_2O
System at 40 and 120°C
(From Reference 13)

APC   Active Path Corrosion   a   Anodic Polarization
ttf   Time to Failure   c   Cathodic Polarization

HEC   Hydrogen Embrittlement
↑
ᴏ   No Failure
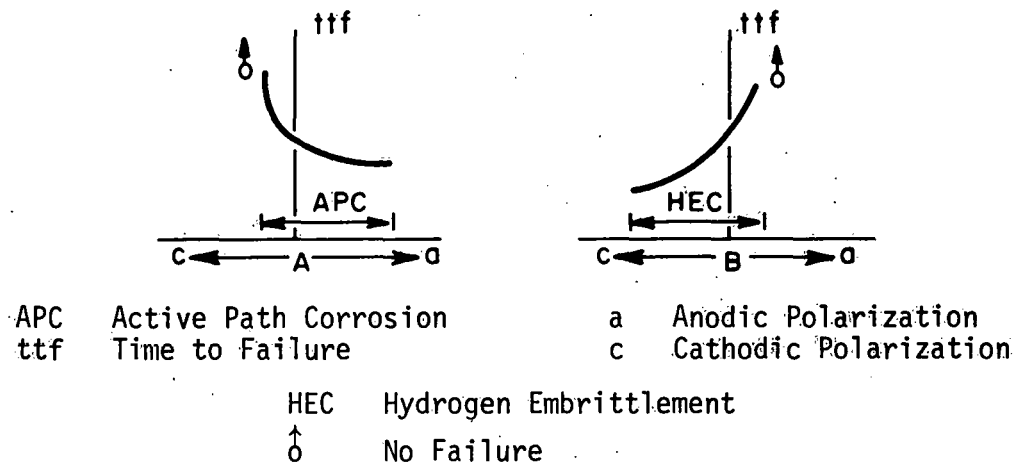
FIGURE 5   Effect of Anodic and Cathodic
           Polarization on Time to Failure
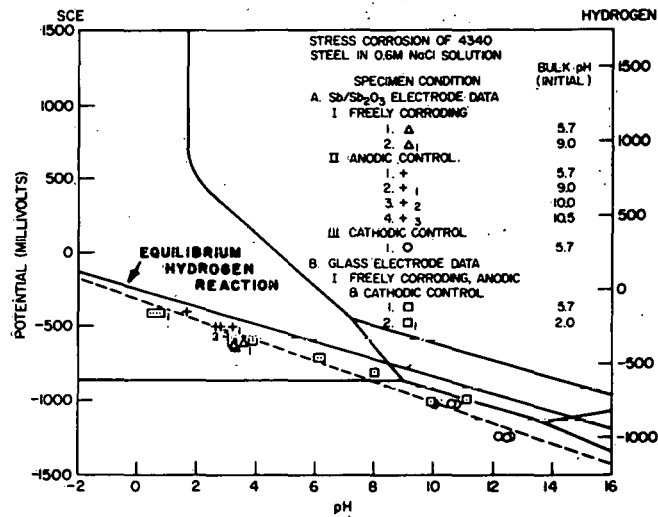
FIGURE 6   Effects of Anodic and Cathodic (impressed) Potential on
           the pH at the Tip of Propagating Stress Corrosion Cracks
           in AISI 4340 Steel. Obviously water may be reduced to
           release hydrogen at the crack tip in every case.
           (From Reference 14)
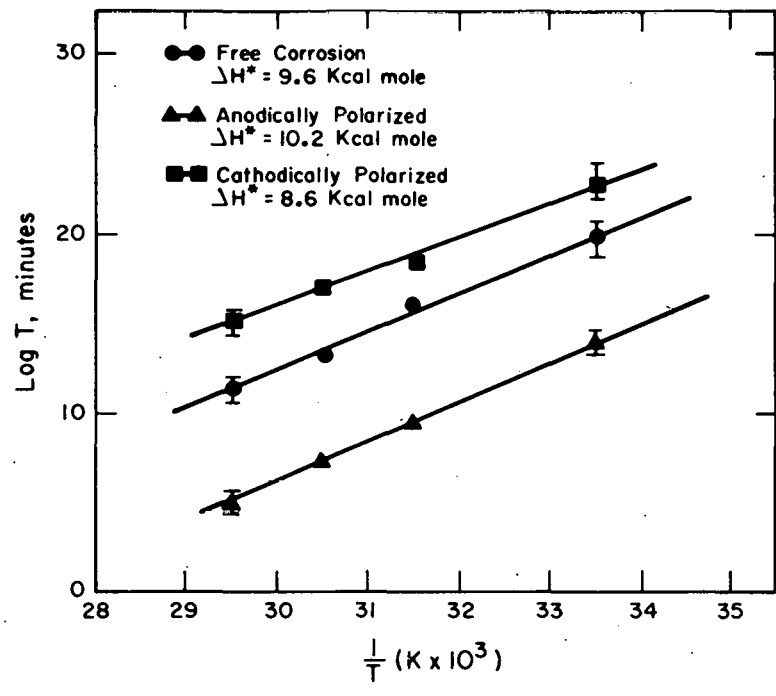
FIGURE 7   The Influence of Temperature on the Crack
Growth Kinetics of a Modified 12% Cr
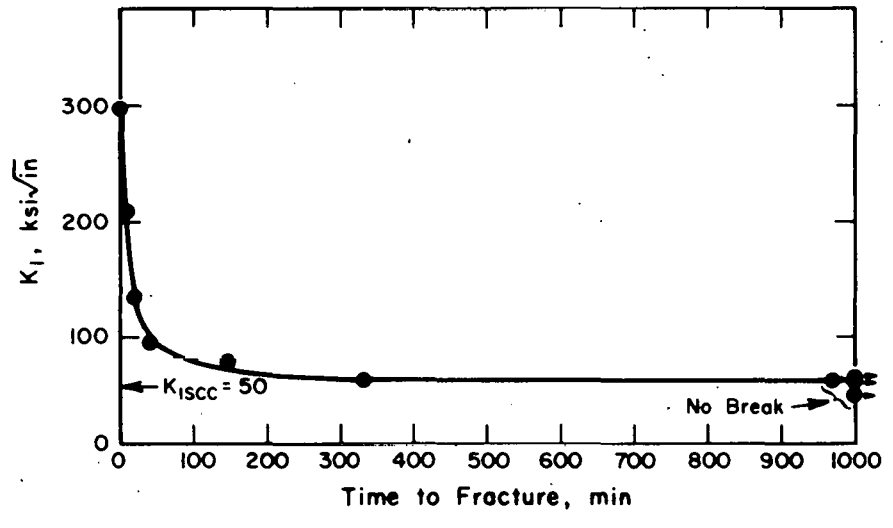Martensitic Alloy in 3% NaCl
(From Reference 6)

FIGURE 8   Effect of Initial Stress Intensity on
Time to Fracture of AISI 4340 Steel
(From Reference 28)
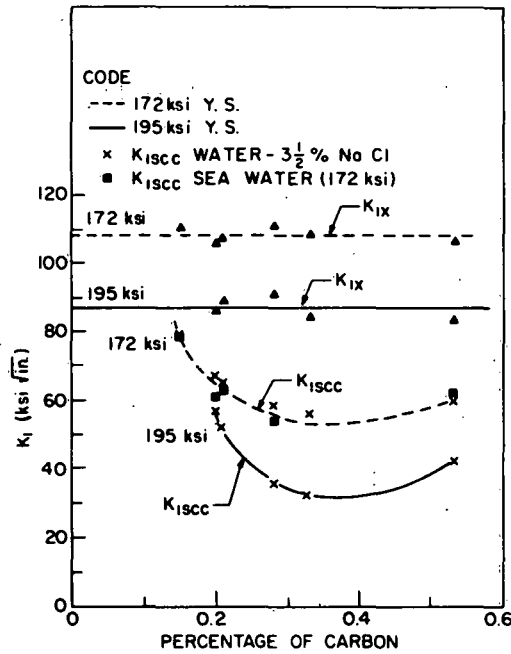
FIGURE 9   The Effects of Carbon on the Stress Corrosion
            Cracking of AISI 4340-Type Steels Quenched and
            Tempered to Either 172- or 195-ksi Yield Strength
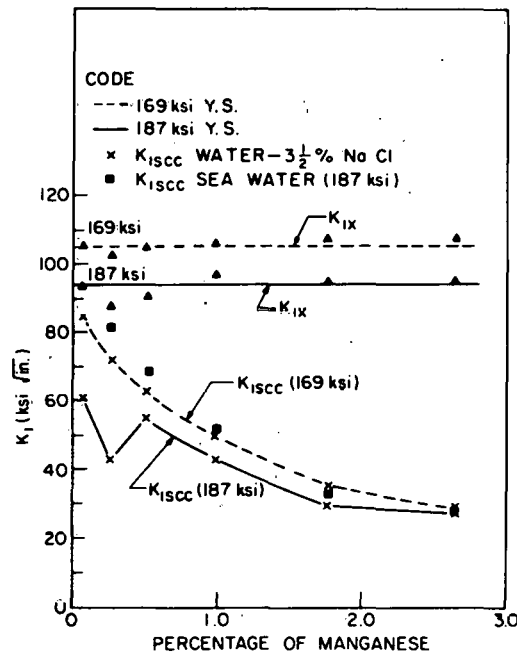   *(Reference 14)*

FIGURE 10   The Effects of Manganese on the Stress Corrosion
            Cracking Resistance of AISI 4340-Type Steels
            Quenched and Tempered to 169- and 187-ksi Yield
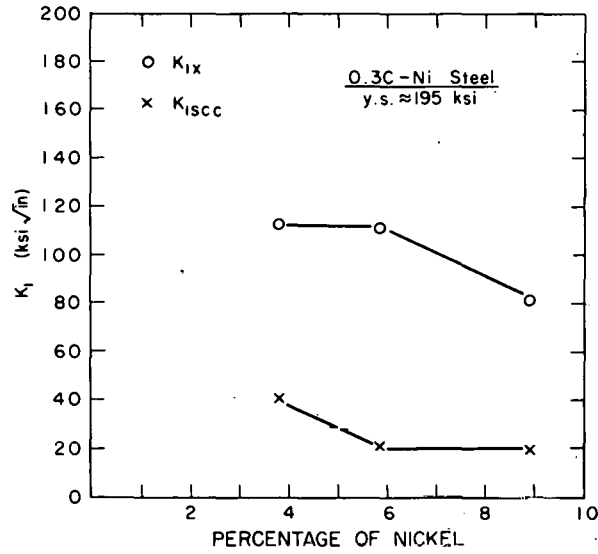   Strength *(From Reference 14)*

FIGURE 11 The Effects of Nickel on the Stress Corrosion Cracking
Resistance of 0.3% C Steel Quenched and Tempered to
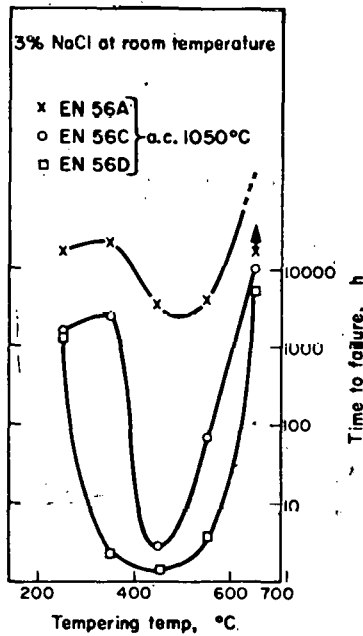About 195-ksi Yield Strength
(From Reference 14)

FIGURE 12. Effect of Tempering Temperature on Time to Failure
(From Reference 33)