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DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

By

George Earl Kerns, M. S. in Met. E.

The Ohio State University
1973

Approved by

Adviser
Department of Metallurgical Engineering
DEDICATION

To my wife, Marie
ACKNOWLEDGEMENTS

I am indeed grateful to the Wright Patterson AFB Materials Laboratory, the Ohio State University Engineering Experiment Station, the Edison Electric Institute, and the Office of Naval Research for their financial support of this study.

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INTRODUCTION

1.1 Purpose and Extent of Investigation

High strength steels are susceptible to hydrogen embrittlement, giving delayed failure in hydrogen-containing environments. Recent studies (1,2,3,4) have shown that slow crack growth occurs in high strength steels stressed in a hydrogen gas environment.

The purpose of this study is to measure crack velocities in high strength steels exposed to a common aqueous environment (3\% NaCl in double distilled water) and in several gaseous environments. Crack velocities are measured in hydrogen gas, and in deuterium gas. Other investigated gaseous species contain hydrogen in their molecular structures, and are NH\(_3\), H\(_2\)S, CH\(_4\), C\(_2\)H\(_2\), HCl, and HBr. Such gaseous species, upon dissociation, are potential sources of hydrogen. In addition, crack velocities are measured
in a molecular chlorine gas environment. The additions of \( \text{H}_2\text{S}, \text{O}_2, \) and \( \text{H}_2\text{O} \) to a hydrogen gas environment are studied, as relating to their effects on crack growth rates.

Fracture mechanics techniques are applied in the investigation in order to define the mechanical aspect of crack propagation.

As a result of the susceptibility to hydrogen embrittlement, two low alloy, high strength steels (D6AC and AISI 4335V) are chosen for the study.

Acoustic emission phenomena are studied in gaseous and aqueous environments in order to determine their relationship to the fracture process.

Specific emphasis is placed on the effects of material strength level, applied stress, and gas pressure on the rate of slow crack growth.
2.1 Introduction

The literature regarding the interaction of hydrogen and gases with metals (or alloys) is reviewed in eight areas:

1) Behavior of hydrogen in metals and alloys
2) Models for the hydrogen embrittlement mechanism
3) Slow crack growth of high strength steels in aqueous media containing hydrogen
4) Adsorption behavior of gases on metals
5) Hydrogen adsorption on iron or steel
6) Adsorption characteristics, on iron or steel, of other hydrogen-containing gas species
7) Permeation of gaseous hydrogen through iron or steel
8) Slow crack growth of high strength steels in gaseous media containing hydrogen

These areas of the literature present information regarding the interaction of hydrogen (or hydrogen-containing gases) with high strength steels, as
relating to crack propagation in gaseous or aqueous media.

The literature regarding acoustic emission phenomena is also surveyed with respect to its application to slow crack growth studies.

The principles of linear elastic fracture mechanics are reviewed to the extent that they define the stress intensity parameter (K) and apply to the measurement of crack velocities in steel.

2.2 Hydrogen in Metals and Alloys

2.2.1 Solubility behavior

The dissolution of atomic hydrogen into an iron lattice is expected, by ideal thermodynamics, to obey Sieverts' law. However, at ambient temperatures (25°C), ideal behavior is not observed. If the hydrogen source is the diatomic gas (H₂), the lattice solubility (by Sieverts' law) is:

\[ C_H = k P_{H_2}^{1/3} \]
where: \( C_H \) = solubility of hydrogen in the metal lattice
\( P_{H_2} \) = pressure of hydrogen gas
\( k \) = proportionality constant

However, it has been shown that, for the case of iron or steel, Sieverts' law is obeyed only at high temperatures (5, 6, 7). Ham and Rast (7), using hydrogen permeation data for iron, showed that the Sieverts' law coefficient at 200°C is 1.08, rather than \( \frac{1}{2} \) (ideal case). The work of Hill and Johnson (6) on hydrogen solubility has related the non-ideal behavior to the interaction of hydrogen with "traps" in iron.

The "trapping" concept was first introduced by Darken and Smith (8) in 1949, and was later applied to the interaction of hydrogen with dislocations in iron (9), as well as to the deviation of hydrogen gas from Sieverts' law behavior in iron at temperatures below 390°C (6). Coe and Moreton (10) have attributed the "trapping" effect in steels to carbide-matrix interfaces, at which hydrogen was believed to segregate.
Calculations by Oriani (11) of the energy difference between "trapped" and "non-trapped" hydrogen, using published solubility data, yield values of -6.0 to -8.7 kcal/mole H, with the reference state being "non-trapped" hydrogen.

2.2.2 Diffusion and permeation behavior

The diffusion coefficient of hydrogen in iron or steel has also been shown to exhibit non-ideal behavior at low temperatures. The apparent diffusivity of hydrogen in low alloy steel has been shown (10) to exhibit a much higher activation energy at low temperatures (below 150 - 300°C), and has also been attributed to "trapping" effects. Studies of hydrogen diffusivity in alpha iron below 200°C (12) have attributed the anomalously low values of the diffusion coefficient (at ambient temperatures) to the interaction of hydrogen with "traps" in iron. An increased temperature dependence of diffusivity at low temperatures, for both hydrogen and deuterium in steel, was observed by Frank, Lee, and Williams (13).
Kim and Loginow (14) studied hydrogen permeation rates through Ni-Cr-Mo steel (yield strength values of 95 to 150 ksi), using electrolytic charging techniques. A higher material strength level was found to result in a lower apparent diffusivity for hydrogen, with a larger apparent solubility. The diffusivity of hydrogen, over the range of strength levels studied, was found to decrease by a factor of 5. No significant effect of strength level on permeation rate (product of solubility and diffusivity) was observed.

Oriani (11) has related the lower apparent diffusivity in higher strength level material to a higher density of "trapping" sites for hydrogen in the structure.

The application of an elastic tensile stress has been shown to enhance the rate of hydrogen permeation through iron or steel. Studies of the permeation rate of hydrogen through Armco iron by Bockris et al (15) have shown an increase of permeation rate with an applied tensile stress. An increase of hydrogen
permeation rate with applied tensile stress was also observed by Beck et al. (16) for AISI 4340 steel (260 ksi strength level), and for Armco iron.

2.3 Hydrogen Embrittlement Theories

The presence of a small amount (<10 ppm) of hydrogen in a high strength steel is known to reduce the mechanical properties of the material. The interaction of hydrogen with the structure of the steel, however, has not been sufficiently explained by any single theory. Although none are sufficient, three hydrogen embrittlement theories are outstanding: (1) Zapffe and Sims "pressure" theory, (2) Troiano theory, and (3) Petch and Stables "surface energy" theory.

2.3.1 Theories and inadequacies

The Zapffe and Sims theory (17) proposes that atomic hydrogen in the lattice is precipitated, at interfaces or subgrains, as molecular hydrogen gas.
Hydrostatic pressures are generated, in excess of the yield strength of the material. The model offers such internal stresses as the explanation for the failure of hydrogen embrittled steels at low externally applied stresses. The original "pressure" theory has since been modified by Tetelman and Robertson (18,19) to suggest that the role of the precipitated hydrogen gas is to provide an additional internal pressure, thus lowering the required external stress for hydrogen-induced cracking.

There are two outstanding objections to the proposed "pressure" theory: (1) microscopically observable fissures or cracks in iron or steel are present only under conditions of severe embrittlement, and (2) internal pressures of hydrogen greater than one atmosphere are unlikely in the case of low pressure hydrogen test gas environments (less than one atmosphere pressure). The latter objection is based on published slow crack growth studies (2,4).

The Troiano model for hydrogen-metal interaction (20) proposes that electrons donated by the interstitial...
hydrogen atoms enter the partially filled d-band of the transition metals. The author suggests that increased "repulsive forces between the metallic cores" result in a decrease in the cohesive strength of the lattice. This is believed to occur in regions of high hydrostatic stress, suggested by Troiano as favored sites for hydrogen in the metallurgical structure. The model, however, assumes that there is localization of the donated electrons, which is a questionable approach with metals.

The "surface energy" theory of Petch and Stables (21) proposes that hydrogen gas adsorbs on the surface of a crack, lowering the surface energy, and thus the energy per unit crack extension required for delayed failure. The kinetics of crack growth are controlled by the rate of arrival of the adsorbing species. As suggested by Bastien (22), cracks formed by dislocations piled up against grain boundaries may serve as sites for hydrogen adsorption in the Petch and Stables model.

The deficiencies of the Petch and Stables model lie in: (1) the difficulty of experimentally
demonstrating the effect of a hydrogen gas environment on the surface energy of iron (or steel) at room temperature, and (2) the questionable significance of surface energy, with respect to the energy of plastic deformation, during the slow crack growth process in steels.

2.4 Stress Corrosion Cracking in Aqueous Media

High strength steels (yield strengths greater than 200 ksi) are notably susceptible to stress corrosion cracking in natural environments, such as neutral saline solutions. By the hydrogen ion discharge reaction in aqueous media \( \text{H}^+ + e^- = \text{H}^0 \), these environments can supply hydrogen as an embrittling species. Also, the detrimental effects of high material strength level and applied tensile stress on cracking in aqueous environments are similar to their effects on hydrogen embrittlement processes observed under static load conditions after the cathodic charging of steels with hydrogen. For these reasons, it is essential that the effects of
material and environmental variables on cracking in aqueous media be reviewed. The effects of solution pH, applied potential, temperature, material strength level, applied stress, grain size, and cathodic poison additions will be examined to characterize the cracking behavior of high strength steels in aqueous media. Reported fractography, observed after the failure of steels in such aqueous media, will also be reviewed.

2.4.1 Effect of material strength level

Strength level itself is, in general, a more significant factor with regard to stress corrosion cracking susceptibility than are other material parameters such as structure, composition, or heat treatment (23). Studies by Farrell and Quarrell (24) have shown that, after cathodic charging with hydrogen, the deleterious effect of a given hydrogen concentration (in an ultra-high-strength steel) on both the fracture ductility and the static fracture stress is also increased by a higher material strength level.
The work of Kim and Loginow (14) has shown, by electrolytic hydrogen permeation and delayed failure studies, that hydrogen exhibits a lower apparent diffusivity and a higher apparent solubility with increasing material strength level (Ni-Cr-Mo steel). The time to failure of tensile specimens, equally stressed in the same environment (with no applied potential), was found to decrease with increasing strength level of the steel. The hydrogen charging and delayed failure environment was an aqueous solution of 3% sodium chloride and 0.5% acetic acid, saturated with hydrogen sulfide. On the basis of the solubility and diffusion behavior of hydrogen in the material, the delayed failure by hydrogen embrittlement was attributed to "trapped" hydrogen in the material structure.

It is therefore seen that both the susceptibility to stress corrosion cracking and the effect of hydrogen on the failure of high strength steels are increased by a higher material strength level.
2.4.2 **Effect of applied stress or stress intensity**

The application of an external tensile stress accelerates the failure of high strength steels which have been either electrolytically charged with hydrogen or stressed in an aqueous environment. An increase of stress intensity, as defined by linear elastic fracture mechanics, also enhances the fracture process in steels exposed to aqueous media.

Van der Sluys (25), using a distilled water environment, showed that crack propagation in AISI 4340 steel (217 ksi yield strength) is accelerated by an increase of applied stress intensity. Additional studies by Landes (3) of cracking in AISI 4340 steel (distilled water environment) also showed an accelerating effect of increased stress intensity on crack growth kinetics.

Delayed failure times were studied by Hughes et al (26) for a low alloy high strength steel, statically loaded in 3% NaCl and 0.1N HCl aqueous environments. An increase of applied tensile stress was shown to
reduce the time to failure in both environments. The accelerating effect of applied tensile stress on cracking in aqueous media has been reviewed by others (27,28).

The effect of an externally applied tensile stress on the failure of hydrogen-charged steels has also been extensively reviewed (20,29,30). In the presence of sufficient hydrogen within the material, an increase of applied stress or stress intensity will accelerate failure.

The effect of stress on crack growth kinetics may well be related to the established effect (16) of stress in enhancing the rate of hydrogen permeation into high strength steels.

The interaction of hydrogen (in aqueous environments) with applied tensile stress has been explained by Tiller and Schrieffer (31) as resulting from the effect of stress on the distribution of electronic charge within the metal. The resulting change of electron density is proposed as the source of a more cathodic potential at regions of high elastic tensile stress.
Such a potential change is expected to favor the hydrogen ion discharge reaction at regions of high tensile stress on the metal surface.

2.4.3 Fractography of aqueous stress corrosion cracking

Crack propagation in high strength steels exposed to aqueous environments is found to occur primarily along prior austenite grain boundaries. The fractography of hydrogen embrittled steels (pre-charged with hydrogen) does not, in general, exhibit such an inter­granular fracture mode.

Using high strength AISI 4330M and AISI 4340 steels, Davis (32) showed that, in a 3% NaCl aqueous solution, fracture occurs along prior austenite grain boundaries. Cathodic or anodic polarization of the specimen showed no observable effect on the fracture mode. Cathodic charging in a 0.25N sodium sulfide solution showed a severe decrease in failure time, with no observable change in fractography.

A detailed fractographic study of AISI 4340 steel, fractured in a 3% NaCl solution, was conducted by Tiner
and Gilpin (33). Both intergranular and transgranular (quasi-cleavage and micro-void coalescence) fracture modes were observed, with intergranular fracture occurring in the early stage of crack growth.

Beachem (34) studied the fractography of 4300 series steels (yield strengths of 172 to 195 ksi) resulting from slow crack growth in a 3.5% NaCl solution. The fracture mode was either quasi-cleavage or intergranular at low stress intensity values. At higher stress intensity values (near catastrophic fracture), the fractography indicated failure by micro-void coalescence. The low stress intensity intergranular fracture was observed with the higher strength material.

Fracture along prior austenite grain boundaries was observed by Van der Sluys (25) in slow crack growth studies of AISI 4340 steel in a distilled water environment.

The fractography of hydrogen-charged ultra-high-strength steels was studied by Farrell et al (24), with quasi-cleavage being the predominant mode of fracture.

The comparison of fractography observed in aqueous cracking studies with that found in the delayed failure
of pre-charged steel is not conclusive with respect to the role of hydrogen in the failure process. Hydrogen entry is not a required step in the fracture process for pre-charged steel. However, for the cases of an external aqueous environment and an external hydrogen gas environment \((2,4)\), the fractography of high strength steels is primarily intergranular, along prior austenite grain boundaries.

The work of Beachem \((34)\) is significant in that it shows that the fractography observed in aqueous environments is a function of the applied stress intensity.

2.4.4 Effect of prior austenite grain size

Since the cracking of high strength steels in aqueous environments is predominantly intergranular, the effect of grain size on crack growth kinetics is significant.

Proctor and Paxton \((35)\) investigated the effect of prior austenite grain size in AISI 4340 steel (yield strengths of 240 to 270 ksi) on the susceptibility to
cracking in a 3½% sodium chloride solution. The investigated range of grain size was ASTM 7-12. Failure times were increased by a decrease in the prior austenite grain size.

The effect of grain size variation from ASTM 7 to ASTM 12 on the failure time, however, was less than a factor of 4.

2.4.5 Effect of temperature

In all reviewed studies, the crack growth rates for high strength steels in aqueous environments were found to increase with increasing temperature (above ambient). However, the effect of temperature on such crack growth kinetics for high strength steels in distilled water or sodium chloride solution is distinctly different from the temperature dependence of the hydrogen embrittlement process in pre-charged steels under static load conditions.

Van der Sluys (25) measured the activation energy for crack growth in AISI 4340 steel (yield strength of
217 ksi) in a distilled water environment. For the investigated temperature range of 27°C to 192°C, the resulting activation energy values were +8.1 to +8.7 kcal/g-mole.

Temperature dependence measurements were made by Landes (3), using AISI 4340 steel in a distilled water environment. The measured activation energies ranged from +8 ± 1 kcal/mole to +12 ± 1.5 kcal/mole. The investigated temperature range was 10°C to 75°C.

In both investigations (3, 25), the activation energy was found to decrease with increasing applied stress intensity.

Johnson and Willner (36) investigated the effect of temperature on the crack growth rate in H-11 steel (yield strength of 230 ksi) exposed to a distilled water environment at temperatures of 1°C to 84°C. The activation energy was found to be approximately 9 kcal/mole.

Studies by Farrell et al (24) clearly show that the degree of embrittlement (as measured by reduction of area at fracture) for ultra-high-strength steel
specimens, electrolytically charged with hydrogen, exhibits a maximum with respect to temperature. This is shown in Figure 1. It is seen that the effect of hydrogen on ductility decreases with increasing temperature (above 0°C). However, the reviewed literature on aqueous environment cracking shows, in all cases, an increase of crack growth rate with temperature over the same temperature range. It is significant to recall that the entry of hydrogen into the steel is not a required process (nor a possible rate-controlling process) in the static fatigue failure of pre-charged high strength steels.

Recent studies by Townsend (37) of the delayed failure of cold-drawn AISI 1075 steel wire (ultimate tensile strength of 244 ksi) have indicated a minimum time to failure at approximately 25°C. The wire specimens (un-notched) were 0.080" in diameter, and the test environment was 3 wt% NaCl + 0.5 wt% acetic acid in distilled water (saturated with H₂S).

It is important to note that delayed failure and sub-critical crack growth involve different processes,
Figure 1 - Effect Of Test Temperature On Ductility Of Hydrogen-Charged Steel Tensile Specimens [From Farrell et al (24)]
and thus the effect of temperature on the final result (time to failure or crack velocity) may give a different indication of the process controlling fracture. This is particularly true for delayed failure testing of smooth (un-notched) specimens in aqueous media, in which crack initiation may constitute the primary process (with respect to time requirement) in the failure of the specimen.

2.4.6 Effects of solution pH and applied potential

In view of the susceptibility of high strength steels to both hydrogen embrittlement and aqueous stress corrosion cracking, the effects of electrochemical variables on both the hydrogen entry process and aqueous cracking are of critical concern. The significant question with regard to electrochemistry is whether a variation of solution chemistry or electrode potential, at a location external to the tip of a stress corrosion crack, will alter the electrochemical conditions within the crack tip region itself.
In this way, factors affecting the hydrogen reduction reaction may be examined with respect to a hydrogen-induced fracture process at the crack tip.

Phelps (23) has proposed that the applied potential may enhance or retard cracking, depending on the failure mechanism. Failure by "active path corrosion", or anodic dissolution, is favored by anodic polarization. Failure by hydrogen embrittlement is favored by cathodic polarization, which increases the driving force for the hydrogen ion discharge reaction.

Tiner and Gilpin (33) have shown that the failure of AISI 4340 steel in a 3% sodium chloride solution was accelerated by either a low solution pH or cathodic polarization. However, the specimens were un-notched tensile coupons, and time to failure was the measured parameter. Crack initiation time, by the time to failure technique, cannot be distinguished from the time of sub-critical flaw propagation. Observations by the authors (33), however, indicated that failure time was primarily the time required for crack initiation. On
this basis, the detrimental effects of low solution pH and cathodic polarization on failure are not related to their effects on the slow crack growth process, but rather to crack initiation.

Studies by Hughes et al (26) of failure times for a low alloy high strength steel were conducted, using 3% NaCl and 0.1N HCl aqueous solutions. The results showed several orders of magnitude shorter failure times in the HCl environment. The specimens were of the un-notched cantilever beam geometry. The authors (26) suggest that the failure time was primarily the time required for crack initiation. In addition, the authors (26) concluded that a hydrogen mechanism could not be discounted, as a contributing cause of failure, in the neutral sodium chloride solution.

From the reviewed studies (26, 33), the effects of low solution pH and an applied cathodic potential on the kinetics of slow crack growth are not defined.

Potential and pH measurements at a growing stress
corrosion crack tip in AISI 4340 steel by Brown et al (38), and in a variety of high strength steels by Brown (39), have shown that the pH and electrochemical potential are independent of the conditions in the bulk solution. In addition, the electrochemical conditions at the crack tip are thermodynamically favorable for hydrogen ion reduction.

The significant result of the reviewed studies is that the measured effects of pH and potential on the failure of high strength steels in aqueous media have not discounted the proposition (32, 40) that hydrogen embrittlement and stress corrosion cracking (in neutral or acidic aqueous media) are inter-related processes.

2.4.7 Effect of cathodic poison additions on aqueous stress corrosion cracking

The relationship of aqueous stress corrosion cracking to hydrogen embrittlement has not, for the case of high strength steels, been fully demonstrated by the enhancement of both processes by cathodic poison additions.
Many elements of groups V and VI of the Periodic Table are known to be catalytic promoters with regard to the electrolytic charging of hydrogen into iron or steel. Such poisons are sulfur, arsenic, selenium, antimony, phosphorus, and tellurium (41). Lead, tin, and bismuth are also effective, but to a lesser degree.

Using low strength (unhardened) steel sheet of 0.002" thickness, Radhakrishnan and Shrier (42) studied the rate of hydrogen permeation as a function of poison additions to a 0.1N H₂SO₄ hydrogen charging solution. Enhanced permeation kinetics (during charging) were found with additions of As (as sodium arsenite), Se (as selenous acid), and tellurium. In the absence of an applied potential, sulfur compounds (sodium sulfide, carbon disulfide, and thiourea) were found to enhance permeation kinetics. Additions of As, Se, or Te were less than 100μg/ml. The order of effectiveness, as a poison, was found to be:

As > Se > Te > S > Pb > Bi
Studies by Wood (43) have shown that the delayed failure stress of SAE 4130 steel (tensile strength of 229-234 ksi) is reduced by an increase of hydrogen content (introduced electrolytically). In addition, the presence of a poison (P in CS₂) in the charging bath (4% H₂SO₄) was found to increase the hydrogen content of the steel by an order of magnitude. Similar results were found by Farrell (44) for a low alloy high strength steel (tensile strength of 270 ksi) in a 4% H₂SO₄ solution poisoned with arsenic metal.

Under environmental conditions which permit hydrogen-induced crack propagation (39), the presence of cathodic poisons would be expected to enhance the kinetics of stress corrosion cracking.

The additions of colloidal sulfur, H₂S (0.11M), NaHS (0.1M), NaHSO₄, NaHSO₃, and H₂SO₃ (0.1M) to a distilled water environment by Tirman et al (45) resulted in detrimental effects on the failure time of AISI 4340 steel tensile specimens. Foil specimens (0.002" thick) ranged in tensile strength from 220 ksi
to 264 ksi. In these environments, however, the failure times were decreased by less than a factor of 4, as compared with the case of pure distilled water.

In studying the failure stress for two low alloy high strength steels in a 0.5% acetic acid solution, Treseder and Swanson (46) showed that the fracture stress for delayed failure is greatly reduced by H₂S additions to the solution. The accelerating effect of H₂S additions, to a 5% NaCl solution, on the aqueous cracking of low alloy high strength steels has also been shown by Hudgins et al (47). In the latter study (47), the failure times were reduced by up to three orders of magnitude, and decreased with increasing sulfide concentration in the solution (≤ 3000 ppm). In the reported studies (43,44,45,46), specimens were unnotched and crack velocities were not measured.

The most severe effect of H₂S additions on the time to failure (47) was observed in the presence of a notch (notched ring specimens).
Townsend (37) has measured hydrogen permeation rates through normalized AISI 1040 steel (0.026" thick evacuated cylinder) from an external aqueous media (3 wt% NaCl + 0.5 wt% acetic acid + H₂S). Permeation rate measurements from 4°C to 82°C resulted in an Arrhenius activation energy for the process of +8.4 kcal/mole, comparing well with that observed during the slow crack growth of high strength steels in aqueous media (3,25,36).

Although specific crack velocity measurements have not been made, the effect of the investigated cathodic poisons on the failure of high strength steels in aqueous media is consistent with their known accelerating effect on processes requiring the entry of hydrogen into iron or steel.

2.5 Adsorption Behavior of Gases on Metals

The mechanical properties of metals are affected by the test environment. Since gaseous environments are the most common, it is of major importance to understand
the surface interaction of gases and metals, as affecting the mechanical behavior of the latter. The explanation of the effect of gaseous media requires an understanding of the activity at gas-metal interfaces with regard to atomic interaction and bonding.

2.5.1 Physical and chemical adsorption

Gases are known to adsorb on metals. There are two types of adsorption: (1) physical adsorption, and (2) chemical adsorption. Physical adsorption, in general, involves a larger inter-atomic bond distance, a lower heat of adsorption, and a negligible activation energy (48). It is the result of van der Waal's bonding, or weak physical forces such as those associated with the condensation of a liquid (49). Chemical adsorption, however, involves small bond distances and large bond energies - comparable to those of chemical compound formation (48). Chemical adsorption also involves the sharing or transfer of electrons (50), not required for physical adsorption.
It is reasonable to view chemical adsorption (chemisorption) as an intermediate step between the existence of two distinct phases and the bulk absorption of the gas into the metal (when thermodynamically feasible). The effect of a gas environment on the mechanical behavior of a metal (or alloy) is thus far more reasonable, on the basis of bonding energies, if it is viewed as the result of chemical, rather than physical, adsorption.

2.5.2 Chemical adsorption isotherms

The heat of chemical adsorption is the energy difference between the desorbed and chemically adsorbed species, and is therefore a measure of the affinity of a gas for adsorbing on a particular metal. In addition to heats of chemisorption, it is of importance to know the relationships between the quantity of adsorbed gas and the thermodynamic variables of the system (pressure, temperature, etc.). The isothermal coverage of a metal surface by a chemically adsorbed gas is related to the
gas pressure by one of three basic adsorption isotherms: (1) the Langmuir isotherm, (2) the Temkin isotherm, or (3) the Freundlich isotherm. The application of any such isotherm to a particular gas-metal system is the result of the effect of surface coverage on the heat of chemisorption. The equilibrium isotherms are obeyed for the case of less than one monolayer coverage by the gas, and are reviewed for the simplest case - that of a non-dissociating gaseous species.

The Langmuir isotherm applies to the simplest type of behavior. The basic assumptions (51) are: (1) the heat of adsorption is independent of surface coverage, (2) each molecule (or atom) striking an adsorbed gas species will immediately desorb, giving a maximum of one monolayer coverage, and (3) the adsorbent surface is uniform, with respect to binding energy for gas adatoms. Under equilibrium conditions, the isothermal coverage (52) is:

$$\theta = \frac{bP}{1 + bP}$$
where: $\theta = \text{fractional coverage of surface sites by adsorbed species}$

$b = \text{constant}$

$P = \text{gas pressure}$

The Freundlich isotherm applies to chemical adsorption in which the heat of adsorption falls logarithmically with increasing surface coverage. The effect of surface coverage may result from surface heterogeneity (with respect to metal-gas binding energy), or from a mutual repulsion of adsorbed species. The resulting form of the equilibrium isotherm is given by Trapnell (53) as:

$$\theta = (a_0 P)^{\frac{RT}{q_m}} (n_0 q_m)$$

where: $\theta = \text{fractional coverage of surface sites by adsorbed species}$

$n_0, a_0, q_m = \text{constants}$

$T = \text{temperature}$

$R = \text{gas constant}$

$P = \text{gas pressure}$
The Temkin isotherm is obeyed in chemical adsorption processes wherein the heat of adsorption falls linearly with increasing surface coverage. As with the Freundlich isotherm, the decrease of the heat of adsorption may result from surface heterogeneity (with respect to binding energy) or from mutual repulsion of adsorbed species. The isothermal dependence of surface coverage on pressure (54) is of the form:

\[ \theta = \frac{RT}{q_0\alpha} \ln (A_0P) \]

where: \( \theta \) = fractional coverage of surface sites by adsorbed species

\( R \) = gas constant

\( T \) = temperature

\( \alpha \) = constant

\( q_0 \) = initial heat of chemical adsorption \((\theta = 0)\)

\( A_0 \) = constant (function of \( q_0 \), \( T \))

\( P \) = gas pressure
Although the Langmuir and Temkin isotherm equations do not reflect such behavior, the coverage of a metal surface by a chemically adsorbed species is a strong function of both temperature and the heat of adsorption.

It is of great significance to recall that chemisorption is an activated process, and thus equilibrium conditions are not necessarily a valid assumption. In addition, not all surface sites are active in the chemisorption process, and the fractional coverage pertains to those which are active.

Surface coverage as a function of temperature, at constant gas pressure, is discussed elsewhere (55).

More extensive discussions of gas chemisorption on metals may be found in the literature (56, 57, 58).

2.5.3 Chemical adsorption behavior of hydrogen gas

Since chemical adsorption is a pre-requisite to the entry of hydrogen into metals and alloys, it is essential to know how chemisorption is affected by the
nature of the metal or alloy (chemical, electronic, etc.).

The heat of hydrogen chemisorption, being a measure of the gas-metal bond strength, will be reviewed for different metals. In addition, the kinetic and equilibrium isotherm behavior will be presented for the case of iron, since this adsorbent is the chemical species of interest in the current study. The latter information will define the effects of pressure and temperature on the chemical adsorption process for the hydrogen \( (H_2) \) - iron system.

2.5.3.1 Chemical adsorption of hydrogen on metals

Dissociative hydrogen chemisorption is found to occur only on alkaline earth or transition metals (59). Chemical adsorption occurs on Ti, Zr, Nb, Ta, Cr, Mo, Fe, W, Co, Ni, Rh, Pd, Pt, and Ba (60). Covalent bonding is believed to occur between hydrogen and the surface atoms of metals having unfilled electronic d-orbitals (59).
For transition metals, however, Bond (61) has shown an inverse trend between the initial heat of hydrogen chemisorption and the number of electrons in the atomic d-shell (as indicated by the group number in the periodic table transition series). Therefore, the heat of chemisorption cannot be directly related to the quantity of electrons in the metallic d-orbitals. An inverse trend does exist between the initial heat of chemisorption and the efficiency of the transition metal (relative to platinum) in hydrogen atom recombination kinetics. In both effects, the change in the heat of chemisorption is approximately a factor of 2.

The significance of the observed electronic effects is an apparent trend between the strength of the metal-hydrogen bond and (1) the immobility of the adatom species, as retarding recombination kinetics, and (2) the requirement for a minimum number of bonding d-orbital electrons in the metal. Further discussion by Bond (61) of transition metal-hydrogen interaction
shows that the number of d-orbital electrons is not related to catalytic and chemisorption activity, but that the bonding of metal surface atoms is significant. The role of d-orbital electrons in hydrogen chemisorption has been suggested by others (59,62).

2.5.3.2 Heat of adsorption of hydrogen on metals

The process of chemical adsorption, in which new atomic bonds are formed, has been approached (from the energy standpoint) by considering the prior binding energies of the gas and metal. The significant assumptions are: (1) that the surface is homogeneous with regard to binding energy, (2) that a single stoichiometry exists for the adsorbed species, and (3) that the thermodynamic energy values obtained for two homogeneous and separate phases may be applied at an interface between the phases.

The Pauling heat of formation for a metal-hydrogen bond \((2M + H_2 = 2MH)\) is given by Trapnell and
Hayward (63) as:

$$E (M-H) = \frac{1}{2} E (M-M) + E (H-H) + 23.06 (X_M - X_H)^2$$

where: $E (M-H) = \text{energy of metal-hydrogen bond}$

$E (M-M) = \text{energy of one metal-metal bond (estimated from heat of sublimation)}$

$X_M, X_H = \text{electronegativities of gas and metal species}$

$E (H-H) = \text{dissociation energy of hydrogen molecule}$

The initial heat of hydrogen chemical adsorption ($q_o$) is given by Trapnell and Hayward (63) as:

$$q_o = 2 E (M-H) - E (H-H)$$

where: $q_o = \text{initial heat of adsorption, per mole of H}_2$

Using 2.1 as the value for the electronegativity of hydrogen, and relating that of the metal to the work function, Stevenson (64) calculated the initial heats
of adsorption for hydrogen on Ta, W, Cr, Mo, Ni, Fe, Mn, Rh, and Pd. These values are presented in Trapnell and Hayward (63), and are compared to the experimentally determined values (ranging from 17 to 45 kcal/mole H₂).

Agreement between predicted and observed heats of adsorption is good for all transition metals except chromium and manganese. The inclusion of electro-negativities in bond energy calculations indicates a partially ionic character for the metal-hydrogen bond (63). Surface potential measurements during hydrogen chemisorption on transition metals (65) also indicate that a surface dipole is formed, with the hydrogen adatom as the negatively charged species.

The bond energy model shows good agreement for the case of tungsten, which is an obvious exception to the d-orbital theory of metallic bonding (66). Therefore, d-orbital electrons do not fully explain the bonding in hydrogen chemisorption. In addition, the model has only been successfully applied to the
simplest case ($H_2$). The data for $O_2$ and $N_2$ chemisorption (67) show errors of up to a factor of 2 between the predicted and observed heats of adsorption. As suggested by Bond (61), the independence of binding energy (with respect to surface coverage) is the exception, rather than the rule.

On the basis of the Pauling and Stevenson calculations, and the discussion by Bond (61), the chemical adsorption of hydrogen on transition metals is indeed related to the electronic structure of the metal, but not simply to the d-orbital characteristics of the individual metal atoms.

2.5.3.3 Chemical adsorption of hydrogen on iron

Since the slow crack growth in high strength steel exposed to molecular $H_2$ gas constitutes a major portion of the current investigation, the process of hydrogen chemisorption on iron is of obvious importance.

Porter and Tompkins (68) measured the kinetics of hydrogen chemisorption on spectroscopically pure iron
at temperatures of 78°K to 140°K. The rate-controlling process was found to be monatomic, and characteristic of a surface having a non-uniform binding energy for gas adatoms. The chemisorption process involved the initial dissociation of hydrogen molecules on lattice sites of low gas-metal binding energy, with the rate-controlling process being the subsequent surface migration of hydrogen adatoms to sites of higher binding energy. The rate equation is given (68) as:

\[
d\theta/dt = \alpha \frac{1}{\theta} (1-\theta) e^{-E_m/RT}
\]

where: \( \theta \) = fraction of sites (of a single binding energy) covered by adatoms

\( P_{H_2} \) = hydrogen gas pressure

\( \alpha \) = temperature dependent constant (containing the condensation coefficient)

\( R \) = gas constant

\( T \) = temperature

\( t \) = time

\( E_m \) = activation energy for surface migration of hydrogen adatoms
The variable \((a)\) is not fully defined in the rate equation. The activation energy \((E_m)\) ranged from 3 to 6 kcal/mole \(H\), and increased with surface coverage. Typical test pressures in the investigation ranged from \(10^{-2}\) to \(10^{-4}\) torr \(H_2\). Above \(140^\circ K\), the rate of hydrogen adsorption was immeasurably rapid.

Additional work by Porter and Tompkins (69) showed that hydrogen chemisorption on iron obeys the Temkin isotherm. Test temperatures in this study were \(148^\circ K\) to \(306^\circ K\), with hydrogen pressures of \(10^{-5}\) to 1.0 torr. The initial heat of chemisorption was found to be 20 kcal/mole.

The prior work (68, 69) on chemisorption for the hydrogen-iron system shows three significant results: (1) above \(140^\circ K\), and at pressures of greater than 1.0 torr, equilibrium conditions are established, (2) hydrogen dissociates during chemisorption, and (3) the Temkin isotherm is obeyed. Therefore, the description of hydrogen chemisorption on iron by a
dissociative Temkin isotherm, at > 1.0 torr pressure and > 140°K, is valid.

Such conditions of pressure and temperature apply to the current investigation. The surface coverage of iron by chemisorbed hydrogen is therefore defined, as a function of pressure, temperature, and the heat of chemisorption, by the dissociative Temkin isotherm. The isotherm, described for the hydrogen-iron system by Sawicki (4), is of the form:

\[
\theta = \frac{a_0 P_{H_2} e^{-\Delta H_0 (1-\alpha \theta)/RT} \frac{1}{\sqrt{1 + \left[a_0 P_{H_2} e^{-\Delta H_0 (1-\alpha \theta)/RT}\right]}}}{1 + \left[a_0 P_{H_2} e^{-\Delta H_0 (1-\alpha \theta)/RT}\right]}
\]

where:
- \( a_0 \) = constant
- \( \Delta H_0 \) = initial heat of adsorption of hydrogen on iron (i.e., \( \theta = 0 \))
- \( \alpha \) = constant
- \( R \) = gas constant
- \( T \) = temperature
- \( P_{H_2} \) = hydrogen gas pressure
- \( \theta \) = fraction of surface sites covered by hydrogen adatoms
2.5.4 Chemical adsorption behavior of other gases on iron

The capacity for hydrogen to chemisorb on iron is not unique. Since other hydrogen-containing gases are of interest in this study, their chemical adsorption behavior is of great significance.

Roberts and Ross (70) have measured the kinetics of H$_2$S chemisorption on iron. The authors have shown that hydrogen sulfide dissociates and chemically adsorbs on iron at temperatures down to -80°C. Simultaneous desorption of molecular hydrogen, from -80°C to +32°C, was found to occur during H$_2$S chemisorption. Dissociative chemisorption of H$_2$S on nickel and tungsten has also been observed at temperatures down to -80°C (71).

Other hydrogen-containing gases, in general, exhibit more complex chemical adsorption behavior. A survey of gas chemisorption by Trapnell and Hayward (60) has shown that very rapid or non-activated chemisorption on iron (at room temperature) occurs with O$_2$,
CO, C₂H₂, C₂H₄, and H₂. The chemical adsorption processes for CH₄, C₂H₆, and N₂ on iron, however, are activated. Wright et al. (72) found that very little or no chemisorption of CH₄ or C₂H₆ occurs on iron below 70°C. Ammonia (NH₃) is believed to undergo dissociative adsorption on iron at 21°C at a rate comparable to that of hydrogen (60,73). It has also been suggested (73) that NH₃ chemisorption on iron results in the formation, and desorption, of molecular hydrogen gas.

Trapnell (59) has compared several gases, with regard to their affinity to chemisorb on any metal surface. The order of affinities is:

\[ O₂ > C₂H₂ > C₂H₄ > CO > H₂ > N₂ \]

If a metal chemisorbs one of the gases, it will also chemisorb any other gas higher in the affinity scale. With respect to iron, the comparison is qualitative, in that adsorption rates and heats of adsorption are
not given (59). All of the above gases were chemically adsorbed, at room temperature, by one group of metals: Ca, Ba, Fe, W, Ta, Mo, Ti, and Zr. Nickel and palladium differ from this most active group of metals only by the absence of nitrogen chemisorption at room temperature.

The generation of molecular hydrogen during the chemisorption of a hydrogen-containing gaseous species is, in an obvious sense, related to the capacity of the metal substrate to release hydrogen from the molecule by strong bonding with the non-hydrogen species. As is indicated by the temperature range over which the dissociative chemisorption process occurs, the kinetics of hydrogen desorption, resulting from CH₄ or C₂H₆ adsorption on iron (72), is notably slower than for the case of H₂S (70). The controlling process in the case of C-containing species is believed to be the breakdown of hydrocarbon radicals on the iron surface (72). An estimate of Fe-C, Fe-N, and Fe-S bond strengths can be obtained from the standard free energies for
the formation of FeS, Fe₂N, and Fe₃C. The values are -23.32 kcal/mole (74), +7.46 kcal/mole (75), and +4.78 kcal/mole (75), respectively. Similarly, the estimates of single bond energies of hydrogen to carbon, sulfur, and nitrogen are found to be 98.8, 81.1, and 93.4 kcal/mole (76), respectively. The thermodynamic values given above suggest that such bonding of the non-hydrogen species to iron is more favorable for the case of sulfur, than for carbon or nitrogen.

The significance of the chemical adsorption behavior of hydrogen-containing gases on iron lies in the expected capacity of each gas to produce atomic hydrogen (the embrittling species of interest) by dissociation on an iron (or steel) surface at room temperature. For the species H₂S, CH₄, NH₃, and C₂H₂, the capacity to dissociate, and produce hydrogen (and in the presence of a hydrogen entry catalyst) is clearly greater for the case of H₂S.

No chemical adsorption information was found in the literature for HCl, HBr, or Cl₂ gases.
2.6 Permeation of Gaseous Hydrogen Through Iron or Steel

The hydrogen embrittlement of iron or steel is attributed to the presence of hydrogen in the metal structure. Also, slow crack growth in a high strength steel exposed to molecular hydrogen gas has recently been attributed (4) to the permeation of hydrogen into the steel. For these reasons, the process of gaseous hydrogen permeation through iron (or steel) is examined. Particular emphasis is placed on the effects of temperature, pressure, and the addition of catalytic poisons on permeation kinetics.

2.6.1 Kinetics of gaseous hydrogen permeation

2.6.1.1 Effects of temperature and pressure

Studies by Smithells and Ransley (77) of hydrogen permeation through iron, at temperatures down to 686°K and pressures of $9 \times 10^{-2}$ to 140 torr, showed that the rate of permeation is of the form:
D = k \sqrt{P} \left[ \frac{(aP)}{(1 + aP)} \right]

where:  
- D = permeation rate, cc H₂ at N.T.P. per sec. per cm² area per mm thickness
- k = 1.63 \times 10⁻³
- P = hydrogen pressure (torr)
- a = 0.75

The units of k must be sec-torr⁻¹/₂ to conform to the units of the permeation rate, D. The form of the equation was attributed (??) to Langmuir adsorption behavior of hydrogen at the entry surface. Only a certain fraction (θ) of surface sites were believed to be covered by molecular H₂ gas, allowing entry of hydrogen into the iron. This fractional coverage was the proposed origin of the Langmuir adsorption term in the rate expression.

By Sieverts' law, the solubility of hydrogen at the entry surface exhibits a P_H₂^{1/3} dependence, giving the same ideal behavior for the permeation process (assuming zero hydrogen concentration at the exit.
surface). Such behavior was observed by the authors (77) at either high pressures or high temperatures. At low temperatures, the deviation is described by the rate equation given above. The data of Borelius and Lindblom (78) exhibit the same low temperature behavior. The results are shown in Figure 2. It is important to note that the deviation from ideal \( P_{H_2}^{3/2} \) behavior occurs at higher pressures, as the temperature is lowered.

The significance of the permeation studies (77,78) is that it is not unreasonable to expect a dependence of hydrogen permeation rate on hydrogen pressure to the three-halves power at room temperature and near-atmospheric pressure. This would occur if \( aP \ll 1 \). The constant \( (a) \) was found to decrease with decreasing temperature (78).

The hydrogen-iron system was later shown by Porter and Tompkins (68,69) to obey the dissociative Temkin isotherm. Therefore the Langmuir isotherm does not explain the observed (77,78) pressure dependence of hydrogen permeation. However, the observed pressure
Figure 2 - Effect Of Pressure On the Permeation Rate, $D \times 10^5$ (cc H$_2$ per cm$^2$ per mm thickness per second) Of Hydrogen Through Iron [From Borelius et al (78)]
dependence is consistent with the low temperature "trapping" effects discussed earlier (Section 2.2.1).

2.6.1.2 Effect of oxygen additions

Smithells and Ransley (77) observed an inhibiting effect of low pressure oxygen gas on the kinetics of hydrogen permeation through iron. Required oxygen levels (to inhibit or halt permeation) were not investigated. Fricke et al (79) found that the embrittlement of low alloy steel in 150 atmospheres of H₂ gas did not occur in the presence of 100 ppm O₂ gas. Permeation rates of hydrogen through low carbon and Cr-Ni steels were found by Eschbach et al (80) to be lower for the case of an oxidized entry surface, although neither the required oxygen levels nor the quantitative effect on permeation kinetics were reported (80).

2.6.1.3 Effect of hydrogen sulfide additions

Hydrogen sulfide, when added to partially
dissociated hydrogen gas, has been shown to enhance the rate of hydrogen permeation through iron by approximately one order of magnitude. The required H₂S levels are less than 0.4 volume percent.

Early studies by Palczewska et al (81) of hydrogen permeation through Armco iron foil have shown that additions of 0.1 to 0.4% H₂S to partially dissociated hydrogen gas enhance the rate of permeation. Quantitative effects on the rate of permeation were not determined in this study. Further studies by Palczewska (82) showed that H₂S additions (0.01 to 0.4 mole percent) to partially dissociated hydrogen gas increased the permeation rate of hydrogen through Armco iron foil (at 29°C) by approximately one order of magnitude. This effect is shown in Figure 3. For the range of H₂S concentrations investigated, the presence of H₂S in the H + H₂ gas phase was found to reduce the activation energy for permeation from +6.7 to +4.6 kcal/mole. Activation energy measurements were obtained from data over the temperature range of 0°C to 50°C.
Figure 3 - Effect of $\text{H}_2\text{S}$ Additions On the Permeation Rate, $P$, Of Hydrogen Through Iron [From Palczewska (82)]
Palczewska (82) described the adsorption of H₂S by assuming that the Langmuir isotherm was obeyed, giving:

\[ \theta_{\text{H}_2\text{S}} = \left( \frac{b P_{\text{H}_2\text{S}}}{1 + b P_{\text{H}_2\text{S}}} \right) \]

where: \( \theta_{\text{H}_2\text{S}} = \) fractional coverage of active surface sites by hydrogen sulfide

\( P_{\text{H}_2\text{S}} = \) hydrogen sulfide pressure

\( b = \) constant

If hydrogen permeation kinetics are proportional to H₂S coverage (\( \theta_{\text{H}_2\text{S}} \)), then \( \dot{P} \) (permeation rate as measured by the pressure rise in an evacuated volume) obeys the following relationship:

\[ \dot{P} \propto \left( \frac{b P_{\text{H}_2\text{S}}}{1 + b P_{\text{H}_2\text{S}}} \right) \]

Dividing by \( P_{\text{H}_2\text{S}} \), and taking the reciprocal, gives:

\[ \left( \frac{P_{\text{H}_2\text{S}}}{\dot{P}} \right) \propto \left( \frac{1}{b} + P_{\text{H}_2\text{S}} \right) \]
As seen in Figure 4, the experimental data (82) were found to agree with the above relationship. The effect of H₂S as a promoter is attributed to a change in the state of hydrogen chemisorbed on the iron (82).

The observed dependence of permeation rate on the non-dissociative Langmuir isotherm suggests that the enhanced entry of hydrogen is due to surface coverage by: (1) undissociated H₂S, or (2) the species of sulfur, which is present as a single atom in the H₂S molecule. Molecular hydrogen from the hydrogen sulfide is not the controlling species, since it dissociates and obeys a dissociative Temkin isotherm (68,69). The consideration of molecular H₂S as the catalytic species on the iron surface is not reasonable, since the work of Roberts and Ross (70) shows that H₂S undergoes rapid dissociative chemisorption on iron, with a consequent desorption of hydrogen gas from -80°C to +32°C. Therefore the enhanced hydrogen permeation through iron in the presence of H₂S is far more reasonable when attributed
Figure 4 - Relationship Between the Rate Of Hydrogen Permeation Through Iron (P) And the Pressure Of H₂S In the Gaseous Hydrogen (Molecular And Atomic) Source [From Palczewska (82)]
to the fractional coverage of active surface sites by adsorbed sulfur.

The role of H$_2$S (or sulfur) in enhancing hydrogen permeation may be the result of a reduction in the kinetics of recombination for hydrogen adatoms on the iron surface. Studies by Palczewska (83) have shown that H$_2$S or AsH$_3$ additions (approximately 0.2%) to partially dissociated hydrogen gas retard atomic hydrogen recombination kinetics on silver, nickel, and iron foils. The equilibrium between dissociated and molecular hydrogen may be written as:

$$2 \text{H}(g) = \text{H}_2(g)$$

At 298°K, the recombination reaction is highly exothermic, with an enthalpy change of -104.2 kcal/mole H$_2$ (83). The reduction in kinetics of the steady state recombination reaction at high temperatures would produce a reduction in temperature for a heterogeneous catalyst, such as a metal foil. Such temperature measurements showed that additions of 0.2 vol% H$_2$S (or AsH$_3$) to partially dissociated hydrogen gas reduced,
on a qualitative basis, the hydrogen recombination kinetics on an iron film at 472 - 505°C. The effect, as measured by the decrease in temperature, was far greater with H₂S (ΔT = -127°C, as opposed to ΔT = -31°C for AsH₃).

The literature on hydrogen gas permeation through iron shows that: (1) oxygen retards, or halts, hydrogen permeation, (2) hydrogen sulfide additions increase the permeation kinetics, and (3) the pressure dependence of permeation is a function of both temperature and pressure.

The significant point with regard to slow crack growth in molecular hydrogen gas is that oxygen and hydrogen sulfide additions should clearly have opposite effects on a cracking process requiring hydrogen entry.

2.6.1.4 Isotope effects in gas phase permeation

Wood (43) has measured the permeation rates for hydrogen and deuterium in SAE 4130 steel (approximate strength level of 230 ksi), using electrolytic
charging and vacuum extraction techniques. At 35°C, the permeation rate of hydrogen was found to be 2.3 times greater than that of deuterium.

Hydrogen and deuterium permeation rate measurements were made by Frank et al. (84) for SAE 1010 steel, using electrolytic charging and vacuum extraction techniques. At 26°C, the permeation rate of hydrogen was found to be 4.5 to 4.8 times greater than that of deuterium.

The relative permeation rates for hydrogen and deuterium in steel are thus seen to differ by at least a factor of 2, in contrast with the ideal diffusivity ratio of 1.414 (84).

2.7 Slow Crack Growth in Gaseous Media Containing Hydrogen

2.7.1 Introduction

It has been shown in several investigations (1,2,3,4) that slow crack growth occurs in high strength steels exposed to dry, molecular hydrogen gas environ-
ments. Recent studies (89,90) have shown crack velocities in a high strength steel exposed to hydrogen sulfide gas (1 atmosphere pressure) to be several orders of magnitude greater than those observed in 1 atmosphere of molecular hydrogen gas. The review presented here describes:

(1) Phenomenological studies of slow crack growth in molecular hydrogen gas environments

(2) The Williams and Nelson (2) chemisorption model for slow crack growth in molecular hydrogen gas

(3) The Sawicki (4) permeation model for slow crack growth in molecular hydrogen gas

(4) Slow crack growth studies in a hydrogen sulfide gas environment

2.7.2 Phenomenological studies of slow crack growth in hydrogen gas environments

Johnson and Hancock (1) showed that slow crack growth will occur in a martensitic high strength steel exposed to dry H₂ gas, and at velocities greater than those observed in a pure water environment. Crack
growth was studied using H-11 steel, hardened to a yield strength of 230 ksi, in one atmosphere of dry hydrogen gas.

An addition of 0.7 vol% oxygen to the hydrogen gas was found to halt crack growth. Of equal significance is the fact that crack growth rates in humidified hydrogen were the same as those observed in liquid water or humidified argon. The effect of oxygen was attributed to a preferential chemisorption, with respect to hydrogen, at the crack tip. This is in agreement with the order of gas affinities in chemisorption given by Trapnell (59), and discussed earlier in Section 2.5.4.

The work of Johnson and Hancock (1) clearly shows that the addition of oxygen can halt the cracking process in hydrogen gas, and that the addition of water vapor can reduce the crack growth kinetics. The effect of applied stress intensity on crack velocity was not investigated.

Landes (3) investigated the slow crack growth behavior of AISI 4340 steel (ultimate tensile strength -
302 ksi) in both triple distilled water and one atmosphere of dry H$_2$ gas, both at 24°C. The effect of applied stress intensity on crack velocity is shown, for both environments, in Figure 5.

The results of the Landes study (3) show three outstanding effects: (1) crack velocities are approximately one order of magnitude higher in hydrogen gas (1 atmosphere) than in distilled water, (2) the stress intensity value required for observable cracking in distilled water is notably lower than that required for cracking in hydrogen gas, and (3) the crack velocity shows both weak and strong dependence on applied stress intensity, in either the hydrogen gas or the distilled water environment. The crack velocity increases more rapidly with increasing applied stress intensity at low values of the stress intensity parameter.

The effect of hydrogen pressure on crack velocity was not investigated by Landes (3), and no mechanism was proposed for cracking in the hydrogen gas environment.
Figure 5 - Effect Of Stress Intensity On Crack Velocity For AISI 4340 Steel In Distilled Water and Hydrogen Gas (1 Atm.) Environments [From Landes (3)]
2.7.3 Chemisorption model for slow crack growth in molecular hydrogen gas

2.7.3.1 Investigation and proposed model

The Williams and Nelson (2) chemisorption model resulted from the first attempt to define the rate-controlling process in the cracking of high strength steel in a molecular hydrogen gas environment. The authors (2) obtained crack velocity values, using crack opening displacement measurements for pre-fatigue cracked constant stress intensity specimens of a double cantilever beam geometry. The test material used in the study was fully-hardened SAE 4130 steel (exact strength level not given).

Crack velocity measurements were obtained at temperatures of -80°C to +80°C, and at hydrogen pressures of 76 to 760 torr. Crack velocity, at constant hydrogen pressure and stress intensity, is shown as a function of temperature in Figure 6. Maximum crack growth kinetics are seen in Figure 6 to occur at near-ambient temperature (20°C). The Arrhenius-type
Figure 6 - Effect Of Temperature On Slow Crack Growth Kinetics For SAE 4130 Steel Exposed To Dry Hydrogen Gas Environment [From Williams and Nelson (2)]
activation energies for crack growth rate were found to be +3.9 kcal/mole (0°C to -80°C) and -5.5 kcal/mole (40°C to 80°C). At low temperatures (-60°C), crack velocity exhibited a hydrogen pressure dependence of $P_{H_2}^{1/3}$. At 23°C, a $P_{H_2}^{1.0}$ hydrogen pressure dependence was observed. At high temperature (60°C), the dependence of crack velocity on hydrogen pressure was $P_{H_2}^{3/2}$.

The rate-controlling process was described by the Porter and Tompkins (68) expression for activated dissociative chemical adsorption of hydrogen on the steel surface. The original adsorption rate equation, as described in Section 2.5.3.3, is:

$$d\theta/dt = \alpha P_{H_2}^{1/3} (1-\theta) e^{-E_m(\theta)/RT}$$

where: $\theta = \text{fraction of sites (of a single binding energy) covered by hydrogen adatoms}$

$P_{H_2} = \text{hydrogen gas pressure}$

$\alpha = \text{temperature dependent constant (containing the condensation coefficient)}$
The authors (2) assumed that the crack velocity, at a constant fractional surface coverage (required for crack growth) is proportional to the adsorption rate:

\[ (\frac{da}{dt})_\theta = k_1 \ (d\theta/dt) \]

where: \( (\frac{da}{dt})_\theta \) = crack velocity, at constant surface coverage

\( (d\theta/dt) \) = adsorption rate, as defined by the time rate of change of fractional surface coverage

\( k_1 \) = constant, independent of temperature or pressure
The variable (α) in the Porter and Tompkins (68) equation is defined, by Williams and Nelson (2), as:

$$\alpha = k_2 \frac{S \sqrt{T_0}}{\sigma_0 + S \sqrt{T_0}}$$

where: $k_2 = \text{constant, independent of temperature or pressure}$

$S = \text{sticking coefficient of hydrogen molecule on the surface}$

$\mathcal{J} = \text{number of molecules impinging on a 1 cm}^2 \text{ surface area per second}$

$\mathcal{T} = \text{mean residence time of undissociated hydrogen molecule on surface}$

$\sigma_0 = \text{total number of sites at which physical adsorption can occur}$

The variable ($\mathcal{J}$) is defined (2) as:

$$\mathcal{J} = k_3 P_{H_2} T^{-\frac{1}{2}}$$

where: $k_3 = \text{constant}$

$P_{H_2} = \text{hydrogen gas pressure}$

$T = \text{temperature}$
The mean residence time of the physically adsorbed hydrogen molecule (τ) is of the form:

\[ \tau = \tau_0 e^{\Delta H/RT} \]

where: \( \tau_0 = \) constant

\( \Delta H = \) heat of physical adsorption of hydrogen molecule

\( R = \) gas constant

\( T = \) temperature

The combination of terms, to give the final rate equation, yields:

\[ \frac{da}{dt} = k_1 k_2 \frac{S k_3 P_{H_2} T^{-1/2} \tau_0 e^{\Delta H/RT}}{\sigma_0 + S k_3 P_{H_2} T^{-1/2} \tau_0 e^{\Delta H/RT}} \]

\( \sigma_0 \) times \( P_{H_2}^{1/2} e^{-E_m/RT} \)

In the limit of low temperatures:

\[ S k_3 P_{H_2} T^{-1/2} \tau_0 e^{\Delta H/RT} >> \sigma_0 \]

\[ \frac{da}{dt} = k_1 k_2 P_{H_2}^{1/2} e^{-E_m/RT} \]
In the limit of high temperatures:

\[
\sigma_0 > S k_3 P_{H_2} T^{-\frac{1}{2}} \tau_0 e^{\Delta H/RT}
\]

and \((da/dt)_0 = k_1 k_2 k_3 (1/\sigma_0) S \tau_0 P_{H_2}^{3/2} T^{-\frac{1}{3}} \times e^{(\Delta H - E_m)/RT}\)

The investigation (2) showed that the predicted pressure dependencies were obeyed. Values for \(\Delta H\) of -9.5 kcal/g-atom H, and for \(E_m\) of +3.9 kcal/g-atom H, were obtained from the original Porter and Tompkins study (68). Such energy values explained the observed activation energies (-5.5 and +3.9 kcal/mole) in the crack velocity study.

The significant conclusion of the Williams and Nelson study was that crack growth kinetics are controlled by a surface process (chemisorption), and that hydrogen entry into (or permeation through) the steel is not the rate-controlling process.
2.7.3.2 Criticisms of the Williams and Nelson model

Although the Porter and Tompkins (68) adsorption rate equation may, indeed, be expanded to explain the observed dependence of crack velocity on hydrogen pressure and temperature, several serious objections to the Williams and Nelson treatment have been presented.

Sawicki (4) and Bond (85) have reported that the heat of physical adsorption, for non-dissociated molecular $H_2$ ($\Delta H$), cannot exceed 2 kcal/mole. Williams and Nelson (2) interpret the term ($\alpha$) as applying to such non-dissociated hydrogen, but apply (in activation energy calculations) a $\Delta H$ value (-9.5 kcal/g-atom H) associated with dissociative chemisorption. This criticism is reviewed by Sawicki (4).

A significant criticism arises from the fact that, in the Porter and Tompkins study, the variable ($\alpha$) in the rate equation is not clearly defined. However, Williams and Nelson interpret ($\alpha$) as the fractional surface coverage by physically adsorbed molecular
hydrogen, obeying a Langmuir isotherm. Such an interpretation is not justified. In addition, Porter and Tompkins (68) report that the hydrogen adsorption rate on iron is immeasurably rapid above 140°K, with the original hydrogen pressures being $10^{-4}$ to $10^{-2}$ torr. Therefore, the Williams and Nelson study was conducted in a range of temperatures and pressures quite different than that of the original kinetic study (68).

The use of a Langmuir coverage term, for ($\alpha$), in the adsorption rate equation, and in prior $H_2$ gas permeation rate equations (77), is discussed by Johnson and Sawicki (86). In the case of early permeation studies (77), the rate of hydrogen permeation is found, experimentally, to be of the form:

$$P = k \frac{P_{H_2}^{\frac{1}{3}}}{(a \frac{P_{H_2}}{1 + a P_{H_2}})}$$

where:  
- $a$ = adsorption parameter, dependent upon temperature
- $k$ = permeation system parameter, containing hydrogen diffusivity, membrane thickness, etc.
By the Johnson and Sawicki (86) treatment, the thermodynamic relationships between gaseous H₂, adsorbed H or H₂, and dissolved H, may be written as:

\[
\begin{align*}
H_2(g) &= H_2(ads) & K_1 &= a_{H_2(ads)}/P_{H_2} \\
H_2(ads) &= 2H(ads) & K_2 &= C_{H(ads)}/a_{H_2(ads)} \\
2H(ads) &= 2H(sol'n) & K_3 &= C_{H(sol'n)}/C_{H(ads)}^2
\end{align*}
\]

The overall equilibrium reaction is:

\[
H_2(g) = 2H(sol'n) & K_4 = C_{H(sol'n)}/P_{H_2}
\]

If a negligible hydrogen pressure exists at the exit surface of the permeation membrane, the rate of atomic hydrogen permeation is proportional to the dissolved hydrogen (atomic) at the input surface, giving:

\[ F = k' P_{H_2}^{\frac{1}{2}} \]

where:  \( k' \) = permeation system parameter, such as \( k \)

\( P_{H_2} = \) hydrogen gas pressure
Thus, by thermodynamics, an ideal Sieverts' law behavior is expected. Johnson and Sawicki (86) concluded that the "ad hoc" insertion of a Langmuir "effective area" term is unjustified in permeation rate equations, as it is in the Williams and Nelson model (2).

A detailed development of hydrogen adsorption kinetics by Oriani (87) has shown direct disagreement with the pressure and temperature dependencies of the Williams and Nelson study (2). If \( n^n \) designates the number of adatoms (per unit area) on final adsorption sites, and \( n' \) designates the number of admolecules on initial adsorption sites, the rate of dissociative chemisorption (as described by the Porter and Tompkins model) may be written as:

\[
\frac{dn^n}{dt} = 2k_m n' \sigma^n (1-\theta)
\]

where:
- \( k_m \) = specific rate constant
- \( \theta \) = fraction of final adsorption sites that are occupied
- \( \sigma^n \) = number of final adsorption sites (per unit area)
- 2 = factor resulting from each admolecule giving 2 adatoms
If \( (\alpha) \) represents the fractional coverage of initial adsorption sites, and \( (\sigma_0) \) is the total number of initial adsorption sites per unit area, then \( n' = \alpha \sigma_0 \). Assuming Langmuir behavior of \( H_2 \) admolecules, we can write:

\[
K = a_{H_2} / P_{H_2} = \frac{1}{k} \left[ \frac{\alpha}{1-\alpha} \right]
\]

where: \( a_{H_2} = \) thermodynamic activity of adsorbed \( H_2 \)

\( k = \) constant, relating to activity reference state

\( P_{H_2} = \) hydrogen gas pressure

The equilibrium constant \( K \), for initial molecular hydrogen adsorption, is expressed as:

\[
K = g \, e^{-\Delta H / RT}
\]

where: \( g = \) thermodynamic term, involving entropy of adsorption

\( \Delta H = \) enthalpy change for molecular hydrogen adsorption

\( R = \) gas constant

\( T = \) temperature
The fractional coverage of initial adsorption sites ($\alpha$) may thus be expressed as:

$$\alpha = \frac{k g P_{H_2} e^{-\Delta H/RT}}{1 + k g P_{H_2} e^{-\Delta H/RT}}$$

Since $\theta = n''/n''$, the rate of adsorption is:

$$\frac{d\theta}{dt} = 2 k_m \sigma_o \alpha (1-\theta)$$

$$= 2 \sigma_o (1-\theta) k_m \frac{k g P_{H_2} e^{-\Delta H/RT}}{1 + k g P_{H_2} e^{-\Delta H/RT}}$$

The specific rate constant ($k_m$) is defined as:

$$k_m = \nu_m e^{-E_m/RT}$$

where: $\nu_m = \text{constant}$

$E_m = \text{activation energy for surface migration of hydrogen adatoms}$

The resulting adsorption rate equation is given by Oriani (87) as:

$$\frac{d\theta}{dt} = 2 \sigma_o k g \nu_m (1-\theta) \frac{P_{H_2} e^{-\Delta H/RT}}{1 + k g P_{H_2} e^{-\Delta H/RT}} e^{-E_m/RT}$$
In the limit of low temperatures:

\[ k g P_{H_2} e^{-\Delta H/RT} >> 1 \]

and \( d\theta/dt \propto P_{H_2}^0 \)

In the limit of high temperatures:

\[ k g P_{H_2} e^{-\Delta H/RT} << 1 \]

and \( d\theta/dt \propto P_{H_2}^1 \)

The significance of the Oriani development (87) is that, with basic thermodynamic relationships and the same assumptions as in the Williams and Nelson investigation (2), the predicted dependence of adsorption rate on hydrogen pressure is shown to be quite different than the observed pressure dependence of crack velocity (2).

Further studies by Williams et al (88) showed crack velocities in SAE 4130 steel (ultimate tensile strength of 220 ksi) to be several orders of magnitude greater in partially dissociated hydrogen gas.
Molecular hydrogen gas, at 8 X 10^-3 torr pressure, was partially dissociated (< 1%) by a heated tungsten filament (2000°C). Crack growth rates, at a stress intensity of 41 ksi-in^(1/2), were approximately three orders of magnitude greater than those predicted by the chemisorption model (2) for a molecular hydrogen pressure of 8 X 10^-3 torr.

The Arrhenius-type activation energy, based on crack velocity measurements from -42°C to +164°C, was +6.8 kcal/mole. On the basis of activation energy measurements for hydrogen permeation (+8.4 kcal/mole), and dissolution (+6.5 kcal/mole), the authors concluded that the rate-controlling process for cracking in partially dissociated hydrogen gas was neither activated hydrogen chemisorption nor hydrogen permeation, but rather the transport of hydrogen to just below the first atomic layer of metal atoms at the crack tip.
2.7.4 Permeation model for slow crack growth in molecular hydrogen gas

2.7.4.1 Investigation and proposed model

The Sawicki permeation model (4) defines crack growth kinetics in a molecular H₂ gas environment as resulting from the rate-controlling process of hydrogen permeation into the steel. The proposed model, based on a hydrogen dissolution and bulk transport process, clearly differs from the surface-controlled chemisorption model of Williams and Nelson (2).

The critical issue in dry H₂ cracking is the question of whether hydrogen enters the steel, and interacts with the structure to give delayed failure, or whether the role of hydrogen is to affect the surface properties of the steel, thus allowing sub-critical crack growth. The Sawicki model is thus consistent with the bulk transport-controlled hydrogen embrittlement processes proposed by Troiano (20) and others. The Williams and Nelson model is consistent with the surface-related processes proposed by Petch
and Stables (21).

Using pre-fatigue cracked H-11 steel specimens of the WOL (wedge-opening-loading) geometry, Sawicki (4) measured crack velocity as a function of hydrogen pressure, temperature, and applied stress intensity. The yield strength of the H-11 steel was 230 ksi. The addition of 0.4 vol% oxygen to the hydrogen prevented cracking between -28°C and +100°C. Additions of up to 0.3 vol% oxygen did not halt the cracking process, but increased the critical stress intensity at which cracking was observed. The required stress intensity was approximately 23 ksi-in\(^{\frac{1}{2}}\) in the presence of 0.3 vol% oxygen, and 15 ksi-in\(^{\frac{1}{2}}\) in the absence of oxygen additions.

Figure 7 shows crack velocity as a function of stress intensity at test temperatures of -28°C to +71°C. The investigation of crack velocity as a function of temperature (-28°C to +71°C) revealed that maximum crack growth kinetics occurred at approximately 24°C. The temperature dependence of crack velocity
Figure 7 - Effect Of Stress Intensity On Crack Velocity For H-11 Steel In Hydrogen Gas Environment At Various Test Temperatures [From Sawicki (4)]
showed the same maximum, at applied stress intensity values of \(25 \text{ ksi-in}^{1/2}\) to \(32.5 \text{ ksi-in}^{1/2}\).

Sawicki (4) also measured the dependence of crack velocity on hydrogen pressure. Figure 8 shows the resulting pressure dependencies at 27°C, 47°C, and 80°C. At a stress intensity of 29 ksi-in^{1/2}, the pressure dependence of crack velocity was \(P_{H_2}^{1}\) at 27°C or 47°C. At 80°C (and the same value of stress intensity), crack velocity exhibited a \(P_{H_2}^{3/2}\) dependence on hydrogen pressure.

The Sawicki investigation resulted in two significant experimental observations: (1) regions of strong and weak dependence of crack velocity on applied stress intensity occur between 2°C and 45°C, and (2) the observed fracture mode was predominantly intergranular at low stress intensities, with increasing amounts of ductile tearing as the stress intensity is increased. The first observation is significant in that it agrees with the behavior observed by Landes (3) in both hydrogen gas and distilled water environments. The second observation is important in that only inter-
Figure 8 - Effect Of Test Temperature On the Pressure Dependence Of Crack Velocity For H-11 Steel Specimens In Hydrogen Gas [From Sawicki (4)]
granular fracture modes (along prior austenite grain boundaries) had been previously reported (2, 88) for the slow crack growth process in hydrogen gas. Beachem (34), however, has shown that the fractography of high strength steels is a function of applied stress intensity in aqueous environments, with exclusively intergranular fracture occurring at low stress intensity values.

The proposed Sawicki model is consistent, in that all terms in the kinetic equation pertain to atomic hydrogen (diffusing species), with no "effective area" terms relating to a physically adsorbed molecular hydrogen precursor. The proposed rate-controlling process is the permeation of atomic hydrogen into steel, and to a region of embrittlement $10^{-4}$ to $10^{-3}$ cm ahead of the crack tip. The rate of permeation is given as:

$$ P' = C_H \cdot D_H $$

where: $D_H = \text{hydrogen diffusivity}$

$$(\text{cm}^2/\text{sec})$$

$C_H = \text{hydrogen concentration at entry surface (unitless, if defined as atom fraction)}$
\[ P' = \text{hydrogen permeation rate} \]
\[ (\text{cm}^2/\text{sec or cm}^3 \text{ per cm thickness per second}) \]

The model proposes that hydrogen entry can only occur at those surface sites covered by hydrogen adatoms, resulting from the dissociative chemisorption of molecular hydrogen. The fraction of total sites which are covered is \( \theta \), and the true permeation rate \( P \) is then \( P' \theta \). By thermodynamics, the equilibrium concentration of hydrogen at the entry surface is related to gas pressure by:

\[ k = \frac{C_H}{(P_{H_2})^n} \]

where: \( k = \text{equilibrium constant} \)
\( C_H = \text{hydrogen concentration, as previously defined} \)
\( n = \text{empirical exponent, being } \frac{1}{2} \text{ for the case of ideal Sieverts' law behavior} \)

The final permeation rate is given by:

\[ P = k P_{H_2}^n D_H' \theta \]
The fractional surface coverage ($\theta$) is then defined by the dissociative Temkin isotherm as:

$$\theta = \frac{[a_o \ P_{H_2} \ e^{-\Delta H_0 (1-\alpha \theta)/RT}]^{1/2}}{1 + [a_o \ P_{H_2} \ e^{-\Delta H_0 (1-\alpha \theta)/RT}]^{1/2}}$$

where: $a_o = \text{constant}$

$\Delta H_0 = \text{initial heat of adsorption of hydrogen on steel}$

(i.e. $\theta = 0$)

$\alpha = \text{constant}$

$R = \text{gas constant}$

$T = \text{temperature (absolute)}$

The diffusion coefficient is expanded as:

$$D = D_0 \ e^{-E_D/RT}$$

where: $D_0 = \text{temperature independent constant}$

$E_D = \text{activation energy for diffusion}$

The equilibrium constant ($k$) is also modified to include the effects of stress and temperature on hydrogen solubility, giving:
\[ k = k_0 \exp \left[ \frac{\Delta H_S - (\sigma_1 + \sigma_2 + \sigma_3) V/3}{RT} \right] \]

where:  \( \sigma_1, \sigma_2, \sigma_3 = \) principal stresses

\( \bar{V} = \) partial molar volume of hydrogen in steel

\( \Delta H_S = \) heat of solution of hydrogen in steel

\( k_0 = \) constant

The resulting permeation rate equation is:

\[ P = k_0 D_0 P_{H_2}^n \frac{[a_o P_{H_2} e^{-\Delta H_o (1-\alpha\theta)/RT}]^1}{1 + [a_o P_{H_2} e^{-\Delta H_o (1-\alpha\theta)/RT}]^1} \]

times \exp \left[ \frac{\Delta H_S - (\sigma_1 + \sigma_2 + \sigma_3)V/3}{RT} \right]

In the limit of low temperatures:

\[ [a_o P_{H_2} e^{-\Delta H_o (1-\alpha\theta)/RT}]^1 \gg 1 \]

and \( P \propto P_{H_2}^n \)

In the limit of high temperatures:

\[ [a_o P_{H_2} e^{-\Delta H_o (1-\alpha\theta)/RT}]^1 \ll 1 \]

and \( P \propto P_{H_2}^{n+\frac{1}{2}} \)
As stated in the earlier review (Section 2.2.1), Sieverts' law is not obeyed by hydrogen in steel at temperatures below 200°C. Therefore the coefficient \((n)\) is not \(\frac{1}{2}\), but may be 1.08 (?) or greater. The expected pressure dependencies for hydrogen permeation rate (and permeation-controlled crack velocity, \(da/dt\)) are thus:

At low temperatures: \(P \alpha P_{H_2}^{1.08}\)

At high temperatures: \(P \alpha P_{H_2}^{1.58}\)

Although the predicted pressure dependencies were observed in the Sawicki study, the temperature dependence of crack velocity (at constant hydrogen pressure and stress intensity) did not agree with the predictions from the permeation rate equation. The Arrhenius-type activation energy for crack growth rate at low temperatures (-28°C to +26°C) was \(+2.15 \pm 0.4\) kcal/mole. At high temperatures (+26°C to +99°C), the activation energy was \(-3.4 \pm 0.4\) kcal/mole.
2.7.4.2 Criticisms of the Sawicki model

The Williams and Nelson model has been extensively reviewed in the literature (4,86,87). The Sawicki model, however, has not been reviewed in the published literature. Therefore, it is of major importance to examine the permeation model in detail.

Several shortcomings of the Sawicki investigation are evident. The dependence of crack velocity on stress intensity, shown in Figure 7, is presented as a series of curves. The actual data points are not given, resulting in a question as to the statistical significance of the curves. In addition, the fractographs presented in the Sawicki work (4) do not include information regarding the test temperature or applied stress intensity. In the study the author stated that fractography is a function of the applied stress intensity.

It is also of critical significance that the region of strong dependence of crack velocity on stress intensity (Region I) and that of weak dependence (Region II) were not investigated with regard to the
isothermal pressure dependence of crack velocity in each region. The pressure dependence data (Figure 8) is obtained at a stress intensity value (29 ksi-in\(^{1/2}\)) which lies in Region I at high temperatures (71°C) and in Region II at low temperatures (26°C).

With regard to the hydrogen pressure dependence of crack velocity, the author concludes that the low temperature pressure dependence of the Williams and Nelson study, \(P_{H_2}^{1/2}\), was not observed. The low temperature Williams and Nelson study was conducted at -60°C. However, the lowest temperature for reported pressure dependence data in the Sawicki study was 27°C. Therefore, the conclusion by Sawicki regarding low temperature pressure dependence is not justified.

The validity of the high and low temperature extrapolations for the permeation rate equation is also of great significance in the Sawicki study. In terms of absolute temperature, the pressure dependence transition occurred with a temperature increase of 10% (47°C to 80°C). Since the proposed model suggests that the pressure dependence transition results from
the effect of test temperature on the Temkin isotherm expression in the permeation rate equation, this hypothesis must be examined. The limiting conditions are:

Low or Ambient Temperature
\[ a_o P_{H_2} e^{-\Delta H_o(1-\alpha\theta)/RT} \frac{1}{2} > 1 \]

High Temperature
\[ a_o P_{H_2} e^{-\Delta H_o(1-\alpha\theta)/RT} \frac{1}{2} < 1 \]

In order to test these assumptions, an acceptable value for \( a_o \) must be obtained. Using the Porter and Tompkins coverage data (69), and the dissociative Temkin isotherm, we find:

For:
\[ \theta = 0.75 \]
\[ P_{H_2} = 0.10 \text{ torr} \]
\[ \Delta H = -12 \text{ kcal/mole H}_2 \]
\[ T = 300^\circ\text{K} \]

\[ 0.75 = \frac{\left[ a_o (10^{-1}) e^{12,000/600} \right]^{1/2}}{1 + \left[ a_o (10^{-1}) e^{12,000/600} \right]^{1/2}} \]

and \[ a_o = 1.8 \times 10^{-7} \text{ torr}^{-1} \]

The previous adsorption data at 10^{-1} torr (69) shows a heat of adsorption \( [\Delta H \text{ or } \Delta H_o(1-\alpha\theta)] \) of
approximately -12 kcal/mole, and therefore this pressure value was used in the Temkin isotherm equation. Based on the calculated value of \((a_o)\) and a typical Sawicki test pressure of 400 torr \(H_2\), we find:

For:

\[ P_{H_2} = 400 \text{ torr} \]
\[ \theta = 0.8 \]
\[ T = 300^\circ K \]

At \(\theta = 0.5\), the value is \(4 \times 10^6\). A heat of chemisorption of -11 kcal/mole was used by Sawicki in an attempt to explain activation energy data, and is in agreement with the heat of adsorption used in the above calculations. For this heat of adsorption, the fractional surface coverage is approximately 0.75, and consequently:

\[
[a_o \ P_{H_2} \ e^{-\Delta H_o(1-\alpha \theta)/RT}]^{\frac{1}{2}} > 1
\]

Therefore, the ambient (or low) temperature assumption in the Sawicki model is correct. However, the change in pressure dependence \((P_{H_2}^{1/2} \text{ to } P_{H_2}^{3/2})\)
is observed on increasing the test temperature from 47°C to 80°C. For the same hydrogen pressure and surface coverage (hence, heat of adsorption), such a temperature change reduces the term on the left by less than a factor of 3. Thus, temperature alone cannot explain the reversal of the inequality, and the increased pressure dependence of crack velocity observed at high temperature.

Although pressure and temperature effects are not fully explained by the Sawicki model, the permeation mechanism does offer an explanation for the observed (3,4) enhancement of crack growth kinetics by increased stress (or stress intensity) in hydrogen gas environments.

2.7.5 Slow crack growth studies in hydrogen sulfide gas environments

Recent studies by McIntyre et al (89,90) have shown that crack velocities in high strength steel stressed in pure hydrogen sulfide gas (one atmosphere pressure) are
at least two orders of magnitude greater than those observed in a pure hydrogen gas environment (one atmosphere pressure). The results are significant from the standpoint that H₂S constitutes a major environmental species in the petroleum industry, giving delayed failure of high strength steels at stress levels of 15% of the ultimate tensile strength (37). However, the recent investigation (89) has been the first reported study of slow crack growth of high strength steels in a pure hydrogen sulfide gaseous environment.

Crack growth rates were measured by the investigators (89) using pre-cracked CKS-type specimens and electrical resistance monitoring techniques. The test material was a 4Ni-1Cr high strength steel (0.2% proof stress of 196 ksi). Figure 9 shows the dependence of crack velocity on applied stress intensity for hydrogen and hydrogen sulfide gaseous environments, and for a sodium chloride (aqueous) solution. The sodium chloride solution consisted of 3.5% NaCl in de-ionized water.
Figure 9 - Effect Of Stress Intensity On Crack Velocity For 835 M30 Steel In H₂ Gas, H₂S Gas, and Aqueous Saline Environments [From McIntyre et al (89)]
Additional studies by McIntyre et al (90) showed direct disagreement with the results of prior hydrogen gas studies (2,4). Slow crack growth studies showed that crack velocities, in both molecular hydrogen gas and in hydrogen sulfide gas, were proportional to the square root of the gas pressure ($P_{H_2}^{1/2}$, $P_{H_2S}^{1/2}$). The investigated pressure range for hydrogen gas testing was 50 to 760 torr. Hydrogen sulfide pressure dependence data was obtained by testing in 1 to 760 torr $H_2S$ (91). The applied stress intensity values in these tests were not given.

The Arrhenius-type activation energies for cracking in $H_2$ gas (760 torr), $H_2S$ gas (760 torr), and sodium chloride solution were found to be +2.80 kcal/g-atom, +1.85 kcal/g-atom, and +8.50 kcal/g-atom, respectively. The temperature range of the testing was not given (90).

Crack growth in hydrogen gas was inhibited by the addition of 1% oxygen gas. However, no effect of oxygen additions was observed for crack growth in a hydrogen sulfide gas environment (90).
The significance of the studies by McIntyre et al (89,90) is that: (1) the \( P_{H_2}^{1/3} \) pressure dependence of crack velocity is lower than the dependence observed by either Sawicki (4) or Williams et al (2), except at cryogenic temperatures in the latter study, (2) the investigation of temperature did not indicate a decrease in crack velocity (in a \( H_2 \) gas environment) with increasing temperature, as observed by both Sawicki (4) and Williams et al (2), and (3) crack growth rates in hydrogen sulfide gas were found to be at least two orders of magnitude greater than those in molecular hydrogen gas.

The activation energy for crack growth kinetics in the aqueous environment (+8.5 kcal/g-atom) agrees with the observed activation energy for slow crack growth in a distilled water environment (3,25,36).

2.8 The Application of Fracture Mechanics to Stress Corrosion Cracking Studies

2.8.1 Introduction

Real engineering materials contain pre-existing
flaws and imperfections. The propagation of such flaws, under sufficient conditions of both stress and environment, constitutes stress corrosion cracking. The stress intensity parameter, as defined by the concepts of linear elastic fracture mechanics, uniquely defines the stress distribution associated with such a flaw in the presence of an applied tensile stress. It has been observed, in both gaseous and aqueous environment testing, that crack growth kinetics are uniquely defined by a particular value of stress intensity, for a given set of environmental conditions. Therefore, the concepts of fracture mechanics provide a stress intensity parameter which: (1) exhibits a reproducible effect on crack growth kinetics, and (2) defines the mechanical aspect of fracture in a stress corrosion environment.

2.8.2 History and principles of fracture mechanics

Linear elastic fracture mechanics is an application of the Griffith (92) concept, later modified by
Orowan (93) and Irwin (94) for application to engineering materials. The basic assumptions are: (1) that all stresses are elastic, and (2) that, under sufficient conditions of geometry, flaw size, and stress distribution, a section of material will undergo brittle, catastrophic fracture. The stress intensity parameter (K) uniquely defines the stress distribution in the volume of material surrounding a flaw (95). The stress intensity, as defined by Irwin, for a notch in the presence of an applied tensile stress, is given as:

\[ K = \lim_{\rho \to 0} \frac{1}{2} \sigma_m \left( \pi \rho \right)^{\frac{1}{2}} \]

where: \( \sigma_m \) = maximum stress at root of notch
\( \rho \) = notch-root radius

For an infinitely sharp crack in an infinitely wide plate, (K) may also be defined (96) as:

\[ K = \sigma \sqrt{\pi c} \]

where: \( \sigma \) = applied stress
\( c \) = crack length
2.8.3 Plasticity considerations

In real materials, the stress concentration due to the presence of a flaw (under load) results in plastic flow at the tip of the crack, although applied stresses are well below those required for general yielding of the section. By equating the stress perpendicular to the crack plane (and at a point in the plane of the crack) to the yield stress of the material, the equation relating normal stress, stress intensity, and distance from the crack tip (95) yields:

$$r_p = \frac{1}{2\pi} \left( \frac{K}{\sigma_{ys}} \right)^2$$

where:
- $r_p =$ radius of the plastic zone
- $K =$ stress intensity
- $\sigma_{ys} =$ tensile yield strength of material

Tetelman and McEvily (97) state that the elastic stress distribution about a "relaxed" crack, of length $(c)$, is the same as that observed about an "elastic" crack of length $(c + r_p)$. Therefore, plastic flow changes the elastic stress distribution, and thus the
apparent stress intensity value, associated with a crack in a material.

With regard to high strength steels and initial cracks on the order of \( \frac{1}{8} \)" long, the magnitude of the stress intensity change, due to plastic flow, is not significant. For values of \( K = 50 \text{ ksi-in}^{\frac{1}{2}} \) and \( \sigma_{ys} = 150 \text{ ksi} \), the value of \( r_p \) is 0.018". If the initial crack length (c) is 0.50", the value (c + r_p) equals 0.52". Recalling that \( K \propto c^{\frac{3}{2}} \), the resulting error in stress intensity, due to plastic deformation, is approximately 2%. Thus, high strength steels approach the ideal condition of an isotropic elastic medium.

Although plastic flow at the crack tip does not significantly affect the stress intensity parameter (for high strength steels), it is important to realize that plastic flow does occur. It is then essential that plasticity not be totally neglected in any model describing the fracture process in real materials.
2.8.4 State of stress

Of equal significance in fracture mechanics applications is the state of stress, i.e. plane stress or plane strain. As discussed by Johnson (98), specimens having thicknesses considerably greater than the plastic zone size \(2r_p\) result in "high constraint at the leading edge of the crack." The resulting condition is that of plane strain, giving lower fracture toughness values \(K_c\) than would be observed under plane stress conditions (infinitely thin specimen). The specimen thickness requirement for plane strain fracture toughness tests is given by Wei (99) as \(2.5 \left(\frac{K_{ic}}{\sigma_{ys}}\right)^2\).

In stress corrosion testing, the crack velocity is measured as a function of stress intensity. Therefore, with increasing applied stress intensity (constant specimen thickness and material strength level), the requirement (99) for plane strain conditions may no longer be fulfilled. This transition must be considered in the analysis of resulting test data.
2.8.5 Mode of deformation

The stress intensity parameter \( K \) is not uniquely defined by stress and flaw size, but is dependent upon the orientation of the applied external load with respect to the crack (mode of deformation). The local modes of deformation are discussed by Paris and Sih (100), as affecting the stress field at the tip of the crack.

With regard to all reported literature pertaining to stress corrosion cracking, and the present study, the displacement of the crack surfaces is directly apart (Mode I). The stress intensity is therefore designated as \( K_I \). This mode is also defined by Tetelman and EcEvily (101) as that which exists when the tensile stress is applied normal to the faces of the crack.

2.9 Acoustic Emission Techniques

2.9.1 Introduction

The existence of flaws in engineering materials, in
the presence of an applied tensile stress, results in stored elastic strain energy. By the propagation of such flaws or cracks in materials, strain energy is released. Either the formation of flaws in a stress field, or the incremental propagation of such flaws, results in detectable strain transients within the material. Since such energy releases often produce audible signals, the releases are termed acoustic emissions. By virtue of the fact that acoustic emissions are generated during slow crack growth processes, the associated technology has been applied in studies of stress corrosion cracking processes.

The significance of acoustic emission technology is that it provides high sensitivity with regard to both the detection and monitoring of either delayed failure or slow crack growth processes. It has not, however, been clearly established that acoustic emission phenomena are related, in a quantitative manner, to the chemical or mechanical aspects of the fracture process itself. At this time, a clearly defined model for the generation of such energy pulses
by a growing crack does not exist.

Acoustic emission technology has been successfully applied in determining: (1) the presence of flaws in materials, and (2) the existence of sub-critical flaw growth processes. However, a definite lack of information exists as to: (1) the quantitative effects of specimen geometry, loading system design, and detection system design on measured acoustic emission parameters, and (2) the characteristics of the actual strain transient (amplitude, energy, frequency content), as affected by the mechanical and chemical parameters of the slow crack growth (or delayed failure) process.

2.9.2 Acoustic emission detection techniques

Since acoustic emissions are very small elastic stress (hence, strain) waves, a detection device must transform strain into a parameter, such as electrical voltage, which is measureable by an external system. The piezoelectric effect permits the transformation of an applied stress (hence, strain) pulse into an
electrical pulse. Therefore, the most common detection techniques employ piezoelectric transducers. The resulting signal (output of the transducer) is then amplified, filtered to remove extraneous electrical noise, and either stored on magnetic tape (for subsequent analysis) or fed into an oscillograph or oscilloscope/counter system (for real-time base analysis). Although piezoelectric transducers are the most common, magnetostrictive transducers (using the Villari effect) may also be employed to detect acoustic emissions (102).

2.9.3 Measured parameters

Since acoustic emissions contain high frequency components (MHz range), the observed electrical signals are not necessarily related to the characteristics of the emission signal (strain transient) itself. This is the result of resonance phenomena (standing waves) within either the test specimen, the detector, or both. It is therefore important to realize that a single
stress wave, when striking the detecting transducer, is capable of producing one or more positive voltage pulses of sufficient magnitude to trigger an electronic counter. Each such positive voltage pulse is called an acoustic emission count, and is the most commonly measured parameter in acoustic emission studies. The observed damped sinusoidal signal (which triggers the counter with each positive voltage rise above the trigger voltage) is shown in Figure 10. In this case (trigger voltage \( V_t \)), 3 counts are recorded as a result of one emission. Therefore, acoustic emission counts are not necessarily acoustic emissions, per se. On this basis, the association of an acoustic emission count with a physical event in the fracture process may be misleading. The obtained value of counts is thus a function of the number of stress waves (events), the amplitude of each stress wave, and the physical characteristics of the test system as relating to the resonance phenomenon.

Acoustic emissions, per se, may also be measured in slow crack growth or delayed failure studies.
Figure 10 - Decaying Sinusoidal Voltage-Time Transient
Associated With Transducer Response To Acoustic Emission Signal [From Harris et al (103)]

\[ V = V_0 e^{-\beta \sin \lambda t} \]
However, increased sensitivity and ease of measurement have resulted in the preferred use of the acoustic emission counts technique.

2.9.4 Prior acoustic emission studies

2.9.4.1 Extent of literature survey

The present investigation of the acoustic emission phenomenon is directed toward its value in providing significant information regarding the slow crack growth process in high strength steels. Although acoustic emission techniques have been applied in studies of microplasticity (104, 105, 106) and flaw detection (107), the subject literature will be reviewed only to the extent that it pertains either to slow crack growth processes or to the determination of acoustic emission characteristics (energy, amplitude, frequency spectrum, etc.).
2.9.4.2 Gerberich and Hartbower investigation

Gerberich and Hartbower (108) have conducted the most extensive investigation of acoustic emission phenomena with respect to the slow crack growth process. Quenched and tempered D6AC steel specimens (pre-fatigue cracked, single-edge-notched geometry) were tested in a distilled water environment, or in air (after electrolytic pre-charging with hydrogen). Hydrogen-charged specimens were also tested in a distilled water environment. The ultimate tensile strength levels for the D6AC steel in the study were 190 and 230 ksi.

For each environment, the authors recorded acoustic emission signals using an instrumentation tape recorder, while measuring the associated crack velocity as a function of applied stress intensity. The experimental objectives were to: (1) quantitatively ascribe each acoustic emission with an incremental jump of the crack, and (2) correlate the kinetics of crack growth (hence,
acoustic emission rate) with a rate-controlling process.

The theoretical jump distance for the crack was obtained using a fracture criterion of Wells (109), such that the jump distance is given by:

\[ 1^* = \frac{2 V_c}{\pi e_f} \] (109)

and:

\[ 2 V_c = \frac{K^2}{m \sigma_{ys} E} \]

where:

- \( 2 V_c \) = theoretical crack tip displacement
- \( e_f \) = fracture strain
- \( m \) = constant
- \( \sigma_{ys} \) = yield strength
- \( E \) = Young's modulus

The predicted jump distance agreed (within a factor of 2) with that observed by experiment. The experimental value was obtained by dividing the observed crack extension by the number of acoustic emissions. The observed crack jump increments were
1.8 \times 10^{-3} \text{ to } 3.3 \times 10^{-3} \text{ inches.}

The slow crack growth in all environments was attributed to the rate-controlling process of hydrogen diffusion within the steel. The model proposed that hydrogen diffused to a region ahead of the crack tip (approximately a distance of $l^*$). When the hydrogen concentration in the advance region reached 10 ppm, the crack jumped a distance of $l^*$, and one acoustic emission occurred. Using assumed values for hydrogen diffusivity and bulk concentration in the steel, the authors obtained good agreement between the observed acoustic emission and crack growth rates, and the rates as predicted by hydrogen diffusion kinetics. The fractographic results showed both intergranular fracture and quasi-cleavage.

The Gerberich and Hartbower model is unique in that it attributes the acoustic emission to an incremental advance of the crack. The observation of acoustic emissions is related, in a quantitative manner, to the kinetics of slow crack growth in high
strength steel.

Although the results of the Gerberich and Hartbower study (108) are undoubtedly significant, it is important to emphasize the highly empirical nature of the study. Neither the hydrogen diffusivity nor the critical hydrogen concentration required for crack advancement was measured in the study. The predicted crack velocity (for hydrogen-induced cracking) is a function of hydrogen diffusivity to the first power, and of the critical hydrogen content to the third power. Since neither variable was determined experimentally, and since the diffusivity could admittedly be an order of magnitude lower (108), the model is highly empirical.

No information is given in the study (108) as to the required size of an emission to be counted as one crack increment. In addition to the emission magnitude criterion, the authors did not report any details of the fractography, except those observed on the final fracture surface. Baker (110) has shown that sub-
surface cracking at inclusions in D6AC steel can result in acoustic emission activity. Dunegan and Tetelman (111), in acoustic emission studies of slow crack growth in a hydrogen-charged AISI 4340 steel, have shown that "island cracks" may form well in advance of the main crack front. In addition to these fractographic considerations, Gerberich and Hartbower (108) did not discuss the existence of secondary cracks (normal to the final fracture surface) or crack bifurcation, as affecting the acoustic emission activity observed in their study.

2.9.4.3 Dunegan and Tetelman investigation

Acoustic emission counts have been related, in an empirical manner, to the applied stress intensity during the slow crack growth process. Dunegan and Tetelman (111) measured both crack extension and acoustic emission counts during the hydrogen-induced cracking of high strength steel. After electrolytic charging with
hydrogen, pre-fatigue cracked double cantilever beam specimens of AISI 4340 steel (yield strength of approximately 220 ksi) were tested at applied stress intensity values of 17.5 to 37.6 ksi-in$^{\frac{1}{2}}$. The number of acoustic emission counts per unit cracked area of the specimen were related to the applied stress intensity by:

$$\frac{dN}{dA} = 2.25 K^4$$

where: 
- $N =$ number of acoustic emission counts 
- $A =$ cracked area (in$^2$) 
- $K =$ stress intensity (ksi-in$^{\frac{1}{2}}$)

Figure 11 gives the experimental data for the above relationship. Crack growth rates were not measured in the study.

The importance of the Dunegan and Tetelman study is that the acoustic emission counts parameter is shown to be strongly increased by increasing applied stress intensity, which also accelerates slow crack growth processes in high strength steels.
Figure 11 - Effect Of Stress Intensity On Acoustic Counts Per Unit Cracked Area For Pre-Charged AISI 4340 Steel [From Dunegan et al (111)]
In examining the fourth power K-dependence of acoustic emission counts, it must be recalled that increased count activity may be the result of a greater number of acoustic emissions, a higher average acoustic emission amplitude, or both. Therefore, the sensitivity of acoustic emission counts to applied stress intensity does not fully define the effect of stress intensity on the elastic energy release process at the crack tip.

Although the counts technique has been applied to the slow crack growth process by Dunegan and Tetelman (111), the experimental data in Figure 11 show several inconsistencies. The authors state that no acoustic emission counts (or crack growth) was observed at a K value of 7.0 ksi-in$^{1/2}$. However, the counts/area equation predicts $5.4 \times 10^3$ counts/in$^2$. The data in Figure 11 indicate that this value of counts/in$^2$ is measureable. Also, the insertion of a typical K value into the "fitted equation" of Figure 11 gives a counts/area value one order of magnitude greater than the value
in Figure 11. By using the actual acoustic emission count and cracked area values, on which Figure 11 was based, the counts/area value (for a given stress intensity) is three orders of magnitude greater than the value given in Figure 11. Therefore, several errors in data reduction are evident, although the sensitivity of acoustic emission counts to stress intensity appears valid.

2.9.4.4 Frequency content of acoustic emissions

As stated in Section 2.9.3, the reflection of acoustic emission signals can occur within the test specimen, the detecting transducer, or both. The resulting resonance (standing wave) phenomena can produce frequency components not associated with the incident emission. It is therefore essential that such phenomena be considered in the frequency spectrum analysis of acoustic emission signals.

Ono and Stern (112) applied correlation analysis to acoustic emission signals to determine the power
density function (hence, frequency distribution) of the emissions. Tests were conducted using a commercial Mg-3Al-1Zn alloy (AZ31B) in the form of sheet tensile specimens by examining the acoustic emission frequency content at various levels of applied stress. Using electronic signal analysis techniques, the authors (112) found that the frequency spectrum contained two primary components, and was a function of applied stress. The largest peak (160 kHz) was attributed to the Dunegan Research Corporation S140B transducer (resonant frequency) used in the study. The second major frequency component was 80 kHz. A minor frequency component (400 kHz) was also observed in the study.

The investigation (112) clearly shows that the generation of acoustic emissions will produce high frequency components in the resulting electronic signal. This is in agreement with the fact that acoustic emission signals have been found to excite resonance in detecting transducers at frequencies of 10 kHz to 30 MHz (113).
Although emissions undoubtedly contain high frequency components, the frequency analysis by Ono and Stern (112) can be shown to result from standing waves within the test specimen itself. The second major frequency component in the spectra (80 kHz) is easily attributed to a standing wave in the reduced section (1.2" long) of the tensile specimen. From published data (114), the velocity of sound in this alloy (as-cast AZ31B) is found to be $1.98 \times 10^5$ in/sec. The text by Mason (115) gives the equation for a first harmonic standing wave in such a section as:

\[ f_r = \frac{V}{2l} \]

where: \( f_r \) = first harmonic resonant frequency (sec\(^{-1}\))
\( V \) = velocity of sound in the material (in/sec)
\( l \) = length of the section (in)

The insertion of \( l = 1.2" \) and \( V = 1.98 \times 10^5 \) in/sec into the above equation gives a resonant frequency of 82.5 kHz, very close to the component observed by
the authors (80 kHz). Similarly, the consideration of a standing wave in the larger of the two specimen cross-section dimensions (0.23") gives $f_r = 431$ kHz, the third frequency component found in the study (400 kHz). The second cross-section dimension gives a first harmonic of approximately 1.5 MHz, and thus was not seen in the experimental study (up to 500 kHz). A fourth frequency component (300 kHz) was observed in the investigation.

On the basis of possible resonance phenomena in the system, the reported frequency analysis data appear to result from the reflection of the signal at the physical boundaries of the system, and not from the spectrum of the signal itself. The time duration of the signal is believed to be quite small (116), and reflections within these specimen dimensions are therefore reasonable. The analysis of this study is not designed to dispute the usefulness of frequency analysis - quite the contrary. It is, however, directed toward illustrating the significance of wave reflection and distortion prior to pulse spectrum studies.
2.9.4.5 **Energy of acoustic emissions**

Since acoustic emissions result from the release of elastic energy during plastic deformation or crack growth processes, the energy of emissions (as affected by experimental variables) may supply information as to both the mechanical nature and energy requirements of the slow crack growth process. For this reason, the elastic strain energy associated with an acoustic emission is of considerable interest.

Gerberich et al (117) studied the effect of applied stress intensity on the amplitude of acoustic emissions. Fracture mechanics predicts that the energy supplied (per unit area) to a moving crack is proportional to $K^2/E$, where $E$ is Young's modulus for the material and $K$ is the stress intensity value (118). This proportionality exists under either plane strain or plane stress conditions. If the surface energy and plastic deformation energy requirements of crack growth (as well as thermal losses) do not vary significantly with applied stress intensity, a certain
fraction of the total energy input for fracture is assumed to be acoustic energy. Such acoustic energy is released as elastic stress waves within the material. Treating the piezoelectric transducer (or accelerometer) as a linear device, the maximum output voltage (or acceleration, in g-units) is directly proportional to the displacement (or strain per unit length). If the elastic energy striking the transducer is then proportional to the square of the strain (or transducer output voltage), then the following relationship is proposed (117):

\[ K^2 \frac{\Delta A}{E} \propto (\Sigma g)^2 \]

where:
- \( K \) = applied stress intensity
- \( E \) = Young's modulus for material
- \( \Delta A \) = area (incremental) created by crack growth
- \( \Sigma g \) = summation of amplitudes of emissions observed during creation of new surface (\( \Delta A \)), expressed as g-units

The fracture of SEN (single-edge-notched) specimens
of a 7075-T6 aluminum alloy, in air, showed fair agreement with the above energy equation. The authors measured stress wave amplitudes (in g-units) at stress intensity values of 32.6 to 61.9 ksi-in\(^2\).

By considering each emission to be a single release of energy, the energy of a series of acoustic emission stress waves would be proportional to the sum of the squared amplitudes for all individual pulses, i.e., \( \sum g_i^2 \) for \( i \) pulses. In the reported study (117), the investigators use the expression \( \left( \sum g_i \right)^2 \) for \( i \) pulses in order to obtain agreement with the experimental data. This could not be explained (119).

The energy correlation also assumes that the accelerometer is a linear device. The response of the accelerometer used in the study was independent of frequency up to 6 kHz (117). However, acoustic emissions have been shown to excite transducer resonance at frequencies up to 30 MHz (113). Therefore, the frequency content of the stress wave, as affecting the accelerometer response, was not considered in the energy analysis.
Baker (120) studied the acoustic emission activity of both D6AC and 18 Ni maraging steels (200 and 300 grade) in the pure bend testing of smooth plate specimens in air. Either the formation of surface cracks or the fracture of inclusions, on the tension side of the specimen, resulted in the generation of acoustic emissions. The formation of cracks, of area $10^{-6}$ in$^2$ or less, resulted in detectable emissions for the case of D6AC steel.

Acoustic emission energies were estimated using the impacts of tungsten pellets onto the specimen from known heights. For impact energies of 1 erg (or less), acoustic emission signals were observed at amplitudes one order of magnitude greater than the minimum detection limit of the system (0.01 g-units).

The importance of the Baker study (120) is that it is the first reported estimate of acoustic emission energy. The value of 1 erg is also an upper limit on the emission energy, since the impact energy does not define either the amount of transmitted energy or the
type of wave produced by the impact (as compared to the type produced in crack formation). The author concludes that the frequency content (and associated pulse shape) of the original stress wave must be considered in the measurement of acoustic emission energy.
3.1 Objectives

The investigation of acoustic emissions, as related to slow crack growth in high strength steel, had three objectives: (1) to determine the effects of strength level and chemical environment on acoustic emission count activity during slow crack growth, (2) to determine the effect of chemical environment on the amplitude and frequency content of acoustic emission signals, and (3) to determine the time of duration and the energy of an acoustic pulse, in the absence of reflection phenomena within the test system.

All studies were conducted at room temperature (25°C).

3.2 Experimental Procedure

3.2.1 Material, specimen geometry, and loading system

The material used in the study was AISI 4335 steel.
The mill analysis is given in Table 1. Single cantilever beam specimens, of the geometry used by Johnson (121), were chosen for the investigation. Figure 12 shows the specimen geometry, with the relationship between applied bending moment and stress intensity. The specimen dimensions (W) and (B) in Figure 12 are 1.0" and 0.5", respectively. The specimen length was approximately 6". Figure 13 shows the static load test apparatus used in the slow crack growth studies. Beam deflection was measured, using a Daytronic DS1000 transducer, in series with a Daytronic Model 201B transducer-exciter-demodulator. The output of the Daytronic system was measured as voltage (mv), using an Esterline-Angus El101S strip chart recorder. The calibration curve for the Daytronic LVDT system (output voltage vs. displacement) is shown in Figure 14.

3.2.2 Slow crack growth environments

Both gaseous and aqueous environments were investigated, using a polyethylene environmental
Table 1 - Chemical (Mill) Analysis Of AISI 4335
Steel Used In Single Cantilever Beam Studies

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>0.71</td>
<td>0.006</td>
<td>0.006</td>
<td>0.45</td>
<td>1.79</td>
<td>0.90</td>
<td>0.35</td>
</tr>
</tbody>
</table>
$$B = \text{Specimen Thickness (in.)}$$

$$W = \text{Specimen Width (in.)}$$

$$L = \text{Specimen Length (in.)}$$

$$A = \text{Crack Length (in.)}$$

$$M = \text{Applied Moment (in.lbs.)}$$

Plane-Strain Stress Intensity Factor

$$K = 4.12M \frac{\sqrt{\frac{L^3}{A^3}} - A}{BW^{\frac{3}{2}}}$$

$$\text{(psi-in}^{\frac{1}{2}})$$

Where: $$\alpha = 1 - \frac{A}{W}$$

Figure 12 - Single Cantilever Beam Specimen Used In Crack Growth Rate And Acoustic Emission Studies [From Johnson (121)]
Figure 13 - Loading Frame For Single Cantilever Beam Specimens
Dispacement Measured From Full Open Position

Linear Portion $1\frac{1}{16}$" Full Span

Nonlinear Zones

Figure 14 - Calibration Curve For LVDT Device Used In Single Cantilever Beam Experiments
chamber (bonded to the test specimen by Plastic Rubber adhesive). The gaseous species used in the acoustic emission studies were hydrogen, oxygen, and argon, all of high purity grade. Further purification of hydrogen/argon gas mixtures was achieved using a gas purification train. Figure 15 shows the purification train used in the study. Gas flow rates were measured, using calibrated multi-range flowmeters. Total gas flow rates of up to 1000 cc/min were used in order to obtain low hydrogen partial pressures (< 5 vol%). The column containing cuprous oxide catalyst pellets (shown in Figure 15) was operated at 130°C or above. The total pressure of the gaseous environment was slightly greater than one atmosphere, as the result of exhausting the gas through a glass wash bottle containing dibutylphthalate. Oxygen gas was used in the study to intentionally halt crack growth in hydrogen or hydrogen/argon gaseous environments.

In aqueous environment studies, specimens were tested either at the corrosion potential or under
Figure 15 - Gas Purification Train Used In Hydrogen Gas Environment Studies With Single Cantilever Beam Specimens
potentiostatic conditions. Potentials were applied using a Magna 4700M potentiostat, and were measured with respect to a saturated calomel electrode by means of a Luggins probe at the machined $90^\circ$ notch of the specimen. A platinum counter electrode was used in potentiostatic tests.

3.2.3 Specimen preparation

With the exception of strength level studies, all heat treatment was done by the National Heat Treating Service Co. of Columbus, Ohio. The standard heat treatment consisted of austenitizing at $1550^\circ F$ ($845^\circ C$) for 1 hour (in neutral salt), oil quenching, and tempering at $400^\circ F$ ($205^\circ C$) for 1 hour (in air). In the strength level studies, all heat treatment was done in an air environment, with 1 hour austenitizing and 1 hour tempering cycles. Strength levels were determined by 4 hardness measurements taken on each specimen (after failure) approximately $1/8''$ from the fracture surface on one side face.

Since the over-all objective of the study was to
relate acoustic emissions to the slow crack growth process (not crack initiation), each specimen was pre-fatigue cracked, using a Krouse cantilever fatigue machine prior to testing. The test specimens were then ground to a 120-grit finish, cleaned in reagent grade acetone, and stored in dessicators (containing indicating drierite) until testing. After pre-fatigue cracking, the crack lengths were approximately 0.20", as measured from the tip of the 90° notch in each specimen.

3.2.4 Acoustic emission systems

Three systems were designed to determine: (1) acoustic emission counts, (2) acoustic emission pulse shape (presence of reflections), and (3) acoustic emission pulse shape (absence of reflections).

Acoustic emission counts were measured using an electronic counter, as in the reviewed work of Dunegan and Tetelman (111). The accelerometer used in the study was an Endevco Model 2272, with a nominal resonance frequency of 37 kHz. Since this frequency
is that of maximum gain (hence, sensitivity) for the transducer, the frequency band chosen for selective filtering was 30 - 40 kHz. Figure 16 shows the electronic system used to measure acoustic emission counts. The Hickok counter (shown in Figure 16) contains a Schmitt trigger circuit which permits setting of the trigger level required to activate the counter. The trigger level, in all tests, was adjusted to give an average count rate of 0.4 counts/min or less, in the absence of a stress corrosion environment. The Endevco accelerometer was attached to each specimen by a threaded 3/16" stainless steel cap screw. The head of each screw was machined to 0.47" diameter, and 0.015" thickness. One such screw was bonded by Metal Set epoxy cement (Smooth-On, Inc.) to the bottom of each specimen, 1" from the center.

The second objective was to examine acoustic emission signal shape, in the absence of transducer resonance. The study therefore required a transducer and signal amplifier of high frequency response, as well as a means of photographing the signals. A Branson
Figure 16 - Electronic System Used To Measure Acoustic Emission Counts As A Function Of Strength Level For Single Cantilever Beam Specimens
Z-103-B transducer, and a Hewlett-Packard 400E voltmeter - pre-amplifier, were chosen for the study. The frequency response of the Branson transducer was determined by electrically exciting it with a Hewlett-Packard Model 650A test oscillator at frequencies up to 10 MHz, and monitoring the output voltage (across the transducer) with a Tektronix Model 543 oscilloscope. At frequencies up to 10 MHz, no change in either output voltage amplitude or wave shape was observed. Frequency response tests of the Hewlett-Packard 400E pre-amplifier showed sine wave distortion only at frequencies of 3.5 MHz or above. In the pre-amplifier response testing, the Hewlett-Packard Model 650A test oscillator signal was used as the input, with the output being measured with the Tektronix Model 543 oscilloscope. Figure 17 shows both the electronic system used in the study and the location of the Branson transducer on the bottom of each test specimen. In all tests, the Branson transducer was coupled to the test specimen with Dow Corning ignition
Figure 17 - Electronic System Used To Study Acoustic Emission Signal Characteristics As Functions Of the Test Environment
sealing compound (DC-4). During the slow crack growth process, oscilloscope traces (triggered by acoustic signals) were randomly photographed, using a Polaroid camera attachment for the Tektronix Model 543 oscilloscope.

The purpose of the third acoustic emission investigation was to determine the characteristics of an acoustic emission stress wave (time of duration, frequency content, and energy). In order to examine such characteristics, the time required for superposition of reflected waves must be greater than the expected duration (time) of the wave itself. Taking the velocity of sound as $2 \times 10^5$ in/sec for AISI 4340 steel (122), and assuming a crack jump distance of $2 \times 10^{-3}$ in, results in a pulse duration on the order of $10^{-8}$ seconds. However, the estimate of pulse duration is based on two assumptions: (1) the crack propagates, for the case of one emission, at the velocity of sound, and (2) the emission is generated only while the crack is moving. Since neither assumption is justified at this time, the estimate of
pulse duration serves as a lower limit for the case of an acoustic emission. Therefore, stress wave reflections, within either the transducer or the specimen, must be eliminated. In order to minimize reflections at the side surfaces of the specimen, sections of the same steel (and heat treatment) were coupled to the sides of each test specimen, using Dow Corning ignition sealing compound (DC-4). The detecting transducers (2) were 0.049" thick discs of a PZT-4 type piezoelectric ceramic, approximately 0.35" in diameter. In order to provide the same detector sensitivity, the discs were both cut from a larger disc of the PZT-4 type material. The ceramic discs were bonded to the bottom of each specimen, using a warm water-soluble cement (Franklin Liquid Hide Glue). Both ceramic detectors were backed by \( \frac{1}{2} \)" sections of the same piezoelectric ceramic. In this way, minimal acoustic impedance mismatch existed, and the backing ceramic served as a wave guide. The presence of a backing ceramic resulted in a travel time
of 8 microseconds, required for the wave to reflect from a free surface and strike the detecting disc a second time. Figure 18 shows the specimen-transducer configuration.

Two detecting discs were used in order to define the location of the wave source. If the acoustic emission is generated by the entire crack front, the travel time to symmetrically-located transducers would be the same. If, however, the emission is the result of a point source, a detectable difference in the time of travel to each transducer may result.

The output signal from each detecting crystal was amplified, using a Hewlett-Packard 400 Series voltmeter - pre-amplifier, and then fed into one section of a two-stage Dytronic Model 724 electronic filter, operating as a high pass device (above 2 kHz). The output of each filter stage was then fed into a Tektronix Model 555 dual beam oscilloscope. In this way, both crystal outputs could be examined with a single Polaroid photograph of the triggered oscilloscope sweep.
Figure 18 - Specimen-Transducer Arrangement Used To Study Acoustic Emission Signals In the Absence Of Reflection Phenomena
An additional consideration in the third acoustic emission study was the sensitivity of each detecting crystal, and its amplifier and filter circuit, to the incoming acoustic signal. A 2 MHz sine wave signal was sent into the circuit which amplified and displayed each crystal output signal. This was done with a Hewlett-Packard Model 650A test oscillator. The oscilloscope sensitivity was adjusted such that, for the same input signal, the 2 MHz continuous wave amplitude was the same (on the oscilloscope) for each amplifying circuit.

3.2.5 Beam deflection - crack extension calibration for single cantilever beam specimens

In order to relate acoustic emission activity to the slow crack growth behavior of high strength steel it is necessary to measure crack extension as a function of time. For the single cantilever beam specimen and the deflection measurements in the present study, the relationship of crack extension to beam
deflection must be established.

To establish the crack extension - beam deflection relationship, pre-fatigue cracks were propagated in a hydrogen/argon gas mixture (approximately 10 vol% H₂) under constant load conditions. Prior to adding the hydrogen gas, each specimen was loaded in argon, and the polyethylene environmental chamber was purged with argon for two hours. Crack propagation in hydrogen gas was stopped by purging the environmental chamber with oxygen gas. The beam deflection associated with crack extension was then measured (in mv.). The crack extension in the hydrogen/argon mixture was measured after the specimen was rapidly loaded to catastrophic failure in oxygen gas. Crack lengths, before and after slow crack growth, were measured with a Starrett micrometer depth gauge. Crack length, beam deflection, and applied load data were tabulated for 14 specimens, with crack extensions of 0.017" to 0.152". The initial applied stress intensity for all specimens was 50.8 ksi-in. Brown and Srawley (123) give parameters for
calibrating crack length, applied load, and crack opening displacement measurements for single cantilever beam specimens loaded by an applied bending moment. The parameters are:

\[(E\nu B)/P\] and \[a/W\]

where:
- \(E\) = Young's modulus (psi)
- \(\nu\) = crack opening displacement (in)
- \(B\) = specimen thickness (in)
- \(P\) = applied bending load (lbs)
- \(a\) = crack length (in)
- \(W\) = specimen width (in)

The specimen dimensions, observed beam deflection (mv reading on recorder), applied load, and crack extension data were analyzed, using a least-squares computer program, to provide the relationship between crack extension and beam deflection (under constant load conditions). Beam deflection \(\delta\) was assumed to be proportional to crack opening displacement \(\nu\).
Crack length \( a \) was replaced by crack length change \( \Delta a \). Since the calibration data are obtained from (and applied to) specimens of the same material and heat treatment (under constant load conditions), the variables \( E \) and \( P \) were not included in the calibration procedure. The experimental data are given in Table 2. The resulting least squares equation is:

\[
\frac{\Delta a}{W} = 0.14 + 0.257 \sigma B
\]

where: \( \Delta a \) = crack extension (in)
\( W \) = specimen width (in)
\( \sigma \) = LVDT output voltage (mv)
\( B \) = specimen thickness (in)

The parameter \( \sigma \) can be converted to beam deflection (in) using the LVDT calibration data given in Figure 14. Figure 19 shows the resulting calibration data, along with the 95% confidence interval for the least squares fit (124).

On the basis of the experimental data in Figure 19, a linear relationship between beam deflection and crack extension (for constant load conditions) is
### Table 2 - Crack Length - Beam Deflection

Calibration Data For Single Cantilever Beam Specimens

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>$\Delta a/D$ (unitless)</th>
<th>$\delta B$ (mv-in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDG - 15</td>
<td>0.066</td>
<td>1.676</td>
</tr>
<tr>
<td>CDG - 16</td>
<td>0.104</td>
<td>3.402</td>
</tr>
<tr>
<td>CDG - 17</td>
<td>0.037</td>
<td>0.871</td>
</tr>
<tr>
<td>CDG - 18</td>
<td>0.065</td>
<td>2.135</td>
</tr>
<tr>
<td>CDG - 19</td>
<td>0.134</td>
<td>4.584</td>
</tr>
<tr>
<td>CDG - 21</td>
<td>0.116</td>
<td>4.316</td>
</tr>
<tr>
<td>CDG - 22</td>
<td>0.097</td>
<td>3.008</td>
</tr>
<tr>
<td>CDG - 23</td>
<td>0.140</td>
<td>5.057</td>
</tr>
<tr>
<td>CDG - 24</td>
<td>0.116</td>
<td>3.795</td>
</tr>
<tr>
<td>CDG - 25</td>
<td>0.079</td>
<td>2.615</td>
</tr>
<tr>
<td>CDG - 26</td>
<td>0.050</td>
<td>1.336</td>
</tr>
<tr>
<td>CDG - 27</td>
<td>0.017</td>
<td>0.301</td>
</tr>
<tr>
<td>CDG - 28</td>
<td>0.026</td>
<td>0.575</td>
</tr>
<tr>
<td>CDG - 29</td>
<td>0.153</td>
<td>5.325</td>
</tr>
</tbody>
</table>
Figure 19 - Calibration Curve Relating Loading Beam Deflection To Crack Extension For Single Cantilever Beam Specimens
established.

3.3 Experimental Results

3.3.1 Acoustic emission count study

The effects of strength level and beam deflection (hence, crack extension) on total acoustic emission counts were determined in two environments: (1) a hydrogen/argon gas mixture (9.1 vol% H₂), and (2) a 3½ wt% sodium chloride aqueous solution (pH = 6.0), with a specimen potential of -1.0 volt wrt SCE.

Figure 20 shows the results obtained from the gaseous environment tests. Figure 21 shows the aqueous environment test results.

3.3.2 Acoustic emission characteristics, in the presence of reflections

A minimum of five acoustic signal photographs (per specimen) were obtained during slow crack growth in
Figure 20 - Acoustic Emission Counts As A Function Of Loading Beam Deflection and Material Strength Level For AISI 4335 Steel In A Hydrogen-Argon Gas Mixture (9.1 vol% hydrogen)
Figure 21 - Acoustic Emission Counts As A Function Of Loading Beam Deflection and Material Strength Level For AISI 4335 Steel In 3.2% Sodium Chloride Solution (pH = 6.0)
specimens exposed to four environments: (1) pure hydrogen gas, (2) a hydrogen/argon gas mixture (23.1 vol% H₂), (3) a 0.1N HCl aqueous solution, and (4) a 3½ wt% sodium chloride aqueous solution. Tests in the HCl solution were conducted at specimen potentials of -1.0 and +1.5 volts wrt SCE. Tests in the sodium chloride solution were conducted at a specimen potential of +1.0 volt wrt SCE, with the solution pH adjusted to 13.0 by the addition of NaOH. Test loads in each case were increased until cracking occurred, and such $K_I$ values varied from test to test, as well as during each test.

The signal photographs showed no consistent differences in pulse shape or amplitude, as a function of the test environment. The actual photographs have been published elsewhere (116).

3.3.3 Acoustic emission characteristics, in the absence of reflections

Although the original Polaroid signal photographs
are not available at this time, Figure 22 shows a drawing of typical signal shapes observed simultaneously with the two PZT-4 detectors used in this study. Signal amplitudes were widely varied, such that the drawing in Figure 22 represents a signal of sufficiently low amplitude to be photographed, in its entirety, on the oscilloscope screen.

3.4 Discussion of Acoustic Emission Results

3.4.1 Acoustic emission count studies

The effect of strength level on the acoustic emission activity (counts per unit crack extension) for the hydrogen/argon gas environment shows an apparent increase with strength levels above 200 ksi. Greater acoustic emission activity is also observed with higher strength level steel in the aqueous environment. There is, in addition, an apparent increase of counts (per unit crack extension) with increasing
Figure 22 - Drawings Of Acoustic Signal Profiles Seen Using Two PZT-4 - Backed Detecting Transducers
applied stress intensity. However, in view of the limited quantity of data, and the variation therein, definite conclusions as to strength level and stress intensity effects cannot be made at this time.

A very definite increase in acoustic emission count activity is observed for high strength material (227 - 237 ksi) in the gaseous environment, as opposed to the aqueous environment. The number of acoustic emission counts, for the same beam deflection, is approximately one half an order of magnitude greater in the gaseous environment. The difference between the number of acoustic emission counts observed in the two environments is not the result of reflection phenomena at the specimen - test environment interface. Using published data for sound velocity and density for 0.1% C hardened steel, argon gas (at 0°C), and sea water (125), the values of acoustic impedance (ρV) may be calculated. For the case of steel, the plane longitudinal wave velocity is used. The impedance values are 45,800, 0.568, and 1570 for steel, argon
gas, and sea water, respectively. The units are gram-meters/cm$^3$-second. From the reflection equations of Mason (126), it is seen that the amplitude of a wave reflected back into steel from an external salt water medium is approximately 93.5% of the incident wave amplitude. This gives a measurable transmission into the salt water. The treatment by Mason is for the simplest case, that of normal incidence. For the case of an external argon gas environment, the reflection is essentially 100%. If such reflections do occur on the upper and lower surfaces of the specimen, the time required for a wave reflected from the lower surface to again strike this surface (and the piezoelectric transducer) is 10 microseconds or less, using a specimen width of 1". The accelerometer used in this study had a nominal resonant frequency of 37 kHz. Experimentally, this was found to be as high as 40 kHz, as determined from signal photographs as the transducer was excited by incident stress waves.
Using the value of 40 kHz, the time required for two counts (twice the period of a 40 kHz sine wave) is 50 microseconds. In this time, five such reflections could occur, reducing the wave amplitude to approximately 72% of its original amplitude. The amplitude reduction is obtained by considering that the wave amplitude is reduced 6.5% on each reflection at a steel - salt water interface. Therefore, the wave amplitude is considerably reduced by such multiple reflections.

Oscilloscope photographs of acoustic signals, detected by the Endevco accelerometer, show that the signal amplitude is above the background noise for 400 microseconds or more. Therefore, reflected waves are significant only in the very early portion of an acoustic signal, as detected by an electronic counter. Also, this treatment neglects possible destructive interference by portions of the same wave reflected from other surfaces of the test specimen. In light of these considerations, the partial transmission of the acoustic wave into the salt water medium does not
account for the substantial difference between the number of acoustic emission counts detected in aqueous and gaseous test environments.

A possible explanation for the difference in acoustic emission counts, in gaseous and aqueous environments, is the occurrence of bifurcation and crack arrest. Crack branching (bifurcation) was observed in both aqueous environment test specimens, after the beam deflection rate was found to continually decrease with time. The beam deflection rate for all gaseous tests was either constant, or increasing with time during the test.

3.4.2 Acoustic emission signal characteristics

Acoustic emission signals, detected with the Branson transducer, had duration times of 100 microseconds or more (116). However, in the absence of reflections, the signal duration is seen to be as small as one microsecond (Figure 22).

The significance of the actual signal duration is
that the signal contains frequency components of sufficient magnitude (> 1 MHz) to explain the detection of emissions by examining narrow frequency bands up to 1 MHz (127). A Fourier analysis of a one microsecond square wave or half-sine wave pulse also gives frequency components in the MHz range (128).

In several cases, the photographs of acoustic emission signals (in the absence of reflections) showed that a second spike-type pulse occurred, 3 to 5 microseconds after the first. This is shown in Figure 22. Since both normal and shear stresses are present at the tip of a stressed crack, the release of stored elastic energy could result in the generation of extensional, flexural, or torsional waves. The wave velocities for these modes of propagation are given by Mason (129) as:

- **Extensional (longitudinal)**: \( V_L = \left( \frac{E}{\rho} \right)^{\frac{1}{2}} \)
- **Flexural**: \( V_f = \left( \frac{E}{\rho} \right)^{\frac{1}{2}} \)
- **Torsional**: \( V_t = \left( \frac{\mu}{\rho} \right)^{\frac{1}{2}} \)
where: \( E = \text{Young's modulus for the propagation medium (steel)} \)

\( \mu = \text{shear modulus for the propagation medium (steel)} \)

\( \rho = \text{density of steel} \)

For elastic behavior of the propagation medium, \( E = \frac{2\mu}{1 + \nu} \), where \( \nu \) is Poisson's ratio. For \( \nu = 0.3 \), the ratio \( V_l/V_t = 1.61 \). If the longitudinal wave velocity is taken to be \( 2 \times 10^5 \text{ in/sec in AISI 4340 steel (122)} \), and a source-to-detector distance of 0.5" is assumed, the time difference for the arrival of a longitudinal (or flexural) and a torsional wave is 1.5 microseconds, and is easily resolvable with the oscilloscope used in pulse shape studies. The maximum time of travel (and time difference for longitudinal and shear waves) exists for the case of a point source on the initial (pre-fatigue) crack front, and at the side surface of the specimen. Using the described wave velocities, and a
measured crack length of 0.364"., the shear wave would strike the farthest transducer approximately 2.5 microseconds after the longitudinal wave. However, the longitudinal wave would then have different travel times to each transducer (difference of approximately 0.8 microseconds). The initial pulses experimentally detected by each transducer were found to differ in arrival time by 0.5 microseconds or less. Therefore, on the basis of available wave velocity information, the second pulse cannot be explained by a slower moving shear wave.

Since it has been shown, both in the present work and in the reviewed work of Ono and Stern (112), that the reflection of acoustic waves significantly affects the voltage-time profile of the resulting signal, it is essential that acoustic emission energy be determined in the absence of super-imposed reflections. Such an energy estimate can be made, for a typical spike pulse in the present study, under the following five assumptions:

1. The emission energy is determined by the maximum amplitude of the acoustic pulse, and
is independent of amplitude variation with time.

(2) Ideal matching, with 100% energy transfer, occurs between the transducer and the pre-amplifier.

(3) The piezoelectric constants of the detecting ceramic are independent of mechanical or electrical loading.

(4) The acoustic emission is a spherical pressure wave, generated by a point source, with the strain component parallel to the direction of wave propagation.

(5) The dilatational strain component of the wave is parallel to the axis of polarization of the piezoelectric ceramic detector.

The piezoelectric constant for a PZT-4 type ceramic \( g_{33} \) has been calculated (131) to be \( 2.49 \times 10^{-2} \) volt-meters/newton. For a detector thickness of 0.049", the resulting sensitivity is 0.214 volts/psi. The amplitude of the signal shown in Figure 22 was 0.2 volts, as measured on the oscilloscope photograph. A gain of 60 dB in the pre-amplifier, with a 30 dB loss in the
Dytronic filter, yields an original transducer output of 6.33 millivolts (stress of $2.96 \times 10^{-2}$ psi). The elastic energy of the pulse is then:

$$E^* = \frac{1}{2} \left( \frac{\sigma^2}{E} \right)$$

where: $\sigma$ = maximum dilatational stress of wave

$E$ = Young's modulus for steel

$(30 \times 10^6 \text{ psi})$

The resulting energy value ($1.47 \times 10^{-11}$ in-lbs) must be further corrected, since only a portion of the spherical wave front strikes the transducer:

Area factor = $A'/A''$

where: $A'$ = area of ceramic disc

$(1.9 \times 10^{-2} \text{ in}^2)$

$A''$ = area of spherical wave front, of radius 0.5"

$(3.17 \text{ in}^2)$

The acoustic mismatch factor $(0.8)^2$ results from wave reflection at the metal-ceramic interface. The wave reflection equations of Mason (126), in conjunction
with the acoustic impedance values for metal and ceramic (128), result in the back reflection of a wave (into the steel) having an amplitude 20% that of the original incident wave. Since, in this analysis, emission energy is proportional to the square of the amplitude, the transmitted energy is 0.64 times that of the incident wave. Thus, the original acoustic emission energy is calculated to be:

\[ E^* = \frac{1.47 \times 10^{-11}}{(0.64) (6.02 \times 10^{-3})} \text{ in-lbs} \]

\[ = 5.2 \times 10^{-3} \text{ ergs} \]

The acoustic emission energy value of one erg given by Baker (110) was obtained for a pulse which was: (1) one order of magnitude greater, in amplitude, than the detection limit of the electronic system, and (2) evaluated on the basis of maximum, rather than measured, energy. In addition to these considerations, the pulse examined in the present study was of measurable amplitude, but not necessarily
representative of the amplitude distribution for all emissions in the study. Therefore, on the basis of the assumptions in the present energy analysis and consideration of the Baker (110) technique, the agreement is felt to be good.

3.5 Conclusions of Acoustic Emission Study

The investigation of acoustic emission phenomena during the slow crack growth process in high strength AISI 4335 steel has shown that:

(1) For the investigated material and strength levels, the emission activity (as measured by acoustic emission counts) is greater in a hydrogen/argon gaseous environment than in a sodium chloride aqueous solution at a cathodic potential.

(2) Under conditions which permit stress wave reflections, there is no significant difference, with respect to pulse shape or amplitude, between the acoustic emission signals observed during slow crack growth in the investigated environments.
(3) The acoustic emission signal is very short, with a time duration as small as one microsecond.

(4) By the elimination of reflection phenomena, the acoustic emission signal is shown to contain frequency components equal to, or greater than, one megacycle.
SLOW CRACK GROWTH STUDIES IN GASEOUS AND AQUEOUS MEDIA

4.1 Introduction

4.1.1 Difficulties in prior testing

A double cantilever beam specimen was chosen for the measurement of slow crack growth rates in both gaseous and aqueous environments. A stainless steel vacuum system was used in the gaseous environment testing. Such an experimental procedure resulted in: (1) reproducible crack growth rate data, and (2) a straight crack front geometry, giving satisfactory results with the application of fracture mechanics analysis.

The acoustic emission and slow crack growth studies described in Section 3 involved several experimental difficulties which prevented the use of single cantilever beam specimens or a polyethylene environmental chamber in the detailed investigation of
slow crack growth kinetics. Crack front profiles attained during slow crack growth were generally parabolic. The difference in crack length from specimen mid-thickness or surface was often 50% of the maximum crack extension during the test. The observed geometry creates doubt as to the significance, in a fracture mechanics analysis, of crack length as measured at the specimen mid-thickness (hence, maximum crack length). The non-linear geometry of the crack front was also found to vary from test to test. Crack propagation did not always occur, in pure hydrogen at stress intensities up to 50% of the $K_{IC}$ value, without mechanical tapping of the loading beam.

Although the use of single cantilever beam specimens proved satisfactory for acoustic emission studies, it did not permit either accurate crack velocity measurements nor a detailed investigation of applied stress intensity and gas pressure effects on crack growth kinetics.
4.1.2 Requirements of the experimental system

The objective of the present investigation is the accurate measurement of crack velocities in aqueous and in several gaseous environments. A specimen geometry was required which permits the determination of stress intensity and gas pressure effects (individually) on the kinetics of slow crack growth. A gaseous environmental chamber was required which did not introduce contaminant species to levels greater than those in the test gas itself. The gaseous testing also required isobaric conditions, and in the presence of highly toxic and corrosive gases.

A test specimen of the double cantilever beam (DCB) geometry, statically loaded by a Satec creep machine, fulfilled the requirements for crack velocity measurement. A hard vacuum system, in conjunction with a bakeable stainless steel test chamber, satisfied the purity requirements for gaseous environment testing.
4.2 Experimental System

4.2.1 Specimen geometry

The specimen chosen for this study was of the Type 2S double cantilever beam geometry, designed by Gallagher (132), and is shown in Figure 23. This specimen geometry was chosen on the basis of three factors: (1) simple machining operations, (2) a large constant-$K_I$ zone, and (3) no reported difficulties due to crack bifurcation during testing in aqueous environments. The specimen length was chosen to be 7", and all other dimensions were proportionally reduced. This was done to reduce the required size of the gaseous environment test chamber. Final specimen dimensions were in standard 1/16" increments, and therefore within 1/16" of the scaled-down dimensions. This was done to simplify the machining operations. Machining tolerances were $\pm 0.005"$. Figure 24 shows the calibration curve for the specimen, obtained by
Figure 23 - Type 2S Specimen Of Double Cantilever Beam Geometry Used In Crack Velocity Studies [From Gallagher (132)]
Gallagher for the case of plane strain conditions. The variable $B^*$ is defined by Gallagher (132) as:

$$B^* = (B - B_n)^{\frac{1}{2}}$$

where: $B =$ specimen thickness, as measured from the side faces

$B_n =$ specimen thickness, as measured from the tips of the side grooves

The variables $B$ and $B_n$, for the specimen used in this study, are seen to be 0.443" and 0.293", respectively. The specimen length ($W$), as described by Gallagher, is measured from the axis of loading, and is 6.625". The crack length ($a$) is also measured from the axis of loading. By the curve in Figure 24, the stress intensity - applied load relationship for $0.25 < a/W < 0.45$ is:

$$K_I = 20.8 P$$

where: $K_I =$ stress intensity (psi-in$^{\frac{1}{2}}$)

$P =$ applied load (lbs)
Figure 24 - Calibration Curve For Double Cantilever Beam Specimen Used In Crack Velocity Studies [From Gallagher (132)]
Under the assumptions of linear elastic fracture mechanics, the critical stress intensity for catastrophic fracture is defined by the required mechanical energy (per unit area) for the process. Assuming a Mode I displacement of the crack surfaces, and plane strain conditions, the relationship is given (133) as:

$$K_{ic} = \left[ \frac{E G_{ic}}{(1 - \nu^2)} \right]^{\frac{1}{2}}$$

where:  
E = Young's modulus (units of stress)  
\(\nu\) = Poisson's ratio (unitless)  
\(G_{ic}\) = plane strain fracture toughness (units of energy/area)

By the fracture mechanics analysis, Kies et al (134) have shown that, for a plate containing a crack, and having the load (P) applied normal to the crack faces, the parameter \(G_I\) may be defined as:

$$G_I = \left( \frac{P^2}{2B} \right) \left[ \frac{d(1/M)}{da} \right]$$

where:  
P = applied load  
a = crack length
Therefore, for the specimen used in this study, the stress intensity is uniquely defined by the applied load. In addition, by the fracture mechanics analysis, the measurement of displacement (along the axis of loading) is an indirect measurement of crack extension. The variable B in the treatment by Kies et al (134) corresponds to the variable $B_n$ for the side-grooved specimen of Gallagher.

For Poisson's ratio ($\nu$) and Young's modulus (E) values of 0.3 and $3 \times 10^7$ psi, respectively, the relationship between crack opening displacement and crack extension was found to be:

$$\frac{d\delta}{da} = 8.22 \times 10^{-6} \, P$$

where: $\delta$ = crack opening displacement (inches)

$a =$ crack length (inches)

$P =$ applied load (pounds)
The erroneous use of 0.313" as the value for \( B_n \) in deriving the above equation, and in the subsequent crack velocity calculations, is seen to produce an error of less than 4%.

With respect to specimen design, a 1/16" wide sawcut, with a 45\(^\circ\) groove at its end, was introduced to facilitate the pre-fatigue cracking operation. All specimens were cut from 0.45/0.50" thick plates of steel, and were of a known orientation with respect to the original plate.

4.2.2 Aqueous environment test apparatus

The aqueous tests were conducted using the same test cell, Satec Model D creep machine, and LVDT system used in prior work (135). The test environment was a 3 1/2 wt% sodium chloride aqueous solution in distilled water, adjusted to \( pH = 6.0 \) by additions of either HCl or NaOH. The specimen grips used in this test environment were machined from 1 1/2" diameter sections of Type 304 stainless steel. All testing was performed at room temperature, and with no
externally applied potential.

4.2.3 Gaseous environment test apparatus

4.2.3.1 Test chamber and pumping system

The use of a hard vacuum system in the gaseous studies permitted the evacuation of the test chamber, prior to backfilling with the desired gas environment. All tests were conducted at room temperature, and the outgassing rate of the system was typically $3 \times 10^{-3}$ torr/hour. The pumping system consisted of a 6" oil diffusion pump, backed by a Welch Model 1397B rotary oil pump. Figure 25 shows a block diagram of the vacuum system. Figure 26 shows a photograph of the system itself. A 4" diameter O-ring sealed gate valve was used to isolate the pumping system, just prior to backfilling of the vacuum chamber and elbow with the test gas environment.

The vacuum chamber used in this study (shown in Figures 25 and 26) was constructed entirely of Type
Figure 25 - Block Diagram of Vacuum System Used in Crack Velocity Studies with Double Cantilever Beam Specimens
Figure 26 - Experimental System Used In Gaseous Environment Testing
304 stainless steel, and all seals were of the rubber (Viton) O-ring type. The gas inlet valve was constructed of brass, and contained an O-ring seal. It was used to backfill the system with relatively non-corrosive gases. These included argon, oxygen, hydrogen (wet or dry), methane, and acetylene. The test chamber itself was machined and heli-arc welded in the Metallurgical Engineering Department machine shop. Following machining, the chamber and 90° Type 304 stainless steel elbow were sand blasted by the Columbus Porcelainizing Company of Columbus, Ohio. No vacuum grease was used on any O-ring seals in the system (including the foreline). The connection between the gas inlet valve and the test chamber was made using an O-ring sealed Ultra-Torr vacuum fitting (VWR Scientific Co., Columbus, Ohio).

Following the sand blasting of the chamber and connecting elbow, all parts of the chamber and pumping system (except the rotary oil pump) were cleaned with reagent grade acetone and white laboratory towels.
This cleaning procedure was also used after a burn-out of the pumping system during the course of the investigation.

4.2.3.2 Pressure measurement

Ultimate vacuum pressures were measured with an NRC Type 507 hot cathode ionization gauge. Foreline pressures were measured with an NRC Type 501 thermocouple gauge. Both gauges were used in conjunction with an NRC Type 710 gauge control unit.

In view of the corrosion behavior of several test gases, two types of gauges were used in the measurement of backfilled gas pressures. For the cases of H₂ (wet or dry), O₂, H₂S (< 1 torr pressure), and CH₄, gas pressures were measured with an NRC Model 820 Alphatron gauge. The gauge was calibrated for sensitivity in the case of each test gas environment. Other pressure gauges used in the study were a Speedi-Vac CG3 gauge (Edwards High Vacuum Co., Grand Island, New York) and a dial-type vacuum gauge (Part No. 31749-006, VWR
Scientific, Columbus, Ohio). Both of the latter gauges were of the Bourdon tube-type, and therefore did not require calibration for each individual test gas. The more accurate, multi-range Alphatron gauge was used only with non-corrosive gases because of the possibility of a radiation hazard resulting from a severe corrosion attack of the gauge head assembly.

4.2.3.3 Loading system and displacement measurement

As described in Section 4.2.1, the measurement of both static load and crack opening displacement, by the concepts of fracture mechanics, permits the calculation of applied stress intensity and crack extension in the test specimen.

Static loads were applied to each specimen (contained in the vacuum chamber) using a Satec Model D creep test machine. Crack opening displacement was measured as the displacement of the upper 3/4" diameter stainless steel loading rod. The lower specimen loading rod was attached to the cross head of the Satec machine (stationary during each test). Each loading
rod was attached to the vacuum chamber using a 0.005" stainless steel bellows seal (Cajon flexible tubing, Part No. X-24-3, Type 321 stainless steel). The test specimen grips were constructed from 1\frac{1}{2}" diameter sections of Warpless drill rod. Following machining, the grips were austenitized, oil quenched, and tempered at 200°F.

Loading rod displacement was measured with a Daytronic DS100 linear voltage differential transducer, in conjunction with a Daytronic Model 300D transducer amplifier-indicator. A high sensitivity Type 71 plug-in unit was used in the Daytronic 300D device. The final read-out instrument was an Esterline Angus strip chart recorder. The Daytronic and Esterline Angus devices have been described in prior work (135).

Figure 27 shows the Daytronic LVDT device. The LVDT output is re-zeroed using the micrometer stem rest-stop for the LVDT device itself. The Daytronic DS100 unit was calibrated to give a full scale output (1 mv) on the Esterline Angus recorder for a 0.005"
Figure 27 - Daytronic Linear Voltage Differential Transducer Used In Crack Growth Studies
displacement. This calibration was performed prior to each test, using a Daytronic Model 115C calibrator. In all tests, as in the calibration, the displacement range of the LVDT is 0.069" to 0.074" from the fully-depressed position. The LVDT output voltage is shown, as a function of displacement, in Figure 28. Each data point is the average of four voltage readings for the same displacement. The range of output voltage (in mv) for the same increasing displacement values in Figure 28 are 0.202/0.208, 0.400/0.409, 0.792/0.803, and 0.990/0.993, respectively.

4.2.3.4 Acoustic emission detection system

Acoustic emissions were recorded during slow crack growth studies in hydrogen gas environments. An Endevco Model 2272 accelerometer was attached to the large end of each specimen, using a Viton rubber O-ring. The polarization direction of the accelerometer was parallel to the direction of crack growth. The central axis of the accelerometer was 1" above the plane defined by the
Figure 28 - Calibration Curve For Daytronic LVDT Device Used In Crack Velocity Studies With Double Cantilever Beam Specimens
specimen side grooves. The Endevco accelerometer is a hermetically-sealed device, and created no apparent difficulty in attaining the desired vacuum in the system. The output of the accelerometer was fed through a glass-sealed Co-var electrical feedthrough, located on the bottom of the vacuum chamber. A Hewlett-Packard 400GL voltmeter - pre-amplifier was used to amplify the transducer output signals. The amplifier gain setting, for all tests, was 60 dB.

Acoustic emission signals were recorded, after amplification, on a Sony TC-105 tape recorder, using a tape speed of 7½ ips and the auxiliary input terminal. The tape recorder Record Level (sensitivity) was adjusted, in each test, to 1/16" below the maximum (as indicated on the dial). Subsequent tape playback and acoustic emission signal analysis was performed using a Dytronics Model 724 electronic filter, a Hewlett-Packard Model 32A oscilloscope, and a Hickok Model DP 150 electronic counter. The acoustic emission detection and analysis system is shown in Figure 29.
Figure 29 - Acoustic Emission Detection System Used In Crack Growth Studies
4.2.3.5 Test gases and gas purification system

The test gases chosen for this study were the result of three considerations: (1) the lack of information regarding their potential as stress corrosion cracking environments, (2) definitely different chemical adsorption behavior on iron, or (3) a definite value of the gas in the discrimination as to the rate-controlling process in dry \( \text{H}_2 \) gas cracking.

Several gases, which were available in large, commercial gas cylinders, were required in the study. These were oxygen, argon, hydrogen, methane \((\text{CH}_4)\), and acetylene \((\text{C}_2\text{H}_2)\). With the exception of oxygen, such cylinder gases were further purified using a gas purification train. Figure 30 shows the purification train used in the study. The glass column containing copper turnings was operated at 300/320\(^\circ\)C, and was used to purify hydrogen or argon. The Englehard Industries De-Oxo unit (10 cfh, 50 psi model) was used only in hydrogen gas purification. The cold trap in
Figure 30 - Gas Purification Train Used In Crack Velocity Studies With Double Cantilever Beam Specimens
Figure 30 contained liquid nitrogen for the case of hydrogen gas purification, and a dry ice - methanol bath for the purification of argon, acetylene, or methane.

Upon changing the test gas environment, the purification system was operated for at least 6 hours, at 1 cc/sec, prior to use of the second purified gas. Except during the change of test gases, the gas purification train was operated continuously, with gas flow rates of ≥ 1 cc/sec.

The hydrogen gas used in the study was of a high purity grade (minimum purity of 99.92%). The nominal impurities in the as-received hydrogen gas (Burdett Oxygen Co., Columbus, Ohio) are:

- Oxygen < 5 ppm
- Nitrogen < 100 ppm
- Nitrogen oxides < 7 ppm
- Methane < 1 ppm
- Carbon dioxide < 10 ppm
- Carbon monoxide < 4 ppm
- Chlorides nil
- Moisture Dew Point of -90°F
The methane gas, obtained from Matheson Gas Products, was of an ultra high purity grade (minimum purity of 99.97%). The nominal impurities in the as-received methane gas are:

- Oxygen - 8-10 ppm
- Nitrogen - 40-50 ppm
- Ethane - 20-30 ppm
- Carbon dioxide - 40-50 ppm
- Propane - 5 ppm
- Moisture - 4-6 ppm

The acetylene gas used in the study was of a commercial purity (99.6%). The nominal impurities in the as-received acetylene (Liquid Carbonic Corp., Columbus, Ohio) are:

- Air - 0.03 - 0.3%
- Oxygen - 0.01 - 0.1%
- Nitrogen - 0.02 - 0.3%
- Hydrogen - trace
- Methane - trace
- Ammonia - none
- Phosphene - 0.0008%
- Hydrogen sulfide - 0.0003%
- Chlorine - 0.00002%
The heated copper column of the gas purification train was not used in acetylene purification. An initial attempt to use the column resulted in an apparent chemical reaction. Conversation with the gas supplier (Gas Cylinder Storage Department, Ohio State University) indicated that residual acetone (required for high pressure stability of acetylene) may explain the reactivity with heated copper.

The argon gas used in the investigation was of a high purity grade, but was not used as a test gas environment.

The gases deuterium, ammonia, chlorine, hydrogen chloride, hydrogen sulfide, and hydrogen bromide were obtained from the Lif-O-Gen, Inc. Co. of Lumberton, New Jersey. The analyses of the research grade gases (performed by the manufacturer) are given in Tables 3 to 6. The hydrogen sulfide gas was of a high purity grade. By communication with the manufacturer, it was learned that the major contaminants (as determined by mass spectrometry) are:
Table 3 - Chemical Analysis of Research Grade Chlorine

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>&lt; 2 ppm</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>35 ppm</td>
</tr>
<tr>
<td>Bromine</td>
<td>&lt; 50 ppm</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>&lt; 50 ppm</td>
</tr>
<tr>
<td>Chloroform</td>
<td>&lt; 25 ppm</td>
</tr>
<tr>
<td>Aromatics</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>&lt; 20 ppm</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>90 ppm</td>
</tr>
<tr>
<td>Methane</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Water</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Balance</td>
</tr>
</tbody>
</table>
Table 4 - Chemical Analysis of Research Grade Ammonia

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>N.D.</td>
</tr>
<tr>
<td>Ethane</td>
<td>N.D.</td>
</tr>
<tr>
<td>Propane</td>
<td>N.D.</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>N.D.</td>
</tr>
<tr>
<td>Oxygen</td>
<td>N.D.</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>N.D.</td>
</tr>
<tr>
<td>Argon</td>
<td>N.D.</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N.D.</td>
</tr>
<tr>
<td>Moisture</td>
<td>Moisture</td>
</tr>
<tr>
<td>Concentration</td>
<td>&lt; 1 ppm</td>
</tr>
<tr>
<td>Concentration</td>
<td>&lt; 1 ppm</td>
</tr>
<tr>
<td>Concentration</td>
<td>&lt; 2 ppm</td>
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<tr>
<td>Concentration</td>
<td>&lt; 2 ppm</td>
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<td>Concentration</td>
<td>&lt; 2 ppm</td>
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<td>Concentration</td>
<td>&lt; 2 ppm</td>
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<tr>
<td>Concentration</td>
<td>&lt; 2 ppm</td>
</tr>
<tr>
<td>Concentration</td>
<td>&lt; 0.2 ppm</td>
</tr>
<tr>
<td>Concentration</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Concentration</td>
<td>&lt; 15 ppm</td>
</tr>
</tbody>
</table>
Table 5 - Chemical Analysis of Research Grade Hydrogen Chloride

<table>
<thead>
<tr>
<th>Component</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>&lt; 8 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&lt; 25 ppm</td>
</tr>
<tr>
<td>Argon</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>&lt; 15 ppm</td>
</tr>
<tr>
<td>Methane</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Hydrogen bromide</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Moisture</td>
<td>Dew Point of -80°F</td>
</tr>
<tr>
<td>Other impurities</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>Balance</td>
</tr>
</tbody>
</table>
Table 6 - Chemical Analysis of
Research Grade Deuterium

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>&lt; 2 ppm</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&lt; 2 ppm</td>
</tr>
<tr>
<td>Moisture</td>
<td>&lt; 1 ppm</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>&lt; 0.3%</td>
</tr>
<tr>
<td>Deuterium</td>
<td>Balance</td>
</tr>
</tbody>
</table>
Methyl mercaptan - 100 - 300 ppm
Carbonyl sulfide - 50 - 150 ppm
Sulfur dioxide - 250 - 750 ppm

A similar investigation into the high purity grade hydrogen bromide gas yielded:

Hydrogen chloride - 1000 - 3000 ppm
Moisture - 100 - 500 ppm, max.

The Lif-O-Gen gases were supplied in 7½" diameter spherical pressure vessels, and admitted to the test chamber by a stainless steel, O-ring sealed, bakeable, two-stage regulator (Model No. 1100-SS-100), supplied by the manufacturer.

Due to the toxicity of the test gases, the exhaust fan in the laboratory (nominal 2000 cfm flow rate) was operated continuously during the test program.
4.2.3.6 Test material and heat treatment evaluation

The steels chosen for this study were two ultra-high strength grades, D6AC and AISI 4335V. The latter steel was obtained from the Republic Steel Company of Cleveland, Ohio. A chemical analysis of each steel was performed by the Car-Tech Research and Development Center in Reading, Pennsylvania. Table 7 gives the chemical analyses of the steels.

In view of the quantity of test specimens (96), two double cantilever beam (DCB) specimens were initially heat treated at the National Heat Treating Service Company of Columbus, Ohio to evaluate the commercial heat treating procedure. The AISI 4335V steel specimens were austenitized at 1550°F (845°C) for 1 hour in neutral salt, oil quenched, and tempered at 400°F (205°C) for 1 hour in air. Hardness measurements (80) were taken on each specimen, 1/8" from the side groove on one face, and 1/8" (minimum) apart. The hardness variation within the constant-\( K_I \) zone was 1.3/1.4 R_c.
Table 7 - Chemical Analyses of Steels
Used in Double Cantilever Beam Studies

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>0.42</td>
<td>0.77</td>
<td>0.22</td>
<td>0.011</td>
<td>0.004</td>
<td>1.01</td>
<td>0.53</td>
<td>1.05</td>
<td>0.10</td>
</tr>
<tr>
<td>4335V</td>
<td>0.36</td>
<td>0.75</td>
<td>0.30</td>
<td>0.009</td>
<td>0.009</td>
<td>0.78</td>
<td>1.74</td>
<td>0.39</td>
<td>0.17</td>
</tr>
</tbody>
</table>

- Compositions in percent
units, with no observable trend of hardness with distance along the specimen. A 3/8" cube of steel was cut from the side groove region of one specimen, and examined for decarburization. The etchant was 5 vol% nitric acid in methanol. No decarburization was found.

4.3 Tensile Strength and Grain Size Measurements

Tensile strength was a principal variable, for both steels, in the slow crack growth investigation. Tables 8 and 9 give the heat treatments chosen for the DCB test specimens (and tensile specimens) in the study.

Tensile tests were performed, using an Instron tensile test machine and standard ASTM 1/4" diameter tensile specimens (136). Test data was obtained for both steels and for all heat treatment conditions. The cross head velocity used in the testing was either 0.02 in/min or 0.04 in/min. The use of two cross head velocities resulted from testing on two Instron machines, one of which was located in the Mechanical
Table 8 - Heat Treatments For AISI 4335V Steel

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Material</th>
<th>Austenitizing Temperature (°C) And Time (Hrs.)</th>
<th>Quenching Temperature (°C)</th>
<th>Tempering Temperature (°C) And Time (Hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4335V</td>
<td>925 (1)</td>
<td>925</td>
<td>205 (1)</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td>315 (1)</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td>425 (1)</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
<td>870</td>
<td>205 (1)</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td></td>
<td>315 (1)</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>925 (3)</td>
<td></td>
<td>205 (1)</td>
</tr>
<tr>
<td>G</td>
<td></td>
<td>870 (1)</td>
<td></td>
<td>205 (1)</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td>315 (1)</td>
</tr>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td>425 (1)</td>
</tr>
<tr>
<td>J</td>
<td></td>
<td></td>
<td></td>
<td>540 (3)</td>
</tr>
</tbody>
</table>
### Table 9 - Heat Treatments For D6AC Steel

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Material</th>
<th>Austenitizing Temperature (°C)</th>
<th>Quenching Temperature (°C)</th>
<th>Tempering Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>And Time (Hrs.)</td>
<td>And Time (Hrs.)</td>
<td>And Time (Hrs.)</td>
</tr>
<tr>
<td>K</td>
<td>D6AC</td>
<td>870 (1)</td>
<td>870</td>
<td>540 (2)</td>
</tr>
<tr>
<td>L</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>595 (2)</td>
</tr>
</tbody>
</table>
Engineering Department of Ohio State University. No consistent differences were found between the results on the two machines for material having very similar heat treatments. The reduced section of each specimen was polished to a 400-grit finish. All threads were cleaned, using an electrically-driven wire polishing wheel. Following the polishing operation, each specimen was cleaned in reagent grade acetone. At least three tensile specimens were tested for each heat treatment condition.

Macroscopic examination of the fracture surface, in several instances, indicated that fracture had originated at the surface of the tensile specimen. The outer shear lip was not symmetric with respect to the longitudinal axis of the specimen. In such cases, the test data were neglected.

For a 1 hour austenitizing treatment, Figure 31 shows the 0.2% yield strength as a function of tempering temperature for AISI 4335V steel. For the same steel and austenitizing treatments, Figure 32 shows the effect of tempering temperature on the ultimate tensile
Figure 31 - Tensile Yield Strength Of AISI 4335V Steel As A Function Of Tempering Temperature
strength of the steel. Table 10 gives the actual tensile test data for AISI 4335V steel. Table 11 gives the tensile data for D6AC steel.

Because of a time requirement for pre-fatigue cracking of the double cantilever beam specimens (contract basis at the Battelle Memorial Institute, Columbus, Ohio), it was not possible to heat treat both the DCB and tensile specimens simultaneously. However, all heat treatments were performed by the same commercial facility (National Heat Treating Service Company).

The heat treatments given in Table 8 for AISI 4335V steel were chosen to give both a wide range of strength levels and a measurable difference in prior austenite grain size. Prior austenite grain size has not been previously studied with regard to its effect on the crack growth kinetics for high strength steels in dry hydrogen gas environments.

Grain boundaries were partially etched, using the technique of Harruff and Underwood (137). Figure 33 shows the results for AISI 4335V steel austenitized at
ULTIMATE TENSILE STRENGTH VS. TEMPERING TEMPERATURE FOR AISI 4335V STEEL

Figure 32 - Ultimate Tensile Strength Of AISI 4335V Steel As A Function Of Tempering Temperature
Table 10 - Tensile Data For AISI 4335V Steel

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>0.2% Yield Strength (Ksi)</th>
<th>Ultimate Tensile Strength (Ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V</td>
<td>A</td>
<td>221.0</td>
<td>286.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>221.0</td>
<td>286.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>217.1</td>
<td>285.1</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>204.7</td>
<td>240.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>217.1</td>
<td>252.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>216.5</td>
<td>251.5</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>184.0</td>
<td>210.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>183.7</td>
<td>210.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>184.0</td>
<td>210.6</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>---</td>
<td>283.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220.0</td>
<td>279.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220.0</td>
<td>281.1</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>204.7</td>
<td>236.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>210.2</td>
<td>243.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220.8</td>
<td>244.0</td>
</tr>
</tbody>
</table>
Table 10 - Continued

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>0.2% Yield Strength (Ksi)</th>
<th>Ultimate Tensile Strength (Ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V</td>
<td>F</td>
<td>222.0, 222.0, 217.9</td>
<td>285.1, 287.2, 279.0</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>225.5, 220.8, 221.6</td>
<td>281.5, 274.7, 282.1</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>209.8, 213.6, 214.9</td>
<td>238.1, 241.8, 244.0</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>190.4, 192.7, 192.7</td>
<td>203.9, 206.1, 208.4</td>
</tr>
<tr>
<td></td>
<td>J</td>
<td>179.2, 179.2, 174.3</td>
<td>190.4, 188.8, 185.1</td>
</tr>
</tbody>
</table>
Table 11 - Tensile Data For D6AC Steel

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>0.2% Yield Strength (Ksi)</th>
<th>Ultimate Tensile Strength (Ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>K</td>
<td>207.7</td>
<td>224.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>207.7</td>
<td>226.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>201.6</td>
<td>220.0</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>201.6</td>
<td>217.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>203.7</td>
<td>220.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>201.6</td>
<td>217.9</td>
</tr>
</tbody>
</table>
1700°F (925°C). Several modifications of the etching technique were used. The addition of a small amount of concentrated nitric, picric, or hydrochloric acid to the initial Calsoft F-90 solution showed no improvement. The application of current (dc) was found to enhance pitting, with no improvement in grain boundary delineation. However, electrolytic etching in 10 wt% chromic acid solution (Cr$_2$O$_3$ in distilled water) resulted in good grain boundary etching at current densities (dc) on the order of 50 amperes per square inch.

Material austenitized at 925°C for 3 hours, and oil quenched from 870°C (heat treatment F) was expected to show the largest prior austenite grain size. The time required to cool the salt bath from 925°C to 870°C was approximately 1½ hours. The smallest prior austenite grain size was expected for the case of an 870°C austenitizing cycle for 1 hour (heat treatment H). However, the ASTM grain size numbers were ASTM 8½ and ASTM 9½, respectively. The insensitivity of prior austenite grain size to austenitizing treatment may be
Figure 33 - Photomicrograph (500X) of Grain Structure in AISI 4335V Steel, Austenitized at 925°C (3 hrs.) and Tempered at 205°C (1 hr.)
due, in part, to the absence of a normalizing cycle in the heat treating procedure. However, in view of the quantity and commercial cost of the heat treatments required in the study, prior normalizing treatments were omitted.

No grain size study was conducted with D6AC steel.

4.4 Experimental Procedure

4.4.1 Specimen preparation

An extensive specimen preparation procedure was used to minimize the amount of surface scale (from heat treatment) or adsorbed contaminants (oxygen and water) on each DCB specimen prior to testing. All acetone used in specimen preparation was of reagent grade.

Following the tempering cycle of heat treatment, each specimen was lightly sand-blasted, along the side groove region. This was done to permit accurate measurement of pre-fatigue crack lengths. All specimens
were then polished to a 400-grit finish, using silicon carbide grinding paper (Wet-or-Dry Tri-M-ite grade). Each specimen was then rinsed in acetone to remove metallic oxide and silicon carbide particles. After the initial rinse, each specimen was ultrasonically cleaned for 5 minutes in a bath of acetone contained in an Acoustica ultrasonic cleaner. As a final preparation step, each specimen was lightly swabbed with a new, white laboratory towel moistened with acetone. If any discoloration of the towel was observed, the specimen was re-cleaned.

After cleaning, each specimen was stored in a sealed plastic bag containing a small amount of 6-mesh indicating drierite. The enclosed specimens were then stored in dessicatots, also containing indicating drierite, until the pre-fatigue cracking operation. Because of the sharp corners on each specimen, the plastic bags were sometimes pierced. When any color change of the drierite was observed, the plastic bag and contained drierite were immediately changed.
4.4.2 Pre-fatigue cracking procedure

On the basis of the Gallagher design of the DGB specimen, the conditions of linear dependence of stress intensity on applied load, and the linear dependence of crack opening displacement on crack extension, are satisfied only in a definite range of the variable \( a/W \). As measured from the tip of the \( 45^\circ \) notch at the end of the 1/16" sawcut, the crack length requirement is: \( 1.21 < a < 2.53 \) inches.

Therefore, crack extension may be measured over a distance of 1.32 inches (for the specimen used in this study). However, crack extension measurements require an initial crack length of 1.21".

In order to minimize the time required to test each specimen, pre-fatigue cracks were propagated to within 0.20" of the constant-\( K_I \) zone. To introduce such fatigue cracks, a Krouse fatigue machine (constant deflection type) was used at the Battelle Memorial Institute in Columbus, Ohio. The fatigue apparatus is shown in Figure 34. Crack extension was monitored
Figure 34 - Krouse Fatigue Apparatus
using a Gaertner travelling-stage microscope. Final crack length measurements were made using the same microscope. The measurements were found to be reproducible to ±0.001". Fatigue loading was of the tension-tension type, with an initial maximum load of 2500 lbs., and a minimum load of 250 lbs. These values were chosen after preliminary fatigue cracking of two trial specimens, described in Section 4.2.3.6. Higher loads (4000 lbs. max., 400 lbs. min.) resulted in rapid running of the crack. Lower loads (2000 lbs. max., 200 lbs. min.) resulted in excessive time requirements for the pre-fatigue cracking operation. The fatiguing of each specimen required 31,000 to 105,000 cycles (depending upon material and heat treatment), with the fatigue load being reset once during the pre-fatigue cracking operation. Final pre-fatigue crack lengths for the AISI 4335V steel specimens were 1.02 to 1.25 inches. The crack lengths for the D6AC steel specimens were in the range 1.07 to 1.15 inches.

In order to determine the accuracy of the pre-
fatigue crack length measurements, the surface of one of the two trial specimens was marked at the apparent tip of the fatigue crack, as measured with the Gaertner microscope. The specimen was then fractured in air, and the center crack length was found to be within 1/16" of the scribe mark on the specimen surface. In nearly all cases, the mid-thickness pre-fatigue crack length was less than the value at the surface, the difference being less than 1/16".

In order to check fatigue machine alignment, crack lengths were measured on both sides of eight test specimens (both grades of steel). In all cases, the crack length difference was \( \leq 0.025" \).

The calibration data for the Krouse fatigue machine, in conjunction with the maximum beam deflection (inches), permit the calculation of the maximum applied load. For the case of an AISI 4335V steel specimen, the calculations were performed, using the deflection value at the end of the pre-fatigue cracking operation. The resulting maximum load value was 1971 lbs.
Following the pre-fatigue cracking operation, the specimens were again stored in dessicators containing indicating drierite. Subsequent handling of the specimens was done using lint-free gloves.

4.4.3 Data analysis techniques

Displacement-time data (up to 20 values) were obtained for each set of test conditions, in either a gaseous environment or in 3 1/2% sodium chloride solution. The data were then treated by least squares analysis (138) to obtain the steady state displacement rate. By the previously described relationship between crack opening displacement and crack extension for this specimen geometry (Section 4.2.1), the crack velocity was calculated. In determining the crack velocity - gas pressure relationships, the velocity-pressure data were again treated by the least squares analysis. Confidence limits on pressure dependence relationships were calculated using regression analysis techniques described by Guttman and Wilks (139). In all cases
where slow crack growth rates were significant, only steady state displacement rates were treated by the first power least squares analysis (138).

4.4.4 Experimental techniques in gaseous environment testing

In conducting gaseous environment tests, it is of major importance that the observed displacement be due to crack growth, and not to extraneous sources (initial formation of plastic zone at crack tip, creep of threads in loading rods, etc.). For this reason, with the test load applied to each specimen, the observed displacement rate was required to be ≤ 50 micro-inches per hour, prior to admission of the test gas. Using the compliance equation (Section 4.2.1) for the specimen, and a $K_I$ value of 20.8 ksi-in$^{1/2}$ (1000 lbs. load), this displacement rate corresponds to an apparent crack velocity of $1.7 \times 10^{-6}$ in/sec, well below any velocity value reported in the study.

Since each specimen was under load, crack growth generally occurred immediately on the admission of a
test gas which produced cracking. In view of this, high gas flow rates (and redundant gas train purification steps) were used to obtain the desired test pressure in the system (approximately 50 liter volume) within a 1 to 3 minute time period. The initial use of an Englehard Industries palladium diffusion purifier (Model 0-50) for hydrogen gas purification did not satisfy this flow rate requirement.

Prior to the evacuation of the test chamber, the specimen was aligned under an applied load of 400 lbs. In order to obtain a relatively clean crack tip surface, this load was not increased to the desired test value until the system pressure was less than $5 \times 10^{-6}$ torr.

In hydrogen gas environments, it was required that the test load be increased to approximately the prior fatigue load (2000 lbs.) in order to initiate slow crack growth. For the case of desired test loads less than 2000 lbs., such pre-loading was done in the presence of approximately 100 torr of hydrogen gas. When cracking occurred, the load was decreased, in
increments of 200-400 lbs., until steady state cracking was observed at the desired test load. Such initial crack growth was observable on the final fracture surface, and therefore not included in the correlation of experimental with predicted crack extensions. Following the initiation procedure, the system was re-evacuated and held at < $3 \times 10^{-6}$ torr pressure for at least one half hour, prior to backfilling to the desired test gas pressure.

The maximum test duration was 3 hours. The pressure rise of the system, as measured with both Alphatron and hot cathode ionization gauges, was typically $3 \times 10^{-3}$ torr/hour. At a test pressure of 100 torr, a 3 hour test duration gives a 100 ppm impurity level in the test gas environment, comparing with the nominal impurities in the test gases themselves.

4.4.5 Pumping and bake-out procedures

Analysis of the residual gases in the test chamber, using an AeroVac Model AVA1 Residual Gas Analyzer
(magnetic sector mass spectrometer), showed the major contaminant to be water vapor. In view of this fact, and the possibility of oil backstreaming, two pumping (and trapping) procedures were employed during the course of the test program.

Initial testing was done using Santovac 5 work fluid (Monsanto Co., St. Louis, Missouri), with external L-shaped glass traps immersed in 1-liter dewars containing liquid nitrogen. Figure 27 shows such a liquid nitrogen trap. A similar trap, containing Ultek molecular sieve material, was used in the foreline. Frequent cracking of the work fluid, however, required a change of pumping procedure. Dow Corning 704 diffusion pump fluid was used, in conjunction with a cryogenic chevron baffle above the diffusion pump. Figure 35 shows the methanol pumping system used to cool the baffle. The circulating pump was a polyethylene centrifugal pump (Part No. 54902-000, VWR Scientific, Columbus, Ohio). The temperature of the methanol at the exhaust of the baffle trap was
CVC Cryogenic Chevron Baffle

Vacuum Hose

Centrifugal Poly - Pump

Double - Walled Vacuum Dewar For Dry Ice - Methanol Bath

Stainless Steel Tubing, \( \frac{1}{4} \) O.D. x 0.005", Immersed in Bath

Figure 35 - Methanol - Dry Ice System Used For Cooling Cryogenic Baffle In Vacuum System
checked on several occasions, and always found to be -40°C or below. No difference was observed in the experimental results, as relating to the change of pumping procedure. The cryogenic chevron baffle trap was used whenever the system was pumped to pressures less than 0.20 torr.

Prior to a change of the test gas environment, the system above the 4" gate valve was baked at 150°C. This was done to remove as much of the prior test gas as possible. The bake-out temperature was measured with a chromel-alumel thermocouple located on the inner wall of the vacuum chamber. The system temperature was controlled using Briskeat heating tapes.

During each bake-out cycle, the system was heated and rough pumped until the foreline pressure allowed operation of the diffusion pump (approximately 0.1 torr). The system was subsequently baked for 24 hours. In all cases, the accelerometer and prior test specimen were removed before bake-out. Prior to (for six hours) and during cooling of the system, the cryogenic baffle trap was operated. In addition, two copper screen trays
(1\frac{1}{2}" X 5" X \frac{1}{2}"), containing Ultek molecular sieve material, were placed in the test chamber prior to bake-out. The sieve trays were in contact with the chamber bottom (not directly heated by Briskeat tapes), and were present in order to trap diffusion or roughing pump oil during the slower cooling of the heated portions of the system.

Following bake-out, the ultimate vacuum was approximately 10^{-7} torr. The vacuum obtained prior to each test was typically 3 \times 10^{-6} torr. Using this procedure, the prior test gas constitutes approximately 3\% of the residual gas in the system - prior to backfilling with the desired test gas environment.

In order to minimize the effect of contaminant gas desorption from the walls of the system during an actual test, the system was backfilled after bake-out with either the subsequent test gas or an inert gas. Prior to testing with \text{H}_2\text{S}, \text{HCl}, \text{HBr}, \text{D}_2, \text{Cl}_2, \text{or NH}_3, the system was backfilled with purified argon. Prior to \text{H}_2, \text{CH}_4, \text{or C}_2\text{H}_2 tests, the system was backfilled
with the actual test gas. After backfilling, it was required that the system be opened to air for $\frac{1}{2}$ to 1 hour in order to place a new specimen and the accelerometer in the test chamber.

4.4.6 Study of slow crack growth in a salt water environment

Crack velocity was measured as a function of both strength level and applied stress intensity for AISI 4335V steel in the aqueous environment (3.5% sodium chloride solution). Three strength levels were chosen as defined by tempering temperatures of 205°C, 315°C, and 540°C. Specific heat treatments to achieve these strength levels (Table 8) were G, H, and J, respectively. Specimens tempered at 205°C and 540°C were tested on the experimental apparatus described in Section 4.2.2. Specimens tempered at 315°C were compared to 205°C tempered specimens using a second loading system and LVDT device. All tests were conducted at room temperature (22 - 27°C).
4.4.7 Slow crack growth studies in a pure hydrogen gas environment

Crack velocities were measured as a function of applied stress intensity and strength level for AISI 4335V steel in 300 torr H₂ gas. The specimen heat treatments were G, H, and J. Crack velocity was also measured as a function of applied stress intensity for D6AC steel (heat treatments K and L).

At stress intensity values of 20.8, 41.6, and 54.1 ksi-in³, crack velocities were measured for 205°C tempered AISI 4335V steel as a function of hydrogen gas pressure. The hydrogen pressure was varied from 77 torr to 760 torr for tests at \( K_I = 20.8 \text{ ksi-in}^\frac{3}{2} \) and \( K_I = 54.1 \text{ ksi-in}^\frac{3}{2} \). For the pressure dependence study at a stress intensity of 41.6 ksi-in³, the hydrogen pressure was varied from 10 torr to 300 torr.

Crack velocity was measured as a function of hydrogen pressure for 315°C tempered AISI 4335V steel (heat treatment H) at stress intensity values of 25.0 and 54.1 ksi-in³. Hydrogen pressure for testing at
\( K_I = 25.0 \text{ ksi-in}^{1/2} \) was varied from 93 to 760 torr. Hydrogen pressures of 70 to 487 torr were investigated in the testing at \( K_I = 54.1 \text{ ksi-in}^{1/2} \).

For the case of D6AC steel, crack velocity was measured as a function of hydrogen pressure for material tempered at 540°C and 595°C. For 540°C tempered steel, the hydrogen pressure was varied from 97 to 403 torr (at \( K_I = 33.3 \text{ ksi-in}^{1/2} \)), and from 85 to 553 torr (at \( K_I = 83.2 \text{ ksi-in}^{1/2} \)). For 595°C tempered D6AC steel, the hydrogen pressure was varied from 72 to 556 torr (at \( K_I = 121 \text{ ksi-in}^{1/2} \)) and from 76 to 760 torr (at \( K_I = 133 \text{ ksi-in}^{1/2} \)).

In all studies of pressure dependence, the hydrogen pressure was increased during the course of the test. All testing was performed at room temperature (22 - 27°C). With the exception of D6AC steel tempered at 595°C, one specimen was used for each hydrogen pressure dependence study.

Acoustic emission signals were recorded during all tests in hydrogen gas environments.
4.4.8 Slow crack growth studies in pure hydrogen sulfide gas

Crack velocity was measured as a function of applied stress intensity for 205°C tempered AISI 4335V steel in 0.40 torr hydrogen sulfide gas. For \( H_2S \) pressures of 0.15 to 1.6 torr, the crack velocity in the same steel (heat treatment A) was measured as a function of \( H_2S \) pressure at \( K_I = 20.8 \text{ ksi-in}^{\frac{3}{2}} \). For the same steel and heat treatment, the crack velocity was measured as a function of \( H_2S \) pressure at \( K_I = 54.1 \text{ ksi-in}^{\frac{3}{2}} \). The hydrogen sulfide pressure, in the latter study, was varied from 0.07 to 0.43 torr.

4.4.9 Study of slow crack growth kinetics in a deuterium gas environment

Of major importance in determining the rate-controlling process in the cracking of high strength steels exposed to molecular hydrogen gas environments is the effect of molecular (or atomic) mass on the kinetics of crack propagation. For this reason, crack
velocities were measured in gaseous deuterium, a hydrogen isotope of atomic mass 2.

A 205°C tempered specimen of AISI 4335V steel (heat treatment F) was used in the study. Crack velocities were measured at applied stress intensities of 25.0 and 52.0 ksi-in\(^{\frac{1}{2}}\). For each stress intensity value, the test chamber was backfilled to 300 torr H\(_2\), and three crack velocity measurements were made. The system was then evacuated to < 2 \times 10^{-6} \text{ torr}, and maintained in this pressure range for two hours. The test chamber was then backfilled to 300 torr pressure with D\(_2\) gas. Three crack velocity measurements were again taken. The crack velocity ratio (H\(_2\) environment vs. D\(_2\) environment) was then calculated for each stress intensity value. Pressure measurements were made using a Speedi-Vac CG3 gauge, described in Section 4.2.3.2.

4.4.10 Slow crack growth studies in other gaseous environments

The purpose of this study is the measurement of
crack growth kinetics in gaseous environments of widely different chemisorption behavior on iron (all containing hydrogen), as well as the cracking behavior of high strength steel in chlorine gas (as a non-hydrogenated species). All gas pressures were measured with Bourdon-tube type gauges. At least two specimens of 205°C tempered AISI 4335V steel were tested in each environment to verify the test results. Test pressures were 100 torr for HCl and HBr environments, and 300 torr for NH₃, C₂H₂, CH₄, and Cl₂ environments. For each environment, crack velocity was measured as a function of applied stress intensity.

4.4.11 Crack velocity studies in H₂/H₂S gaseous mixtures

Crack velocities were measured for AISI 4335V steel (tempered at 315°C) as a function of H₂S additions to the gaseous hydrogen environment.

In the first portion of the study, small amounts of H₂S (< 0.1 torr) were admitted to the test chamber, and quickly diluted with molecular hydrogen gas. The
resulting molecular hydrogen gas pressure, in all cases, was 100 torr. Crack velocities were measured (at $K_I = 25.0 \text{ ksi-in}^{1/2}$) as a function of hydrogen sulfide pressure, and for the same test specimen.

In the second study, the objective was to illustrate the effect of sulfur, in addition to hydrogen, on the cracking process. Crack velocity was again measured as a function of $H_2S$ partial pressure for AISI 4335V steel tempered at $315^\circ C$. The applied stress intensity was $25.0 \text{ ksi-in}^{1/2}$. In each test, 0.42 torr $H_2S$ was admitted to the test chamber. The crack velocity was measured. The $H_2S$ was then diluted to 2.1 vol% (admission of 20 torr $H_2$) and 4.4 vol% (admission of 9.5 torr $H_2$). Crack velocities were estimated immediately after dilution, and were also measured after a steady state crack growth rate was again attained.

4.4.12 Crack velocity studies in $H_2/H_2O$ and $H_2/O_2$ gaseous mixtures

The effects of oxygen gas and water vapor on the
crack growth kinetics in a H\textsubscript{2} gas environment were studied by individually admitting these species to the H\textsubscript{2} environment. The effect of water vapor is significant in that it is the primary contaminant species in the test chamber. Oxygen gas has been shown in the literature to halt the crack growth process in H\textsubscript{2} gas environments.

In the water vapor study, crack velocities were measured for an AISI 4335V steel specimen (tempered at 315°C) in both wet and dry hydrogen gas. Crack velocities were initially measured as a function of dry H\textsubscript{2} gas pressure (at K\textsubscript{I} = 41.6 ksi-in\textsuperscript{1/2}) at pressures of 100 to 500 torr. The test chamber was then re-evacuated to < 2 X 10\textsuperscript{-6} torr. To provide a H\textsubscript{2}/H\textsubscript{2}O mixture, the liquid nitrogen - cooled cold trap in the gas purification train was replaced by two gas washing bottles (Kimax 34/28), each containing approximately 150 cc. of distilled water. After bubbling the purified hydrogen through the water baths for 6 hours (at approximately 5 cc/sec), the humidified hydrogen was admitted to the test chamber. At a stress intensity
of 41.6 ksi-in$, crack velocities were measured as a function of hydrogen pressure, for the humidified hydrogen environment, at hydrogen pressures of 100 to 500 torr.

For the case of a humidified hydrogen environment, hydrogen gas pressures were determined under the assumption that the admitted hydrogen was saturated with water vapor.

In determining the effect of oxygen, the gas was admitted to the test chamber (prior to hydrogen) from a glass vacuum vessel (approximately 250 cc volume). Prior to filling and purging (6 hours) with oxygen, the vessel was opened to the system during pumpdown to $10^{-5}$ torr. The oxygen vessel was then valved off from the system, and purged with oxygen gas until the test. The oxygen gas was of a medical grade (99.5% pure), and was further purified only by passage through a container of indicating drierite.

The pressure rise, on opening the oxygen-filled container to the system, was 4.7 to 4.8 torr. This quantity of oxygen was initially added in each test,
with subsequent rough pumping to the desired oxygen pressure prior to backfilling with hydrogen gas. The reason for the backfilling procedure was the accurate measurement of the oxygen pressure on the low pressure range of the Alphatron gauge. Glass stopcock valves on the oxygen vessel did not permit a regulated flow of oxygen gas into the chamber, and therefore 4.7 torr was a required initial pressure. In addition, the stopcock valves constituted the only required use of vacuum grease in the study. The system was, however, baked prior to additional studies after the H₂/O₂ gaseous testing.

In each test, hydrogen gas was admitted to give pressures (hydrogen) of 100, 250, and 500 torr. The specimens (2) used in the study were 315°C tempered AISI 4335V steel, tested at \( K_I = 41.6 \text{ ksi-in}^\frac{1}{2} \). The investigated oxygen pressures were 0.04, 0.10, 0.40, 0.90, and 4.7 torr.
4.4.13 Fractography studies

Fracture surfaces of 205°C tempered AISI 4335V steel, fractured in dry hydrogen gas, were examined with a Materials Analysis Co. scanning electron microscope. The surfaces of specimens used in hydrogen pressure dependence studies (at $K_I = 20.8, 54.1 \text{ ksi-in}^{\frac{1}{2}}$) were examined. Since hydrogen gas pressure was increased during each crack velocity study, the effect of hydrogen pressure (at constant $K_I$) was determined by examining the fractography of $3/8"$ long specimens cut from the initial and final regions of the slow crack growth zone. A similar study was conducted with 315°C tempered material tested in hydrogen gas a stress intensity values of 25.0 and 54.1 ksi-in$^{\frac{1}{2}}$.

The fractography of 205°C tempered AISI 4335V steel was examined after fracture in a gaseous H$_2$S environment at $K_I$ values of 20.8 and 54.1 ksi-in$^{\frac{1}{2}}$.

D6AC steel specimens, tempered at 540°C and 595°C, were examined with the scanning electron microscope.
For applied stress intensities of 33.3 and 83.2 ksi-in$^{\frac{1}{2}}$, the fractography of 540°C tempered steel was examined in the low and high hydrogen pressure regions of the specimens. The fractography of 595°C tempered material ($K_I = 121, 133$ ksi-in$^{\frac{1}{2}}$) was examined using scanning electron microscope techniques.

Fracture surfaces of 205°C tempered AISI 4335V steel specimens, fractured in 100 torr HCl ($K_I = 45.8$ ksi-in$^{\frac{1}{2}}$), 100 torr HBr ($K_I = 45.8$ ksi-in$^{\frac{1}{2}}$), and 300 torr Cl$_2$ ($K_I = 41.6$ ksi-in$^{\frac{1}{2}}$), were also examined using the same scanning electron microscope.

Transmission electron microscope replicas (two-step plastic carbon) were obtained from the fracture surfaces of 205°C tempered AISI 4335V steel specimens, fractured in hydrogen gas at $K_I = 20.8$ ksi-in$^{\frac{1}{2}}$ and at $K_I = 54.1$ ksi-in$^{\frac{1}{2}}$. After shadowing with chromium (60° angle), the replicas were examined using a Phillips 100B electron microscope.

4.4.14 Auger electron spectroscopy analysis

A 540°C tempered specimen of AISI 4335V steel,
fractured in 30 torr H₂S gas at \( K_I = 25.0 \text{ ksi-in}^\frac{1}{2} \), was examined by Auger techniques.
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STRESS CORROSION CRACKING IN
GASEOUS AND AQUEOUS
ENVIRONMENTS

Volume II

DISSETATION

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George Earl Kerns, M. S. in Met. E.

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1973

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Engineering
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Crack growth in 315°C tempered specimens was seldom confined to the region containing the side grooves (for a 1" crack extension). For this reason, and because of testing on a different loading system, these data were not shown in Figure 36. All crack growth data were, however, obtained from displacement measurements prior to crack growth out of the side
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<th>Stress Intensity (ksi-in$^{\frac{1}{2}}$)</th>
<th>Crack Velocity (in/sec)</th>
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<tr>
<td>4335V</td>
<td>G</td>
<td>16.6</td>
<td>3.45 X 10^{-5}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.0</td>
<td>4.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33.3</td>
<td>5.44</td>
</tr>
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<td></td>
<td></td>
<td>37.4</td>
<td>5.97</td>
</tr>
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<td></td>
<td></td>
<td>41.6</td>
<td>6.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>47.8</td>
<td>7.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.9</td>
<td>7.07</td>
</tr>
<tr>
<td>4335V</td>
<td>J</td>
<td>81.1</td>
<td>6.93 X 10^{-7}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>83.2</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<th>Crack Velocity (in/sec)</th>
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<tr>
<td>4335V</td>
<td>J</td>
<td>85.3</td>
<td>2.24 x 10⁻⁷</td>
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Table 13 - Stress Intensity and Crack Velocity Data for AISI 4335V Steel (Heat Treatment H) in 3½% Sodium Chloride Solution

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4.5.2 Crack growth kinetics in dry hydrogen gas environments

Figure 37 shows the effects of applied stress intensity and strength level on crack velocity for AISI 4335V steel in 300 torr H$_2$ gas. The test data are given in Table 14. Figure 38 shows strength level and stress intensity effects on crack velocity for D6AC steel in 300 torr H$_2$ gas. The data are given in Table 15.

The effect of hydrogen pressure on crack velocity for 205°C tempered AISI 4335V steel, at $K_I = 41.6$ ksi-in$^{1/2}$, is shown in Figure 39. The resulting pressure dependence relationship, by least squares analysis, is:

$$K_I = 41.6 \text{ ksi-in}^{1/2}$$

$$\log (da/dt) = -6.0 + 1.2 \log P_{H_2}$$

where: $da/dt =$ crack velocity,  
(in/sec)  
$P_{H_2} =$ hydrogen pressure,  
(torr)
Figure 37 - Crack Velocity As A Function Of Applied Stress Intensity And Tempering Temperature For AISI 4335V Steel In Hydrogen Gas.
Table 14 - Stress Intensity and Crack Velocity Data for AISI 4335V Steel (Heat Treatments G, H, and J) in 300 Torr Dry H₂ Gas

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Figure 38 - Crack Velocity As A Function Of Applied Stress Intensity And Tempering Temperature For D6AC Steel In Hydrogen Gas
Table 15 - Stress Intensity and Crack Velocity Data for D6AC Steel (Heat Treatments K and L) in 300 Torr Dry H₂ Gas

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Figure 39 - Crack Velocity As A Function Of Hydrogen Pressure For AISI 4335V Steel At $K_I = 41.6$ KSI-in$^{1/2}$
The hydrogen pressure and crack velocity data are given in Table 16.

At stress intensity values of 20.8 and 54.1 ksi-in\(^{3}\), the dependence of crack velocity on hydrogen pressure (for the same material and heat treatment) obeys the following relationships:

\[
K_I = 20.8 \text{ ksi-in}^{3/2}
\]

\[
\log \left( \frac{da}{dt} \right) = -7.8 + 1.7 \log \ P_{H_2}
\]

\[
K_I = 54.1 \text{ ksi-in}^{3/2}
\]

\[
\log \left( \frac{da}{dt} \right) = -5.2 + 0.95 \log \ P_{H_2}
\]

where: \( \frac{da}{dt} = \text{crack velocity,} \) 
\( \text{in/sec} \)

\( P_{H_2} = \text{hydrogen pressure,} \) 
\( \text{torr} \)

The hydrogen pressure and crack velocity data are given in Tables 17 and 18. Figure 40 shows the crack velocity dependence on hydrogen pressure at both stress intensity values.
Table 16 - Hydrogen Pressure and Crack Velocity Data for AISI 4335V Steel (Heat Treatment G) At $K_I = 41.6$ ksi-in$^{\frac{1}{2}}$

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<td>&quot;</td>
<td></td>
<td>52</td>
<td>10.9</td>
</tr>
<tr>
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<td>10.4</td>
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</table>
Table 16 - Continued

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V</td>
<td>G</td>
<td>79</td>
<td>12.3 x 10^-5</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>16.5</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>30.2</td>
<td></td>
</tr>
<tr>
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<td>&quot;</td>
<td>32.4</td>
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</tr>
<tr>
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<td>&quot;</td>
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<td></td>
</tr>
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<td>&quot;</td>
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<tr>
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<td>&quot;</td>
<td>43.3</td>
<td></td>
</tr>
<tr>
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<td>&quot;</td>
<td>60.8</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>62.8</td>
<td></td>
</tr>
<tr>
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<td>&quot;</td>
<td>61.8</td>
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</tr>
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<td>&quot;</td>
<td>&quot;</td>
<td>59.6</td>
<td></td>
</tr>
</tbody>
</table>
Table 17 - Hydrogen Pressure and Crack Velocity Data for AISI 4335V Steel (Heat Treatment A) At $K_I = 20.8$ ksi-in$^{1/2}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V A</td>
<td>71</td>
<td>1.69 x 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>2.13</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>161</td>
<td>8.38</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>7.51</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>242</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>371</td>
<td>36.6</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>37.2</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>530</td>
<td>63.1</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>66.2</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>760</td>
<td>105</td>
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</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>102</td>
<td></td>
</tr>
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</table>
Table 18 - Hydrogen Pressure and Crack Velocity Data for AISI 4335V Steel (Heat Treatment A) At $K_I = 54.1$ ksi-in$^{1/2}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V A</td>
<td></td>
<td>77</td>
<td>$4.08 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>163</td>
<td>8.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>249</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>373</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>553</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>760</td>
<td>34.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.8</td>
<td></td>
</tr>
</tbody>
</table>
Figure 40 - Crack Velocity As A Function Of Applied Stress Intensity And Hydrogen Pressure For AISI 4335V Steel Tempered At 205°C
The hydrogen pressure dependence of crack velocity in 315°C tempered AISI 4335V steel was determined at stress intensity values of 25.0 and 54.1 ksi-in$^{1/2}$. Figure 41 shows the observed pressure dependencies. The least squares analysis of hydrogen pressure and crack velocity data results in the following relationships:

\[
\frac{K_I}{25.0 \text{ ksi-in}^{1/2}} = \log \left( \frac{\text{da/dt}}{\text{in/sec}} \right) = -8.2 + 1.9 \log P_{H_2}
\]

\[
\frac{K_I}{54.1 \text{ ksi-in}^{1/2}} = \log \left( \frac{\text{da/dt}}{\text{in/sec}} \right) = -5.7 + 1.1 \log P_{H_2}
\]

where: \( \text{da/dt} = \text{crack velocity, (in/sec)} \)

\( P_{H_2} = \text{hydrogen pressure, (torr)} \)

The hydrogen pressure and crack velocity data are given in Tables 19 and 20.

The hydrogen pressure dependence of crack velocity in D6AC steel, tempered at 540°C, showed similar
ENVIRONMENT - H₂ GAS

MATERIAL - AISI 4335V STEEL TEMPERED AT 315°C (ULTIMATE TENSILE STRENGTH ~ 241 KSI)

Figure 41 - Crack Velocity As A Function Of Applied Stress Intensity And Hydrogen Pressure For AISI 4335V Steel Tempered At 315°C
Table 19 - Hydrogen Pressure and Crack Velocity Data for AISI 4335V Steel (Heat Treatment H) At $K_I = 25.0 \text{ ksi-in}^{\frac{1}{2}}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V</td>
<td>H</td>
<td>93</td>
<td>$2.01 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>176</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>271</td>
<td>9.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>427</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>533</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>760</td>
<td>36.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>104</td>
<td></td>
</tr>
</tbody>
</table>
Table 20 - Hydrogen Pressure and Crack Velocity Data for AISI 4335V Steel (Heat Treatment H) At $K_I = 54.1$ ksi-in$^{\frac{1}{2}}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V</td>
<td>H</td>
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<td>$1.70 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>121</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>211</td>
<td>3.56</td>
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<tr>
<td></td>
<td></td>
<td>313</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>408</td>
<td>6.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>487</td>
<td>6.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1313</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1408</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1487</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1537</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1547</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1548</td>
<td>15.4</td>
</tr>
</tbody>
</table>
behavior. Figure 42 shows the observed pressure dependencies. The pressure dependence equations are:

\[
K_I = 33.3 \text{ ksi-in}^{\frac{1}{2}}
\]

\[
\log (\frac{da}{dt}) = -9.7 + 2.3 \log P_{H_2}
\]

\[
K_I = 83.2 \text{ ksi-in}^{\frac{1}{2}}
\]

\[
\log (\frac{da}{dt}) = -6.4 + 1.2 \log P_{H_2}
\]

where: \( \frac{da}{dt} = \text{crack velocity,} \)
\( (\text{in/sec}) \)
\( P_{H_2} = \text{hydrogen pressure,} \)
\( (\text{torr}) \)

The hydrogen pressure and crack velocity data are given in Tables 21 and 22.

For D6AC steel tempered at 595°C, hydrogen pressure dependencies were determined at stress intensity values of 121 and 133 ksi-in^{\frac{1}{2}}. Figure 43 shows the observed pressure dependence behavior. The resulting hydrogen pressure dependence equations are:
Figure 42 - Crack Velocity As A Function Of Applied Stress Intensity And Hydrogen Pressure For D6AC Steel Tempered At 540°C
Table 21 - Hydrogen Pressure and Crack Velocity Data for D6AC Steel (Heat Treatment K) At $K_I = 33.3$ ksi-in$^{\frac{3}{2}}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC K</td>
<td></td>
<td>97</td>
<td>$0.77 \times 10^{-5}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.68</td>
</tr>
<tr>
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<td>154</td>
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<td>244</td>
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<td>7.49</td>
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<td>&quot;</td>
<td>283</td>
<td>11.3</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>11.2</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>325</td>
<td>14.3</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>14.7</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>403</td>
<td>20.9</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>22.1</td>
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</table>
### Table 21 - Continued

<table>
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<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>K</td>
<td>484</td>
<td>$31.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;33.3&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>691</td>
<td>&quot;52.3&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;53.0&quot;</td>
</tr>
</tbody>
</table>
Table 22 - Hydrogen Pressure and Crack Velocity Data for D6AC Steel (Heat Treatment K) At $K_I = 83.2$ ksi-in$^\frac{1}{2}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>K</td>
<td>85</td>
<td>$8.44 \times 10^{-5}$</td>
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<td>7.89</td>
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<td>127</td>
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<td>15.6</td>
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<td>&quot;</td>
<td>166</td>
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<td>&quot;</td>
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<td>84.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>81.1</td>
</tr>
</tbody>
</table>
ENVIROMENT - H_2 GAS

MATERIAL - D6AC STEEL
TEMPERED AT 595°C
ULTIMATE TENSILE STRENGTH - 219 KSI

\[ K_1 = 120.64 \text{ ksi} \cdot \text{in}^{1/2} \left( P_{H_2}^{1.07} \right) \]

\[ K_1 = 133.12 \text{ ksi} \cdot \text{in}^{1/2} \left( P_{H_2}^{1.06} \right) \]

Hydrogen Pressure (Torr) - Log Scale

Figure 43 - Crack Velocity As A Function Of Applied Stress Intensity And Hydrogen Pressure For D6AC Steel Tempered At 595°C
where: $\frac{da}{dt} = \text{crack velocity, (in/sec)}$

$P_{H_2} = \text{hydrogen pressure, (torr)}$

The hydrogen pressure and crack velocity data are given in Table 23.

4.5.3 Crack growth kinetics in hydrogen sulfide gas environments

Figure 44 shows crack velocity as a function of applied stress intensity for 205°C tempered AISI 4335V steel in 0.40 torr $H_2S$ gas. The stress intensity and crack velocity data are given in Table 24. In Figure 44 results are also shown for the same material
Table 23 - Hydrogen Pressure and Crack Velocity Data for D6AC Steel
(Heat Treatment L) At $K_I = 121 \text{ ksi-in}^{\frac{1}{2}}$
And $K_I = 133 \text{ ksi-in}^{\frac{1}{2}}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress Intensity (ksi-in$^{\frac{1}{2}}$)</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>121</td>
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<td>2.03</td>
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<td>241</td>
<td>3.95</td>
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<td>4.40</td>
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<td>301</td>
<td>6.25</td>
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<td>6.56</td>
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<td>9.71</td>
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<td></td>
<td></td>
<td>10.3</td>
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</table>
Table 23 - Continued

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress Intensity (ksi-in$^{1/2}$)</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>121</td>
<td>760</td>
<td>$18.6 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>133</td>
<td>76</td>
<td>1.84</td>
</tr>
<tr>
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<td>&quot;</td>
<td>&quot;</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
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<td>7.92</td>
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<td>&quot;</td>
<td>10.8</td>
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</tbody>
</table>
Table 23 - Continued

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress Intensity (ksi-in²)</th>
<th>Hydrogen Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>133</td>
<td>556</td>
<td>20.0 x 10⁻⁵</td>
</tr>
<tr>
<td>&quot;</td>
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<td>&quot;</td>
<td>760</td>
<td>31.7</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>23.4</td>
</tr>
</tbody>
</table>
Crack Velocity (in/sec) - Log Scale

\[ \text{Fractured at } K_I = 70.7 \text{ ksi - in}^{\frac{1}{2}} \]

Environments:
- ○ - 0.40 Torr H\(_2\)S
- □ - 300 Torr H\(_2\)
- △ - 3\(\frac{1}{2}\) % NaCl Solution, pH = 6.0

MATERIAL - AISI 4335V STEEL
TEMPERED AT 205°C
Ultimate Tensile Strength - 286,000 psi

Figure 44 - Crack Velocity As A Function Of Applied Stress Intensity For AISI 4335V Steel (Tempered At 205°C) In Salt Water, H\(_2\) Gas, And H\(_2\)S Gas Environments
Table 24 - Stress Intensity and Crack Velocity Data for AISI 4335V Steel (Heat Treatment A) In 0.40 Torr Hydrogen Sulfide Gas

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Stress Intensity (ksi-in(^{1/2}))</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V</td>
<td>A</td>
<td>20.8</td>
<td>4.88 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.0</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29.1</td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37.4</td>
<td>29.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45.8</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.8</td>
<td></td>
</tr>
</tbody>
</table>
(and heat treatment) in gaseous hydrogen and in aqueous sodium chloride environments.

Figure 45 shows the effect of hydrogen sulfide pressure on crack velocity, at stress intensity values of 20.8 and 54.1 ksi-in$^{1/2}$. The resulting pressure dependence relationships, for 205°C tempered AISI 4335V steel, were found to be:

For $K_I = 20.8$ ksi-in$^{1/2}$

$$\log (da/dt) = -2.3 + 1.4 \log P_{H_2S}$$

For $K_I = 54.1$ ksi-in$^{1/2}$

$$\log (da/dt) = -2.0 + 1.1 \log P_{H_2S}$$

where: $da/dt =$ crack velocity, (in/sec)

$P_{H_2S} =$ hydrogen sulfide pressure (torr)

The crack velocity and hydrogen sulfide pressure data are given in Tables 25 and 26.
MATERIAL - AISI 4335V STEEL
TEMPERED AT 205°C
(ULTIMATE TENSILE STRENGTH = 286 KSI)

Figure 45 - Crack Velocity As A Function Of Applied Stress Intensity And Hydrogen Sulfide Pressure For AISI 4335V Steel Tempered At 205°C
Table 25 - Hydrogen Sulfide Pressure
And Crack Velocity Data for AISI 4335V
Steel (Heat Treatment A) At
$K_I = 20.8$ ksi-in$^{1/2}$

<table>
<thead>
<tr>
<th>Material Treatment</th>
<th>Hydrogen Sulfide Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V A</td>
<td>$1.51 \times 10^{-1}$</td>
<td>$2.75 \times 10^{-4}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>2.76 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.50 &quot;</td>
<td>6.47 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>6.88 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>3.37 &quot;</td>
<td>14.6 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>14.9 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.10 &quot;</td>
<td>18.3 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>16.8 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>5.03 &quot;</td>
<td>21.5 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>24.1 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>7.69 &quot;</td>
<td>31.3 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>31.4 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>16.0 &quot;</td>
<td>72.8 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>73.4 &quot;</td>
</tr>
</tbody>
</table>
Table 26 - Hydrogen Sulfide Pressure and Crack Velocity Data for AISI 4335V Steel (Heat Treatment A) At $K_I = 54.1 \text{ ksi-in}^{\frac{1}{2}}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Hydrogen Sulfide Pressure (torr)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V A</td>
<td>&quot;</td>
<td>$0.67 \times 10^{-1}$</td>
<td>$6.17 \times 10^{-4}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>$1.38$</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>$2.21$</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>$2.50$</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>$2.95$</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>$3.27$</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>$4.26$</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
4.5.4 Crack growth kinetics in other pure gaseous environments

Crack velocities in deuterium gas (300 torr pressure) are given in Table 27 for 205°C tempered AISI 4335V steel. Table 27 also gives crack velocity data for the same test specimen in 300 torr hydrogen gas. At an applied stress intensity value of 25.0 ksi-in$^{1/2}$, the crack velocity ratio ($H_2$ environment vs. $D_2$ environment) was 2.50/2.75. For a stress intensity value of 52.0 ksi-in$^{1/2}$, the crack velocity ratio was 2.11/2.44.

Figure 46 shows crack velocity as a function of applied stress intensity for 205°C tempered AISI 4335V steel in the pure gases NH$_3$, CH$_4$, C$_2$H$_2$, HCl, HBr, and Cl$_2$. Also shown in Figure 46 are the crack velocities observed in the hydrogen - deuterium study.

4.5.5 Crack growth kinetics in $H_2/H_2S$ gaseous mixtures

Figure 47 shows crack velocity values in 315°C tempered AISI 4335V steel as a function of hydrogen
Table 27 - Crack Velocity Data for AISI 4335V Steel Specimen (Heat Treatment F) Tested In 300 Torr Hydrogen Gas and 300 Torr Deuterium Gas

<table>
<thead>
<tr>
<th>Stress Intensity (ksi-in$^{\frac{1}{2}}$)</th>
<th>Environment (H$_2$ or D$_2$)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>H$_2$</td>
<td>$3.08 \times 10^{-4}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>3.11</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>3.10</td>
</tr>
<tr>
<td>&quot;</td>
<td>D$_2$</td>
<td>1.20</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.13</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.23</td>
</tr>
<tr>
<td>52.0</td>
<td>H$_2$</td>
<td>$10.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>11.4</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>10.9</td>
</tr>
<tr>
<td>&quot;</td>
<td>D$_2$</td>
<td>4.68</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>5.16</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>4.74</td>
</tr>
</tbody>
</table>
AISI 4335V Steel, Tempered at 205°C (Ultimate Tensile Strength - 284 KSI)

Figure 46 - Crack Velocity As A Function Of Stress Intensity In Several Gaseous Environments
sulfide partial pressure in a H₂/H₂S gaseous mixture. Table 28 gives crack velocity data for 315°C tempered AISI 4335V steel (at $K_I = 25.0$ ksi-in$^{1/2}$) in pure H₂S gas, prior to and after dilution of the H₂S gas with H₂ gas.

4.5.6 Crack growth kinetics in moist and dry hydrogen gas environments

Figure 48 shows the effect of water vapor on crack growth kinetics in 315°C tempered AISI 4335V steel exposed to a hydrogen gas environment. For an applied stress intensity value of 41.6 ksi-in$^{1/2}$, the crack velocity and hydrogen pressure data were found to obey the following relationships:

\[
\begin{align*}
\text{Dry H}_2 & : & \log (\frac{da}{dt}) &= -4.5 + 0.80 \log P_{H_2} \\
\text{Wet H}_2 & : & \log (\frac{da}{dt}) &= -4.6 + 0.52 \log P_{H_2}
\end{align*}
\]

where: $\frac{da}{dt} = \text{crack velocity,}$

\[\text{in/sec}\]

$P_{H_2} = \text{hydrogen pressure,}$

\[\text{torr}\]
Crack Velocity (in/sec) x 10^4

100 torr H₂ Gas, with Additions of H₂S at $K_I = 25.0$ ksi - in^{1/2}

AISI 4335V Steel, Tempered at 315°C (Ultimate Tensile Strength - 248 KSI)

Figure 47 - Crack Velocity In A Hydrogen - Hydrogen Sulfide Gas Mixture As A Function Of Hydrogen Sulfide Concentration
Table 28 - Crack Velocities Observed
In 0.42 Torr Hydrogen Sulfide Gas, Before
And After Dilution With Pure Dry Hydrogen\(^a\)

<table>
<thead>
<tr>
<th>Initial Velocity (in/sec)</th>
<th>Volume % H(_2)S</th>
<th>Crack Velocity After Dilution</th>
<th>Final Velocity, Time to Reach Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td>In 0.42 Torr H(_2)S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.02 (\times 10^{-3})</td>
<td>4.4</td>
<td>6.8 (\times 10^{-4})</td>
<td>1.90 (\times 10^{-3}) 24 sec.</td>
</tr>
<tr>
<td>2.10</td>
<td></td>
<td></td>
<td>2.02</td>
</tr>
<tr>
<td>2.20</td>
<td>2.1</td>
<td>4.4 (\times 10^{-4})</td>
<td>1.80 (\times 10^{-3}) 86 sec.</td>
</tr>
<tr>
<td>2.22</td>
<td></td>
<td></td>
<td>2.00</td>
</tr>
</tbody>
</table>

\(^a\) - Data obtained using AISI 4335V steel (Heat Treatment B) At \(K_I = 25.0\) ksi-in\(^{\frac{1}{2}}\)
**MATERIAL - AISI 4335V STEEL**
*Tempered at 315°C*
**Ultimate Tensile Strength - 248 KSI**
($K_I = 41.60$ KSI $\cdot$IN$^{-2}$)

**Figure 48 - Effect Of Water Vapor On the Crack Velocity**
For AISI 4335V Steel (Tempered At 315°C) In Hydrogen Gas
The calculations for a moist H\textsubscript{2} environment are based on the assumption that the hydrogen gas was saturated with water vapor. The vapor pressure of water was found in published data (140) to be 24 torr at 25\degree C. The total gas pressure (H\textsubscript{2} + H\textsubscript{2}O) in the gas train was assumed to be 760 torr.

Calculation of the velocity - gas pressure relationship in the latter case (wet H\textsubscript{2}) was also performed under the assumption that no moisture was present in the hydrogen gas. The resulting pressure dependence equation is:

\[
\log (\frac{da}{dt}) = -4.6 + 0.50 \log P_{H_2}
\]

where: \( \frac{da}{dt} \) = crack velocity, (in/sec)

\( P_{H_2} \) = hydrogen pressure, (torr)

4.5.7 Crack growth kinetics in H\textsubscript{2}/O\textsubscript{2} gaseous mixtures

Figures 49 and 50 show the effect of oxygen additions (up to 0.9 torr) on the crack velocity in
315°C tempered AISI 4335V steel in hydrogen gas environments. The applied stress intensity was 41.6 ksi-in$^{1/2}$. On the addition of 4.7 torr O$_2$ gas, no crack growth was observed in 665 torr H$_2$ gas during a 30 minute exposure. At lower oxygen pressures (0.04 to 0.9 torr), no incubation times were observed for cracking in H$_2$ gas ($\equiv$ 100 torr pressure).

4.5.8 Acoustic emission results

The acoustic emission pattern for a 205°C tempered AISI 4335V steel specimen, fractured in 300 torr H$_2$ gas, was examined by measuring both acoustic emissions, per se, and acoustic emission counts. Figure 51 shows acoustic emission rate and acoustic emission count rate as functions of applied stress intensity. Tables 29 and 30 give the acoustic emission, acoustic emission count, and applied stress intensity data for the test. Table 31 gives average crack velocity and crack increment (crack extension per acoustic emission) values for the stress intensities used in the test.
Figure 49 - Effect Of Oxygen Additions On the Crack Velocity In Hydrogen Gas For AISI 4335V Steel Tempered At 315°C

MATERIAL - AISI 4335V STEEL TEMPERED AT 315°C
ULTIMATE TENSILE STRENGTH - 248 KSI
($K_I = 41.60$ KSI $\cdot $IN$^{1/2}$)
Figure 50 - Effect Of Oxygen Additions On the Crack Velocity In Hydrogen Gas For AISI 4335V Steel Tempered At 315°C
Figure 51 – Acoustic Emission and Count Rates As Functions Of Applied Stress Intensity For AISI 4335V Steel (Tempered At 205°C) Fractured In Hydrogen Gas
<table>
<thead>
<tr>
<th>Stress Intensity (ksi-in(^2))</th>
<th>Time (minutes)</th>
<th>Total Acoustic Emissions (3 measurements)</th>
<th>Average Emission Rate (emissions per minute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.7</td>
<td>0.5</td>
<td>0,0,0</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.0,0,0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>2,3,2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>3,4,3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>3,4,3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>3,4,3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>5,6,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>5,6,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>5,6,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>6,7,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>6,7,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>6,7,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stress Intensity (ksi-in$^2$)</td>
<td>Time (minutes)</td>
<td>Total Acoustic Emissions (3 measurements)</td>
<td>Average Emission Rate (emissions per minute)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>----------------</td>
<td>------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>20.8</td>
<td>0.5</td>
<td>0,0,0</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0,0,0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0,0,0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1,0,1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>2,1,2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>2,1,2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>2,1,2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>3,1,3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>5,4,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>5,4,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>5,4,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>5,4,5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stress Intensity (ksi-in(^3))</td>
<td>Time (minutes)</td>
<td>Total Acoustic Emissions (3 measurements)</td>
<td>Average Emission Rate (emissions per minute)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>---------------</td>
<td>------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>25.0</td>
<td>0.5</td>
<td>3,3,3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4,4,4</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>4,4,4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>5,5,5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>6,6,6</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>6,6,6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>6,6,6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>6,6,6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>6,6,6</td>
<td></td>
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<tr>
<td></td>
<td>5.5</td>
<td>6,6,6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>6,6,6</td>
<td></td>
</tr>
<tr>
<td>Stress Intensity (ksi-in^2)</td>
<td>Time (minutes)</td>
<td>Total Acoustic Emissions (3 measurements)</td>
<td>Average Emission Rate (emissions per minute)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------</td>
<td>------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>33.3</td>
<td>0.5</td>
<td>5, 5, 5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>9, 7, 8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>12, 10, 11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>13, 11, 12</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>15, 13, 14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>16, 14, 15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>24, 22, 23</td>
<td></td>
</tr>
<tr>
<td>41.6</td>
<td>0.5</td>
<td>3, 4, 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>10, 10, 10</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>12, 13, 13</td>
<td></td>
</tr>
<tr>
<td>58.2</td>
<td>0.5</td>
<td>7, 7, 6</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>18, 18, 18</td>
<td></td>
</tr>
</tbody>
</table>
Table 30 - Stress Intensity and Acoustic Emission Count Data for AISI 4335V Steel Specimen (Heat Treatment D) In 300 Torr Hydrogen Gas

<table>
<thead>
<tr>
<th>Stress Intensity (ksi-in^{1/2})</th>
<th>Time (minutes)</th>
<th>Total Acoustic Emission Counts (3 measurements)</th>
<th>Average Count Rate (counts/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.7</td>
<td>0.5</td>
<td>0, 1, 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1, 1, 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>3, 2, 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>3, 2, 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>3, 2, 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>5, 3, 5</td>
<td></td>
</tr>
<tr>
<td>20.8</td>
<td>0.5</td>
<td>2, 0, 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2, 2, 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>4, 4, 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>11, 6, 8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>13, 7, 11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>16, 9, 15</td>
<td></td>
</tr>
<tr>
<td>Stress Intensity (ksi-in$^{1/2}$)</td>
<td>Time (minutes)</td>
<td>Total Acoustic Emission Counts (3 measurements)</td>
<td>Average Count Rate (counts/min)</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>----------------</td>
<td>-----------------------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>25.0</td>
<td>0.5</td>
<td>30,26,27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>48,50,46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>64,69,63</td>
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</tr>
<tr>
<td></td>
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<td>2.5</td>
<td>110,110,107</td>
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<td>3.0</td>
<td>121,122,118</td>
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<tr>
<td>33.3</td>
<td>0.5</td>
<td>37,29,32</td>
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<td>1.5</td>
<td>70,53,65</td>
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<td>81,59,76</td>
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<td>2.5</td>
<td>101,91,94</td>
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<td></td>
<td>3.0</td>
<td>119,101,112</td>
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Table 30 - Continued

<table>
<thead>
<tr>
<th>Stress Intensity (ksi-in$^2$)</th>
<th>Time (minutes)</th>
<th>Total Acoustic Emission Counts (3 measurements)</th>
<th>Average Count Rate (counts/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.6</td>
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<td></td>
<td>1.0</td>
<td>87,70,89</td>
<td>92.0</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>159,106,149</td>
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</tr>
<tr>
<td>58.2</td>
<td>0.5</td>
<td>71,49,59</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>148,102,136</td>
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</tr>
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</table>
Table 31 - Crack Velocity and Acoustic Emission Rate Data for AISI 4335V Steel Specimen (Heat Treatment D) In 300 Torr Hydrogen Gas

<table>
<thead>
<tr>
<th>Stress Intensity (ksi-in^½)</th>
<th>Average Crack Velocity (in/min)</th>
<th>Average Emission Rate (emissions per minute)</th>
<th>Inches Crack Extension Per Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.7</td>
<td>$3.0 \times 10^{-3}$</td>
<td>1.0</td>
<td>$3.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>20.8</td>
<td>8.2 &quot;</td>
<td>0.78</td>
<td>11 &quot;</td>
</tr>
<tr>
<td>25.0</td>
<td>22 &quot;</td>
<td>1.0</td>
<td>22 &quot;</td>
</tr>
<tr>
<td>33.3</td>
<td>45 &quot;</td>
<td>6.6</td>
<td>6.8 &quot;</td>
</tr>
<tr>
<td>41.6</td>
<td>70 &quot;</td>
<td>8.4</td>
<td>8.3 &quot;</td>
</tr>
<tr>
<td>58.2</td>
<td>84 &quot;</td>
<td>18</td>
<td>4.7 &quot;</td>
</tr>
</tbody>
</table>
The tape recording of the emission signals was filtered (band pass, 5 to 15 kHz) and examined using the Hewlett-Packard Model 32A oscilloscope. To count emissions, the gate output signal of the oscilloscope (100 msec sweep time) was used to trigger the Hickok counter. Whenever an acoustic signal, of duration 100 msec or less, occurred, the oscilloscope sweep was triggered, and one emission was counted. In order to measure acoustic emission counts, the oscilloscope channel output was used to trigger the counter.

During tape playback, the counter trigger level was chosen such that emissions (or counts) were recorded only when the emission was audibly detected using a Bogen Challenger audio amplifier and an 8-ohm speaker (in parallel with the filter-oscilloscope-counter circuit). If count increments were observed in the absence of an audible signal, the counter trigger level was increased. After the choice of a satisfactory trigger level, the amplifier and triggering controls were not adjusted during subsequent playback.
4.5.9 Fractographic results

Figure 52 shows SEM fractographs of 205°C tempered AISI 4335V steel (H₂ pressure dependence specimen), fractured in pure hydrogen gas at $K_I = 20.8$ ksi-in$^{\frac{3}{2}}$. Figure 53 shows the fractographs of a 205°C tempered specimen, tested at $K_I = 54.1$ ksi-in$^{\frac{3}{2}}$. The latter specimen had also been used to determine the dependence of crack velocity on hydrogen pressure. Plastic-carbon replicas, obtained from the two pressure dependence specimens, were used for the transmission electron fractographs shown in Figure 54. Scanning electron fractographs of 315°C tempered AISI 4335V steel, tested in pure hydrogen gas, are shown in Figures 55 and 56.

Figures 57 and 58 show the fractography, as a function of hydrogen pressure and applied stress intensity, for D6AC steel (tempered at 540°C) tested in pure hydrogen gas. Figure 59 shows the fracto-
Figure 52 - SEM Fractographs Of AISI 4335V Steel Tempered At 205°C And Fractured In Hydrogen Gas At $K_I = 20.8$ KSI-in$^{1/2}$
Figure 53 - SEM Fractographs Of AISI 4335V Steel Tempered At 205°C And Fractured In Hydrogen Gas At $K_I = 54.1$ Ksi-in$^2$
Figure 5 - Electron Fractographs (Plastic - Carbon Replicas) Of AISI 835V Steel Tempered At 205°C And Fractured In Hydrogen Gas At $K_I = 20.8$ KSI-in$^2$ And $K_I = 54.1$ KSI-in$^2$

$K_I = 20.8$ KSI-in$^2$

$K_I = 54.1$ KSI-in$^2$
Figure 55 - SEM Fractographs Of AISI 4335V Steel Tempered At 315°C And Fractured In Hydrogen Gas At $K_I = 25.0$ Ksi-in$^{0.5}$
Figure 56 - SEM Fractographs Of AISI 4335V Steel Tempered At 315°C And Fractured In Hydrogen Gas At $K_I = 54.1 \text{ Ksi-in}^2$
Figure 57 - SEM Fractographs Of D6AC Steel Tempered At 540°C And Fractured In Hydrogen Gas At $K_I = 33.3$ Ksi-in$^{\frac{1}{2}}$
Figure 58 - SEM Fractographs Of D6AC Steel Tempered At 540°C And Fractured In Hydrogen Gas At $K_I = 83.2$ Ksi-in$rac{1}{2}$
graphic results for 595°C tempered D6AC steel.

Figure 60 shows the SEM fractographs for 205°C tempered AISI 4335V steel fractured in pure hydrogen sulfide gas at $K_I$ values of 20.8 and 54.1 ksi-in$^{\frac{1}{2}}$. For the same steel and heat treatment, Figures 61, 62, and 63 show SEM fractographs obtained after testing in HCl, HBr, and Cl$_2$ gaseous environments. Figure 64 shows additional fractographs of 205°C tempered AISI 4335V steel fractured in 300 torr Cl$_2$ gas.

4.5.10 Auger spectroscopic results

Surface analysis, by Auger spectroscopy, of a 540°C tempered specimen of AISI 4335V steel, fractured in 30 torr H$_2$S gas, showed three primary chemical species - iron, sulfur, and oxygen. Continuous ion bombardment of the surface reduced the intensity of the sulfur and oxygen peaks, relative to that of iron. Figure 65 shows the peak amplitudes, as functions of sputtering time, for the species oxygen, sulfur, iron, and chromium.
Figure 59 - SEM Fractographs Of D6AC Steel Tempered At 595°C And Fractured In Hydrogen Gas

$$K_I = 121 \text{ KSI-in}^{\frac{1}{2}}$$

$$K_I = 133 \text{ KSI-in}^{\frac{1}{2}}$$
Figure 60 - SEM Fractographs Of AISI 4335V Steel Tempered At 205°C And Fractured In Hydrogen Sulfide Gas

$K_I = 20.8 \text{ Ksi-in}^\frac{1}{2}$

$K_I = 54.1 \text{ Ksi-in}^\frac{1}{2}$
Figure 61 - SEM Fractograph Of AISI 4335V Steel Tempered At 205°C And Fractured In 100 Torr Of Hydrogen Chloride Gas At $K_I = 45.8$ Ksi-in$^{rac{1}{2}}$
Figure 62 - SEM Fractograph Of AISI 4335V Steel Tempered At 205°C And Fractured In 100 Torr Of Hydrogen Bromide Gas At $K_I = 45.8$ Ksi-in$^{\frac{1}{2}}$
Figure 63 - SEM Fractograph Of AISI 4335V Steel Tempered At 205°C And Fractured In 300 Torr Chlorine Gas At $K_I = 41.6$ KSI-in$^{\frac{1}{2}}$
Figure 64 - Additional SEM Fractographs Of AISI 4335V Steel Tempered At 205°C And Fractured In 300 Torr Chlorine Gas At $K_I = 41.6$ Ksi-in$^2$
Figure 65 - Auger Analysis Of Surface Species For AISI 4335V Steel Specimen Fractured In 30 Torr Of Hydrogen Sulfide Gas At $K_I = 25.0$ Ksi-in$^2$
4.6 Discussion of Experimental Results

4.6.1 Crack growth studies in aqueous sodium chloride solution

Crack growth kinetics are shown, in Figure 36, to be a strong function of stress intensity and strength level (as defined by tempering temperature) for AISI 4335V steel. Crack velocities for material tempered at 205°C or 315°C are approximately two orders of magnitude greater than those observed in 540°C tempered material.

The crack velocities are on the order of $10^{-6}$ in/sec for 540°C tempered steel at stress intensities greater than 80 ksi-in$^{\frac{1}{2}}$. In contrast, tempering temperatures of 205°C or 315°C give crack velocities greater than $10^{-5}$ in/sec, and at stress intensity values of 20 to 60 ksi-in$^{\frac{1}{2}}$.

For a stress intensity value of 49.9 ksi-in$^{\frac{1}{2}}$, the crack velocity for 205°C tempered AISI 4335V steel is $7 \times 10^{-5}$ in/sec. The data of Landes (3), presented in Figure 5, show a crack velocity of approximately
5 X 10^-4 in/sec for a higher strength level AISI 4340 steel in a distilled water environment. In view of the different material strength level and environment, the agreement is felt to be good.

The major effect of increased tempering temperature (540°C vs. 205°C) is a decrease in crack growth kinetics (approximately two orders of magnitude), with a clear difference in the range of stress intensity values in which comparable crack velocities are observed.

4.6.2 Crack growth studies in pure hydrogen gas environments

The effects of strength level on crack velocities for AISI 4335V steel in pure hydrogen gas (Figure 37) are the same as those observed in a sodium chloride solution: (1) crack velocities in Region II are approximately two orders of magnitude higher in steel tempered at 205°C or 315°C than in 540°C tempered material, and (2) comparable crack velocities in the
lower strength material are observed at clearly higher values of applied stress intensity. In addition, the dependence of crack velocity on stress intensity, for both D6AC and AISI 4335V steels, is a function of strength level. Higher strength level material exhibits the Region I - Region II behavior seen by others (3,4) in hydrogen gas environments. Low strength material shows a definite increase of crack velocity with increasing applied stress intensity.

It is important to compare the Region II crack velocities for high strength level AISI 4335V steel with the results observed by others (3,4). The data of Landes (3), presented in Figure 5, show a crack velocity of approximately $3 \times 10^{-3}$ in/sec (at $K_I = 40$ ksi-in$^{1/2}$) for AISI 4340 steel (tensile strength - 302 ksi) in one atmosphere of hydrogen gas. The present study shows a crack velocity of $8 \times 10^{-4}$ in/sec for 205°C tempered AISI 4335V steel (tensile strength - 279 ksi) in 300 torr $H_2$ gas ($K_I = 42$ ksi-in$^{1/2}$). A first power hydrogen pressure dependence at this $K_I$ value,
shown in Figure 39, gives a crack velocity of $2 \times 10^{-3}$ in/sec in 760 torr $H_2$. Therefore, the agreement of crack velocity data, for the same environment and similar material, is good. The crack velocity data of Sawicki (4), for H-11 steel in 800 torr $H_2$ gas (Figure 7), show a crack velocity value of $2.5 \times 10^{-3}$ in/sec at $26^\circ C$ and a $K_I$ value of 40 ksi-in$^{1/2}$. The extrapolation of the present data to one atmosphere hydrogen pressure is again seen to result in good agreement with prior work. The crack velocity data of McIntyre et al (89), presented in Figure 9, show a velocity value of $1.3 \times 10^{-4}$ in/sec, for 835M30 steel in 760 torr $H_2$ ($K_I = 40$ ksi-in$^{1/2}$). This velocity value is significantly different than that of the present study, or those of other investigators (3,4).

The significant result of the present work is that the crack velocity at a Region I stress intensity is clearly shown to exhibit a different (higher) hydrogen pressure dependence than do velocities in Region II. The value of this result is in the explanation of the
hydrogen pressure dependence of crack velocity observed at high temperatures. At a stress intensity value of 29 ksi-in$^{1/2}$, the data of Sawicki (4), presented in Figure 8, show that the pressure dependence at 80°C is $P_{H_2}^{3/2}$, whereas at lower temperatures ($\leq 47^\circ$C) a first power pressure dependence is observed. The actual crack velocity vs. stress intensity data of Sawicki (4), presented in Figure 7, show that a $K_I$ value of 29.0 ksi-in$^{1/2}$ lies in Region II at 26°C and in Region I at 71°C. Therefore, an increase of test temperature simply increases the stress intensity range for Region I behavior. At high temperatures (71°C), the applied stress intensity (29 ksi-in$^{1/2}$) then lies in Region I. Consequently, the dependence of crack velocity on hydrogen gas pressure depends on the applied stress intensity, relative to the entire crack velocity-stress intensity curve, and cannot be adequately explained by the effect of temperature on the rate-controlling process for crack growth. The negligible effect of temperature on hydrogen permeation, in the
Sawicki model, has been discussed earlier (Section 2.7.4.2).

It is also important to note that the pressure dependence of crack velocity in the Williams and Nelson study (2) can be explained by the results of the present study. The applied stress intensity in the earlier work (36 ksi-in$^1$) is approximately 2/3 of the $K_{ic}$ value for the steel (2). On the basis of the present investigation and the results of Sawicki (4), this $K_I$ value lies in Region II at room temperature. If, as in the Sawicki study (4), Region I is extended to higher $K_I$ values by increasing the test temperature, the $P_{H_2}^{3/2}$ dependence observed at 60°C by Williams and Nelson (2) is the result of the $K_I$ value being in Region I of the crack velocity vs. stress intensity curve.

In the present $H_2$ gas environment studies, the pressure dependence of crack velocity is seen to be a function of both applied stress intensity and the crack velocity itself. Figure 66 shows the range of
crack velocities, the applied stress intensity, and the observed pressure dependence for each crack velocity - hydrogen pressure study. A low crack velocity, or a low value of applied stress intensity, results in an increased dependence of crack velocity on hydrogen pressure. This result is significant in that neither the H\textsubscript{2} gas studies of Sawicki (4) nor those of Williams and Nelson (2) suggest any effect of these variables on the pressure dependence of crack velocity.

The comparison of aqueous and gaseous (H\textsubscript{2}) environment crack velocities with those of prior studies results in a reasonable agreement. For the case of 205\degree C tempered AISI 4335V steel, at $K_I = 40-42$ ksi-in\textsuperscript{1/2}, the Region II crack velocities in 760 torr H\textsubscript{2} (extrapolated from 300 torr data) and in 3\% sodium chloride solution are $2 \times 10^{-3}$ in/sec and $6 \times 10^{-5}$ in/sec, respectively. The ratio of velocities (approximately 30) agrees, within a factor of 3, with the order of magnitude difference observed by Landes (3).
Figure 66 - Effects Of Crack Velocity And Applied Stress Intensity On Observed Pressure Dependence Coefficient Of Crack Velocity
The Landes results are shown in Figure 5.

The comparison of present crack velocity data with published results is significant only if the present data are accurate and reproducible. Since the crack velocities in gaseous hydrogen environments could not be determined by optical measurements, the observed crack extensions, for the specimens of pressure dependence studies, were compared to the crack extension values predicted from crack opening displacement measurements by Gallagher (132). After each pressure dependence study, the test chamber was evacuated. The specimen was catastrophically fractured in a hard vacuum, and the resulting slow crack growth zones were measured to within 0.10" with an FWP caliper. Table 32 gives the predicted and observed crack extension values. The difference ranges from 4% to 20%, and is felt to be satisfactory for the present study. Calibration data for the Esterline-Angus strip chart recorder, used in displacement rate measurements, are given in Table 33. The chartspeeds
Table 32 - Crack Extension Data for Specimens Used In Hydrogen Pressure Dependence Studies

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Stress Intensity (ksi-in(^{\frac{1}{2}}))</th>
<th>Predicted Crack Extension (inches)</th>
<th>Observed Crack Extension (inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>L</td>
<td>121, 133</td>
<td>0.85</td>
<td>0.92</td>
</tr>
<tr>
<td>&quot;</td>
<td>K</td>
<td>33.3</td>
<td>1.07</td>
<td>1.03</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>83.2</td>
<td>0.52</td>
<td>0.58</td>
</tr>
<tr>
<td>4335V</td>
<td>H</td>
<td>25.0</td>
<td>1.18</td>
<td>1.08</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>54.1</td>
<td>0.91</td>
<td>0.96</td>
</tr>
<tr>
<td>&quot;</td>
<td>A</td>
<td>20.8</td>
<td>1.59</td>
<td>1.28</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>54.1</td>
<td>1.28</td>
<td>1.36</td>
</tr>
<tr>
<td>Chart Speed</td>
<td>Expected Travel Distance (X) In</td>
<td>Time Required To Travel (Seconds)</td>
<td>Error (%)</td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>---------------------------------</td>
<td>-----------------------------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>8 in/hr</td>
<td>0.67 inches</td>
<td>296</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>1/2 in/min</td>
<td>2.50 &quot;</td>
<td>299</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>1 in/min</td>
<td>5.00 &quot;</td>
<td>299</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>2 in/min</td>
<td>10.0 &quot;</td>
<td>297</td>
<td>1.0</td>
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</tr>
<tr>
<td>4 in/min</td>
<td>20.0 &quot;</td>
<td>298</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>8 in/min</td>
<td>40.0 &quot;</td>
<td>298</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>
were checked, using a Hanhart stopwatch. The errors, shown in Table 33, are less than 2%. The reproducibility of test data was determined by two techniques: (1) testing of a second specimen under the same gas pressure and load conditions, and (2) comparison of crack velocities from $K_I$ - dependence (constant pressure) studies with those predicted from pressure dependence (constant $K_I$) relationships. Table 34 gives crack velocity and stress intensity data for a second D6AC steel specimen ($540^\circ$C temper) tested in 300 torr $H_2$ gas. Test data for the first specimen are given in Table 15. Measured crack velocities, and those predicted from pressure dependence equations, are given for both steels in Table 35. In all cases, the reproducibility of test data was found to be good. The confidence limits for pressure dependence coefficients, calculated by regression analysis techniques (139), are given in Table 36. The pressure dependence relationships were determined using least squares techniques. For the case of $540^\circ$C tempered D6AC steel, at $K_I = 33.3$ ksi-in$^{\frac{1}{2}}$, the crack velocity
Table 34 - Stress Intensity and Crack Velocity Data for D6AC Steel (Heat Treatment K) in 300 Torr Dry H₂ Gas

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Stress Intensity (ksi-in$^{\frac{1}{2}}$)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>K</td>
<td>29.1</td>
<td>3.11 x 10^{-5}</td>
</tr>
<tr>
<td></td>
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<td>33.3</td>
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<td>41.6</td>
<td>7.36</td>
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<td>49.9</td>
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<td>54.1</td>
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<td></td>
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<td>62.4</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>74.9</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>82.4</td>
<td>34.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>91.0</td>
<td>38.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>40.5</td>
</tr>
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</table>
Table 34 - Continued

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Stress Intensity (ksi-in²)</th>
<th>Crack Velocity (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6AC</td>
<td>K</td>
<td>91.5</td>
<td>40.3 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
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<td>45.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>404</td>
<td>46.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>404</td>
<td>40.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>404</td>
<td>42.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>404</td>
<td>50.8</td>
</tr>
</tbody>
</table>
Table 35 - Crack Velocity Data
In 300 Torr H₂ Gas

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Stress Intensity (ksi-in²)</th>
<th>Predicted Crack Velocity In 300 Torr H₂ (P₂ Dependence)</th>
<th>Measured Crack Velocity In 300 Torr H₂ (inches/second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V</td>
<td>H</td>
<td>25.0</td>
<td>22.9 x 10⁻⁵</td>
<td>14.8/15.7 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>54.1</td>
<td>95.5</td>
<td>122</td>
</tr>
<tr>
<td>D6AC</td>
<td>K</td>
<td>33.3</td>
<td>10.2</td>
<td>9.56/9.81</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>83.2</td>
<td>40.7</td>
<td>42.9/50.5</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>121</td>
<td>6.16</td>
<td>7.49/11.9</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>133</td>
<td>8.90</td>
<td>17.0/18.5</td>
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</table>
Table 36 - Confidence Limits (95%) For Crack Velocity - Hydrogen Pressure Relationships

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Treatment</th>
<th>Stress Intensity (ksi-in$^\frac{3}{2}$)</th>
<th>Hydrogen Pressure Dependence Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>4335V</td>
<td>A</td>
<td>20.8</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>&quot;</td>
<td>H</td>
<td>25.0</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>54.1</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>D6AC</td>
<td>K</td>
<td>33.3</td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>83.2</td>
<td>1.2 ± 0.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>L</td>
<td>121</td>
<td>1.1 ± 0.3</td>
</tr>
</tbody>
</table>
data shown in Figure 42 do not show a significantly greater pressure dependence than $P_{\text{H}_2}^2$.

4.6.3 Slow crack growth in pure hydrogen sulfide gas environments

The observed crack velocities for AISI 4335V steel in hydrogen sulfide gas were several orders of magnitude greater than the measured velocities in pure hydrogen gas, or in aqueous sodium chloride environments.

It is significant to compare pure $\text{H}_2$ gas and pure $\text{H}_2\text{S}$ gas as crack growth environments, for the same conditions of gas pressure, material, and applied stress intensity. For $205^\circ\text{C}$ tempered AISI 4335V steel tested at $K_I = 54.1$ ksi-in$^{\frac{1}{2}}$, the pressure dependence relationships are:

\begin{align*}
\text{H}_2 \text{ gas :} & \quad \log (\frac{\text{da}}{\text{dt}}) = -5.2 + 1.0 \log P_{\text{H}_2} \\
\text{H}_2\text{S} \text{ gas :} & \quad \log (\frac{\text{da}}{\text{dt}}) = -2.0 + 1.1 \log P_{\text{H}_2\text{S}}
\end{align*}

where: $\frac{\text{da}}{\text{dt}} = \text{crack velocity, (in/sec)}$
For an isobaric (1 atm.) comparison of environments, i.e. $P_{H_2}, P_{H_2S} = 760$ torr, the ratio of crack velocities ($H_2S$ environment vs. $H_2$ environment) is found as follows:

$$[\log (da/dt)]_{H_2S} - [\log (da/dt)]_{H_2} = 3.5$$

Therefore, the crack velocity (at $K_I = 54.1$ ksi-in$^{1/2}$) is predicted to be more than three orders of magnitude greater in 1 atm $H_2S$ than in 1 atm $H_2$ gas.

For the testing in pure $H_2$ and pure $H_2S$ environments at $K_I = 20.8$ ksi-in$^{1/2}$, the pressure dependence relationships are:

$\underline{H_2 \text{ gas}}$ : $\log (da/dt) = -7.8 + 1.7 \log P_{H_2}$

$\underline{H_2S \text{ gas}}$ : $\log (da/dt) = -2.3 + 1.4 \log P_{H_2S}$

where: $da/dt = \text{crack velocity, (in/sec)}$

$P_{H_2}, P_{H_2S} = \text{gas pressures, (torr)}$
At gas pressures ($H_2$, $H_2S$) of 760 torr:

$$[\log (da/dt)]_{H_2S} - [\log (da/dt)]_{H_2} = 4.7$$

Therefore, the Region I crack velocity (at $K_I = 20.8$ ksi-in$^{\frac{3}{2}}$) is predicted to be more than four orders of magnitude greater in 1 atm $H_2S$ gas than in 1 atm $H_2$ gas.

The gaseous environments, at one atmosphere pressure, were compared by McIntyre et al. (89) for slow crack growth in 835M30 steel. The results, shown in Figure 9, are in agreement (within one order of magnitude) with the present predictions. Since the pressure dependence of crack velocity in $H_2S$ gas is extrapolated to a pressure four orders of magnitude greater than the actual test pressures, the agreement is good.

In order to verify the $H_2S$ effect, a 205°C tempered specimen of AISI 4335V steel was fractured at $K_I = 17.9$ ksi-in$^{\frac{3}{2}}$ in 20 torr $H_2S$ gas. The observed crack opening displacement rate corresponded to a crack
velocity of approximately $2 \times 10^{-2}$ in/sec. Using the Region I ($K_I = 20.8$ ksi-in$^{1/2}$) pressure dependence equation, the predicted crack velocity was found to be $3 \times 10^{-1}$ in/sec. However, the pressure dependence equation was derived at $K_I = 20.8$ ksi-in$^{1/2}$. Therefore, in view of the strong dependence of crack velocity on stress intensity in Region I, the order of magnitude difference can easily be seen to result from the difference in applied stress intensity values.

The test in 20 torr $H_2S$ shows that high crack velocities ($> 10^{-2}$ in/sec) are observed in $H_2S$ gas at stress intensities below those for measurable crack velocities in pure $H_2$ gas. The McIntyre et al (89) results in Figure 9 are in complete agreement with this observation.

The dependence of crack velocity on gas pressure shows a first power (or greater) relationship for both $H_2$ and $H_2S$ gaseous environments. Since both gas molecules contain two hydrogen atoms, it is reasonable (under the assumption of the same cracking mechanism)
to expect similar pressure dependence relationships for the two gases. Also, the pressure dependence of crack velocity is greater, for either gas environment, in Region I than in Region II. At room temperature, both Williams and Nelson (2) and Sawicki (4) found a first power hydrogen pressure dependence of crack velocity, in agreement with the present results. McIntyre et al (89), however, found that crack velocity is proportional to the square root of the gas pressure, whether it be H$_2$ or H$_2$S. Therefore, there is still disagreement, in the published literature, as to the hydrogen pressure dependence of crack velocity at ambient temperature.

The H$_2$S study has clearly shown that crack velocities are several orders of magnitude greater in H$_2$S gas than in H$_2$ gas. Also, Region I cracking is seen to occur at lower stress intensity values in an H$_2$S environment, as compared to H$_2$ gas. The dependence of crack velocity on gas pressure is very similar in either H$_2$ or H$_2$S gaseous environments.
4.6.4 Slow crack growth in deuterium gas environments

The comparison of crack velocities in H₂ gas, for the same test specimen and stress intensity, with those observed in D₂ gas are in agreement with the relative permeation rates of these gases through high strength steel. In all cases, the velocity ratio (H₂ environment vs. D₂ environment) is greater than the ratio of the ideal diffusivities (1.414). The permeation rates and diffusion coefficients have been discussed in Section 2.6.1.4.

The significance of the deuterium results is in the discrimination as to the rate-controlling process for slow crack growth. Since both the solubility and diffusivity of deuterium in steel are lower than the values for hydrogen (43,84), a velocity ratio greater than the ratio of the diffusivities is explainable if hydrogen dissolution and diffusion are both required in the cracking process.

In reviewing the proposed Williams and Nelson model (2), the rate-controlling process is seen to be
the surface migration (diffusion) of adsorbed hydrogen atoms. The proposed rate-controlling process does not include the dissolution of hydrogen into the steel. Thus, the expected rates of surface diffusion, for hydrogen and deuterium, would be proportional to the relative diffusivities, giving a crack velocity 1.414 times lower in deuterium gas. Such a velocity ratio was not observed. The Sawicki model (4) proposes a rate-controlling process of hydrogen permeation through the steel. On this basis, both dissolution and diffusion are required. Such relative permeation rates for hydrogen and deuterium in hardened SAE 4130 steel (43) are in excellent agreement with the observed crack velocity ratios for the two environments in this study.

The isotope effect on gaseous environment crack growth \((H_2, D_2)\) is in agreement with the prediction for a permeation-controlled crack growth process.

4.6.5 Crack growth in \(H_2/O_2\) gaseous environments

The observation of a higher hydrogen pressure
dependence of crack velocity at low velocity values (Figure 66) presents the question of contaminant gas effects on the observed pressure dependence. A lower crack velocity is expected to allow the less mobile oxygen species to compete with hydrogen for adsorption sites at the crack tip. Oxygen gas additions have been shown to halt crack growth in hydrogen gas environments (1,4). However, the presence of oxygen did not explain the pressure dependencies observed in the present study.

The addition of oxygen gas, at pressures up to 0.9 torr, did not significantly affect the magnitude or hydrogen pressure dependence of crack velocity. It is important to recall that the oxygen pressures investigated in the study (> 4 X 10^{-2} torr) are at least one half an order of magnitude greater than the pressure rise in the test chamber during a 3 hour test (10^{-2} torr).

The effect of oxygen gas on crack growth indicates that the absolute oxygen level, rather than its level
relative to hydrogen (1,4), is the critical factor in halting crack propagation. Crack growth kinetics were not significantly affected by the addition of 0.9 torr O\textsubscript{2} to 100 torr H\textsubscript{2} gas (Figure 50). The oxygen level corresponds to 0.9 vol\%. However, no crack growth was observed for one half hour in the presence of 4.7 torr O\textsubscript{2} and 665 torr H\textsubscript{2} gas. The latter oxygen level is 0.7 vol\%.

It is important to compare the effect of oxygen in the present study with that observed in prior work. In a detailed study of oxygen effects on crack growth kinetics, Sawicki (4) found that the addition of 0.4 vol\% oxygen was sufficient to stifle slow crack growth in a hydrogen gas environment. However, it is significant to examine the result in terms of the experimental technique. The prior study (4) was conducted by the addition of oxygen to a flowing stream of hydrogen gas, at a total pressure of 813 torr. If the present study had been conducted in flowing hydrogen gas at 665 torr pressure, the absence of cracking at
oxygen levels of 0.9/4.7 torr would correspond to 
0.14/0.70 vol% oxygen, in excellent agreement with 
the value observed by Sawicki (4).

4.6.6 Crack growth in H$_2$/H$_2$O gaseous environments

The addition of water vapor to the hydrogen gas 
environment is seen to reduce both the magnitude of 
the crack velocity, as well as its dependence on 
hydrogen pressure. Therefore, the presence of water 
vapor as the major contaminant in the test system 
does not explain the increased pressure dependence 
observed in Region I.

The effect of water vapor on crack growth kinetics 
in hydrogen gas compares well with the results of 
others (1,3). Using high strength H-11 steel, Johnson 
and Hancock (1) have shown that the crack velocity in 
moist hydrogen (1 atm pressure) is the same as that in 
a liquid water environment. The data of Landes (3), 
shown in Figure 5, give crack velocities (Region II) 
one order of magnitude lower in distilled water than in
hydrogen gas (1 atm). Therefore, the crack velocity in dry H₂ gas (1 atm) is expected to be one order of magnitude greater than the velocity in moist H₂ gas (1 atm).

The dependencies of crack velocity on gas pressure, for wet and dry H₂ environments, were found to be:

\[
\begin{align*}
\text{Dry H}_2: \quad \log (\frac{da}{dt}) &= -4.5 + 0.80 \log P_{H_2} \\
\text{Wet H}_2: \quad \log (\frac{da}{dt}) &= -4.6 + 0.52 \log P_{H_2}
\end{align*}
\]

where: \( \frac{da}{dt} = \text{crack velocity, (in/sec)} \)
\( P_{H_2} = \text{hydrogen pressure, (torr)} \)

For a total gas pressure of 760 torr:

\[
[\log (\frac{da}{dt})]_{\text{Dry H}_2} - [\log (\frac{da}{dt})]_{\text{Wet H}_2} = 0.9
\]

Thus, the crack velocity in the present study is predicted to be 8 times greater in dry H₂ gas than in moist H₂ gas, for a total pressure of one atmosphere. This result shows good agreement with the prior published work (1,3).
4.6.7 Crack growth in H$_2$/H$_2$S gaseous environments

Figure 47 shows enhancement of crack growth kinetics, in 100 torr H$_2$ gas, on the addition of H$_2$S at levels of 0.01 mole%. Hydrogen sulfide data at pressures greater than 0.01 torr are not shown in Figure 47 because of non-steady state crack growth rates (increasing with time).

If crack velocity, as suggested by the Sawicki model (4), is proportional to the rate of hydrogen permeation in the steel, the dependence of crack velocity on H$_2$S concentration should be the same as that observed for hydrogen permeation kinetics. Such a dependence has been described in Section 2.6.1.3. On replacing the hydrogen permeation rate ($P$) with the crack velocity ($da/dt$), the data of Figure 47 are shown in Figure 67. It is clearly seen that, for the same range of H$_2$S concentrations, the dependence of crack velocity on mole% H$_2$S is the same as that observed for the rate of hydrogen permeation through iron. The permeation rate data of Palczewska (82) are
Figure 67 - Relationship Between Crack Velocity And Hydrogen Sulfide Pressure In Hydrogen - Hydrogen Sulfide Gas Environment
shown in Figure 4.

The most significant observation in the \( H_2/H_2S \) studies is that the addition of 2.1% \( H_2S \) to a molecular hydrogen gas environment results in a crack velocity more than two orders of magnitude greater than that observed in the molecular hydrogen alone. The data in Table 28 show that the crack velocity in a gaseous mixture (20 torr \( H_2 + 0.4 \) torr \( H_2S \)) is the same as that observed in 0.4 torr \( H_2S \), and is therefore defined by the \( H_2S \) species alone. The data in Figure 39 show that the crack velocity in 20 torr \( H_2 \) gas is approximately \( 10^{-5} \) in/sec at a \( K_I \) value of 41.6 ksi-in\(^{1/2}\). The effect of stress intensity on crack velocity, shown in Figure 37, indicates that the crack velocity at \( K_I = 25.0 \) ksi-in\(^{1/2}\) is approximately one half an order of magnitude lower than that observed at \( K_I = 41.6 \) ksi-in\(^{1/2}\) (for the same hydrogen gas pressure). Therefore, the expected crack velocity in 20 torr \( H_2 \) gas is less than \( 10^{-5} \) in/sec. The observed crack velocity at \( K_I = 25.0 \) ksi-in\(^{1/2}\) in the same amount of \( H_2 \), with 0.4 torr \( H_2S \), is \( 2 \times 10^{-3} \) in/sec.
(two orders of magnitude greater).

As with the deuterium gas study, the result is of great value in examining the proposed rate-controlling processes for slow crack growth. The Williams and Nelson model (2) is based on the rate-controlling process of chemisorption. The kinetics are defined by surface coverage (molecular and atomic hydrogen), as well as the hydrogen pressure itself. The addition of \( \frac{2.1}{1} \times H_2S \) in the present study produces a negligible change in hydrogen pressure, even if the \( H_2S \) is totally dissociated. Since Roberts and Ross (70) have shown that \( H_2S \) does dissociate on iron (at temperatures of \(-80^\circ C\) to \(+32^\circ C\)), the surface coverage by hydrogen (from the \( H_2S \)) would be equal to or less than that observed with an equivalent amount of pure hydrogen gas. In addition, the presence of sulfur, as a chemisorption product, is not expected to affect the activation energy for surface diffusion of adsorbed hydrogen. Therefore, the increase of crack velocity by two orders of magnitude upon the addition of \( 2.1\% H_2S \) cannot be
explained by the Williams and Nelson model.

The addition of H$_2$S to a gaseous hydrogen environment has been shown to enhance hydrogen permeation through iron (82), and at H$_2$S levels of less than 0.4%. Additions of H$_2$S have also been shown (83) to reduce the kinetics of atomic hydrogen recombination on the surface of iron. On the basis of such observed effects, the results of the present study are consistent with a rate-controlling process for crack growth which requires the entry of hydrogen into the steel.

Since H$_2$S is known to dissociate on iron (70), the effect of H$_2$S on crack growth kinetics may be attributed to the presence of adsorbed sulfur on the surface of the steel. Upon the dilution of 0.4 torr H$_2$S with pure H$_2$ gas, the crack velocity was found to decrease, with a subsequent return to its initial value. By the prior work (70), the dissociation of H$_2$S on iron may be described by a reaction of the form:

\[ \text{H}_2\text{S}(g) + \text{Fe}(\text{site}) = \text{Fe-S}^* + \text{H}_2(g) \]

The Fe-S$^*$ species is assumed to be chemically adsorbed
sulfur on an iron lattice site. If the chemisorbed sulfur is the critical species in the H$_2$S environment, the addition of excess hydrogen could retard the above reaction by: (1) simply diluting the H$_2$S gas, retarding crack growth kinetics by its lower gas phase diffusion (relative to hydrogen), (2) competition of H$_2$ with H$_2$S in the chemical adsorption process, or (3) reducing the equilibrium activity of Fe-S* by Le Chatlier's principle. In any event, the observed effect of hydrogen addition is not consistent with the rate-controlling chemical adsorption process proposed by Williams and Nelson (2). The results are, however, consistent with the catalytic effect of sulfur on hydrogen permeation into iron or steel.

4.6.8 Crack growth in other gaseous environments

The comparison of gaseous environments in Figure 46 shows that the presence of atomic hydrogen in the molecular structure of the gaseous environment species is neither a necessary, nor a sufficient, condition
for slow crack growth in high strength steel.

Crack velocity studies of 205°C tempered AISI 4335V steel in NH₃, CH₄, and C₂H₂ environments did not show significant crack growth rates below the Kᵢc value for the steel. Ammonia is believed to chemisorb on iron at a rate comparable to that of hydrogen at 21°C (60,73), whereas methane chemisorption does not occur below 70°C (72). Therefore, chemical adsorption, per se, does not appear to satisfy the requirements for slow crack growth in gaseous environments. Since the acetylene gas used in this study was not analyzed, and could contain a maximum of 0.1% oxygen (Section 4.2.3.5), the conclusion as to the absence of significant crack growth in this environment is tentative.

Crack velocities in Cl₂, HCl, and HBr gaseous environments are at least one order of magnitude greater than the velocities observed in pure H₂ gas, for the same material, heat treatment, gas pressure, and applied stress intensity. The crack growth in Cl₂ is
unique in that prior studies of slow crack growth in gaseous environments (1,2,3,4,89) have been limited to those species which contain hydrogen, i.e. H₂, H₂S.

The accelerated crack growth in a gaseous Cl₂ environment is not readily explainable by a hydrogen-induced cracking mechanism. Since water vapor is the primary contaminant in the test system, however, the possibility of hydrogen-induced cracking in an aqueous medium must be considered. The conditions for HCl and Cl₂ environments will be considered, with HBr showing very similar behavior to HCl. For the Cl₂ - H₂O system, the possible reaction is:

\[ \text{Cl}_2 + \text{H}_2\text{O} = 2 \text{Cl}^- + 2 \text{H}^+ + \frac{1}{2} \text{O}_2 \quad E_0^o = +1.6 \text{ V} \]

Considering the half-cell reactions, and the standard free energy data, the oxidation potentials (141) may be obtained:

\[ 2 \text{Cl}^- = \text{Cl}_2 + 2 \text{e}^- \quad E_0^o = +2.7 \text{ V} \]
\[ \text{H}_2\text{O} = 2 \text{H}^+ + \frac{1}{2} \text{O}_2 + 2 \text{e}^- \quad E_0^o = +0.5 \text{ V} \]

Since hydrogen-induced cracking is only possible
(on a thermodynamic basis) at potentials below the oxidation potential of hydrogen ($E_0^O = 0.0$), it is easily seen that the rest potential of the $\text{Cl}_2 - \text{H}_2\text{O}$ system is $+0.5/2.7$ volts, and does not permit hydrogen ion discharge and slow crack growth by a hydrogen process.

For the case of dissolved HCl (in water), the reaction may be written as:

$$\text{HCl} = \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 \quad E_0^O = +1.4 \text{ V}$$

Again considering the half-cell thermodynamics, we may write:

$$\text{H}_2 = 2 \text{H}^+ + 2 \text{e}^- \quad E_0^O = 0.0 \text{ V}$$

$$2 \text{Cl}^- = \text{Cl}_2 + 2 \text{e}^- \quad E_0^O = +2.7 \text{ V}$$

Therefore, the rest potential of the system is equal to or above the oxidation potential of hydrogen, and hydrogen-induced cracking by ionic hydrogen discharge is unlikely. If, on the basis of the studies by Brown (39), hydrogen reduction is favored by the environment-insensitive electrochemical conditions at the crack tip, then the expected crack velocities would
be on the order of those observed in aqueous solutions (obviously not the case). Therefore, cracking in the investigated halogen or halide gas environments is not the result of electrochemical reduction of hydrogen ions, as in aqueous media.

4.6.9 Additional considerations in gaseous environment studies

The accelerated cracking in gaseous environments such as HCl, HBr, and H₂S is also examined from the standpoint of a direct chemical reaction of the gaseous species with the steel, resulting in the generation of molecular hydrogen gas. Using published thermodynamic data (142,143,144), equilibrium hydrogen pressures are calculated for the following reactions:

\[
\begin{align*}
2 \text{HCl}(g) + \text{Fe}(s) & = \text{FeCl}_2(s) + \text{H}_2(g) \\
2 \text{HBr}(g) + \text{Fe}(s) & = \text{FeBr}_2(s) + \text{H}_2(g) \\
\text{H}_2\text{S}(g) + \text{Fe}(s) & = \text{FeS}(s) + \text{H}_2(g) \\
4 \text{H}_2\text{O}(l) + \text{Fe}(s) & = \text{Fe}_3\text{O}_4(s) + \text{H}_2(g) \\
\text{C}_2\text{H}_2(g) + 6 \text{Fe}(s) & = 2 \text{Fe}_3\text{C}(s) + \text{H}_2(g)
\end{align*}
\]
The pressures of HCl, HBr, and H\textsubscript{2}S are assumed to be $10^{-1}$ atmospheres. Test pressures of 300 torr are used for the cases of NH\textsubscript{3}, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{2} calculations. The activity of water (H\textsubscript{2}O) is assumed to be unity (pure liquid water). For the case of Cl\textsubscript{2} (99.97% pure), the impurities are assumed to be HCl gas. At a Cl\textsubscript{2} pressure of 300 torr, the resulting HCl pressure is $9 \times 10^{-2}$ torr. The Cl\textsubscript{2} data point is determined using this pressure and the HCl reaction with iron.

The resulting hydrogen pressures are compared to the experimentally observed crack velocities for 205\textsuperscript{\circ}C tempered AISI 4335V steel at $K_I = 45-52$ ksi-in\textsuperscript{1/2}. The velocity in hydrogen sulfide gas is obtained by the extrapolation of pressure dependence data at $K_I = 54.1$ ksi-in\textsuperscript{1/2}. The velocity for the case of H\textsubscript{2}O is obtained from data in the aqueous sodium chloride environment.

The resulting hydrogen pressures and crack...
velocities are shown in Figure 68. Although an apparent trend exists for the HBr, HCl, and H₂ environments, Cl₂ and H₂S species show significant positive deviation from such a trend. In addition, a substantial negative deviation is seen for the cases of H₂O, CH₄, NH₃, and C₂H₂ environments. Figure 68 shows the relationship between observed crack velocities and equilibrium hydrogen pressures for the environments H₂, HCl, and HBr. The slope of this line, on a log-log plot, is 0.07 and clearly different from the first power pressure dependence of crack velocity in H₂ or H₂S environments. The experimentally observed case, a line of slope 1.0, is also shown in Figure 68. Therefore, the equilibrium activity of hydrogen, as generated by dissociative chemisorption, does not explain the observed crack growth behavior in these gaseous environments.

The high crack velocities in Cl₂ gas, relative to a pure H₂ environment, were also considered as resulting from contaminant gases in the chlorine itself.
Figure 68 - Observed Crack Velocities And Predicted Hydrogen Pressures For Water (Liquid) And Gaseous Environments
The purity of the chlorine used in the study is 99.97%. At a chlorine gas pressure of 300 torr, the impurity gas pressure is then $9 \times 10^{-2}$ torr. If the total impurity gas content is assumed to be $H_2$, $HCl$, or $H_2O$, the associated crack velocity may then be calculated for each environment. A first power dependence of crack velocity on gas pressure is assumed for each species. The resulting velocity values are given in Table 37. There is clearly no basis for assuming that the impurity gas concentrations are sufficient to explain the crack velocities observed in a $Cl_2$ gas environment. Therefore, the cracking behavior must be attributed to the $Cl_2$ species itself. A further discussion of chlorine and halide gas cracking has been published (145).

4.6.10 Fractography of crack growth in gaseous environments

The fractographs shown for gaseous hydrogen environment fractures (Figures 52 - 59) indicate that fractography, as well as hydrogen pressure dependence, is a
Table 37 - Crack Velocity Estimates Due to Residual Contaminant Gases in Chlorine Gas Environment

<table>
<thead>
<tr>
<th>Impurity Vapor Species</th>
<th>Crack Velocity&lt;sup&gt;a&lt;/sup&gt; (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (liquid)</td>
<td>$7 \times 10^{-5}$</td>
</tr>
<tr>
<td>Water (vapor at $9 \times 10^{-2}$ torr pressure)</td>
<td>$3 \times 10^{-7}$</td>
</tr>
<tr>
<td>Hydrogen (at $9 \times 10^{-2}$ torr)</td>
<td>$3 \times 10^{-7}$</td>
</tr>
<tr>
<td>Hydrogen chloride (at $9 \times 10^{-2}$ torr)</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Dry chlorine (at 300 torr)</td>
<td>$1 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

<sup>a</sup> All at $K_T = 45.8/47.8$ ksi-in<sup>1/2</sup> stress intensity. Crack velocity assumed to be linear function of gas pressure for $H_2$ and HCl.

<sup>b</sup> Crack velocity assumed to be linear function of water vapor pressure, with equilibrium vapor pressure being 24 torr at $25^\circ$C; velocity in sodium chloride solution ($pH = 6.0$) is taken as crack velocity in pure liquid water.
function of applied stress intensity. For high strength level steel at high stress intensity values, ductile fracture occurs, accompanied by secondary cracking normal to the final fracture surface. Such Region II fractography is then of a mixed mode, in contrast to the primarily intergranular fracture (along prior austenite grain boundaries) observed in Region I. This fracture mode transition, associated with Region I - Region II behavior, is evident in AISI 4335V steel, tempered at 205°C or 315°C. Such fractographic differences are not clearly observed for the case of D6AC steel, tempered at 540°C (shown in Figures 57 and 58). Studies of slow crack growth in hydrogen gas environments by Sawicki (4) have also shown increasing amounts of ductile tearing with increasing applied stress intensity. At constant applied stress intensity, other studies have shown primarily intergranular fracture in hydrogen gas environments (2,88). Studies in aqueous environments by Beachem (34) have shown fractography to be a function of applied stress intensity.
In the present study, it is significant that a first power dependence of crack velocity on hydrogen pressure is observed for the cases of either a mixed mode fracture or a ductile, transgranular fracture. The first fracture mode is seen with high strength steel in Region II. The latter fracture mode is seen with low strength level D6AC steel at high stress intensity values. For a high strength level steel tested in Region I, the fractography shows primarily intergranular fracture, with a higher hydrogen pressure dependence of crack velocity \( P_{H_2}^{3/2} - P_{H_2}^2 \).

The fractography of specimens tested in hydrogen sulfide gas (Figure 60) shows an exclusively intergranular fracture at a Region I stress intensity value, with some evidence of ductility (on grain surfaces) at a Region II stress intensity value. The significant observation in the \( H_2S \) environment fractography is that there is no secondary cracking, to depths greater than one grain diameter, in Region II. This is clearly different than the fractography observed, for the same
material and heat treatment, in a molecular hydrogen gas environment. The presence of secondary cracks will be discussed further.

The fractography observed in chlorine and halide gas environments is of a mixed mode, with evidence of corrosion products on the fracture surface (Figures 61 and 64). All SEM specimens in the study had been cleaned by the same procedure - ultrasonically, in a bath of acetone. Attempts to identify the corrosion products seen in Figures 61 through 64, using a General Electric x-ray diffractometer, were unsuccessful.

4.6.11 Discussion of plasticity and crack bifurcation

The region of plastic deformation at the crack tip, and its effect on the state of stress, must be considered in the present study. By the specimen thickness requirement of fracture mechanics, plane strain conditions were found to exist under all test conditions.

The radius of the plastic zone at the crack tip
(described in Section 2.8.3) is:

$$r_p = \frac{1}{2\pi} \left( \frac{K_I}{\sigma_{ys}} \right)^2$$

For the range of stress intensities and material strength levels in the present study, the minimum and maximum values of \(r_p\) may be calculated. As seen in Table 10, AISI 4335V steel tempered at 205°C and 540°C have the maximum and minimum strength levels, with 0.2% yield strength values of 221 and 179 ksi, respectively. The largest plastic zone radius in the study is \(1.12 \times 10^{-1}\) inches, for 540°C tempered AISI 4335V steel at \(K_I = 150 \text{ ksi-in}^{\frac{1}{2}}\). The minimum plastic zone radius is \(1.44 \times 10^{-3}\) inches, for 205°C tempered AISI 4335V steel at \(K_I = 21 \text{ ksi-in}^{\frac{1}{2}}\).

As discussed by Johnson (98), a specimen thickness of \((2r_p)\) is required for plane strain conditions at the crack tip. The minimum thickness dimension for the specimen used in this study is 0.293", as measured at the tip of the side grooves. Therefore, the fracture mechanics requirement for plane strain conditions has been satisfied under all test conditions.
The phenomenon of crack branching (bifurcation) has been observed in high strength steels during aqueous environment slow crack growth by Carter (146) and others. Based on a stress intensity criterion model by Anthony and Congleton (147), Carter has proposed that crack bifurcation occurs, for a constant crack velocity, at a particular value of stress intensity:

\[ K_{IBr} = n K_{Iscc} \]

where: \( K_{IBr} \) = stress intensity value at which crack branching occurs

\( K_{Iscc} \) = minimum stress intensity for observable crack growth in the environment

\( n \) = constant, a value of 2 for small plastic zone sizes

The crack branching criterion was established by
Carter (146), using single-edge-notched specimens (0.5" thick), tested by 4-point loading or cantilever bending. In the testing of seven high strength steels in an aqueous 3½% sodium chloride solution, Carter found that the values for \( n \) ranged from 2 to 4. For quenched and tempered AISI 4330V steel (196 ksi yield strength), the \( n \) values ranged from 1.8 to 2.0, with crack branching observed at \( K_I = 44-50 \) ksi-in\(^{\frac{3}{2}}\). For a quenched and tempered AISI 4340 steel (230 ksi yield strength), the \( n \) value was 2.4, with crack branching occurring at \( K_I = 53-58 \) ksi-in\(^{\frac{3}{2}}\). In view of the 0.5" specimen thickness, and the material strength levels, the test conditions met the plane strain requirements of fracture mechanics (98).

The significant point in the Carter criterion is that neither the environment itself nor the use of side grooves in the specimen are considered in the crack branching criterion. In the present study, neither significant secondary cracking nor crack bifurcation was observed in AISI 4335V steel (221 ksi yield strength) at \( K_I = 54.1 \) ksi-in\(^{\frac{3}{2}}\) in a hydrogen.
sulfide gas environment. As shown in Figure 44, the $K_{isc}$ value in 0.40 torr $H_2S$ gas is less than 21 ksi-in$^{\frac{1}{2}}$. Therefore, the Carter model, for an $(n)$ value of 2.5, predicts crack branching at $K_1 = 53$ ksi-in$^{\frac{1}{2}}$. No branching was observed. Therefore, the data of the present study clearly show that the Carter criterion is not applicable to all specimen geometries and slow crack growth environments.

4.6.12 Auger analysis of fracture surface from an $H_2S$ environment

The presence of sulfur on the $H_2S$ environment fracture surface suggests a dissociative chemical adsorption of $H_2S$ on steel. Although the use of x-ray diffraction techniques, as with $Cl_2$ and halide gas fractures, did not reveal a stoichiometric compound, the Auger results do agree with the Roberts and Ross (70) results, in that chemically adsorbed sulfur is present on iron exposed to $H_2S$ at room temperature. The adsorbed sulfur may indeed play a
significant role in the slow crack growth process in gaseous H$_2$S environments.

It is important to note that the Auger specimen was exposed to air for several days, prior to analysis, and therefore the presence of oxygen (on the surface) is expected.

4.6.13 Acoustic emission activity in hydrogen gas environments

In contrast to crack velocity, both the acoustic emission rate and the acoustic emission count rate increase continuously with increasing applied stress intensity for 205°C tempered AISI 4335V steel in 300 torr H$_2$ gas (Figure 51). No Region I - Region II behavior is observed in the acoustic emission results. In addition, the correlation of acoustic emission rate with crack velocity (Table 31) shows a maximum crack extension increment per acoustic emission value at approximately $K_I = 25.0$ ksi-in$.^4$. Such behavior can be explained by the secondary cracking observed at stress intensity values in Region II.
Since the polarization direction of the accelerometer (during testing) is parallel to the specimen side grooves, it is expected that the transducer would be more sensitive to strain components in that direction. Such strains would be generated by the formation of secondary cracks, normal to the plane of the specimen side grooves. In addition, such secondary cracks, as well as the motion of the main crack front, would be expected to result in stress wave activity. Since only the growth of the main crack is considered in the fracture mechanics analysis, and subsequent crack increment calculations (Table 31), it is seen that secondary cracking could result in both: (1) additional acoustic emission activity at Region II stress intensity values, and (2) a lower apparent crack jump distance in Region II, as determined by acoustic emission measurements.

4.7 Rate-Controlling Process for Slow Crack Growth In Gaseous Hydrogen Environments

In the study of slow crack growth in gaseous H₂
environments, the requirements for hydrogen entry into, and diffusion through, steel (i.e. permeation) have been strongly supported by: (1) the relative crack velocities in hydrogen and deuterium gaseous environments, (2) the substantial (two order of magnitude) increase in crack velocity on the addition of 2.1 vol% H₂S to the hydrogen gas, and (3) the similar dependence of both hydrogen permeation rate and crack velocity on the hydrogen sulfide concentration in H₂/H₂S gaseous mixtures. All results agree with those expected for a hydrogen permeation-controlled slow crack growth process in gaseous hydrogen environments. Therefore, the results of the present study, in conjunction with the Sawicki model (4) and the fractography observed in this study, will be examined to show that hydrogen permeation is a feasible rate-controlling process for the cracking in gaseous H₂ environments.

It has been shown in Section 2.7.4.2 that the effect of test temperature on the pressure dependence of hydrogen permeation, proposed by Sawicki, does not explain the results observed in the prior work (4), nor
those of the present study. However, if fractography is defined by the applied stress intensity (i.e., Region I or Region II of the crack velocity-stress intensity curve), the pressure dependence results of both studies may be explained. As described in Section 2.7.4, the limiting condition for a first power dependence of crack velocity on hydrogen pressure, in the Sawicki model, is:

$$[a_0 P_{H_2}^3 e^{-\Delta H_0 (1 - \alpha \theta)/RT}]^{\frac{3}{2}} > 1$$

The limiting condition for a higher pressure dependence ($P_{H_2}^{3/2} - P_{H_2}^2$) of crack velocity is:

$$[a_0 P_{H_2}^3 e^{-\Delta H_0 (1 - \alpha \theta)/RT}]^{\frac{3}{2}} < < 1$$

The significant point in the analysis is that the magnitude of the term on the left is an exponential function of the heat of adsorption of hydrogen on steel [$\Delta H_0 (1 - \alpha \theta)$]. For a hydrogen pressure of 400 torr, and an adsorption heat of -2 kcal/mole (approximately one monolayer coverage), the adsorption term on the left is 0.05 at 300°K. If the heat of
chemisorption is -8 kcal/mole, the value of the expression is 7.1 at 300°K. Therefore, for a heat of adsorption of -8 kcal/mole, the pressure dependence of crack velocity is \( P_{H_2}^{1/2} \). For an adsorption heat of -2 kcal/mole, the expected pressure dependence is \( P_{H_2}^{3/2} - P_{H_2}^2 \), with all dependencies being obtained at room temperature. It is also important to recall that the fractional surface coverage values, for the heats of adsorption, are more than 0.5 monolayers. Such a coverage is reasonable, in view of the pressure range investigated in the Sawicki work and in the present study (100 to 800 torr H\(_2\)).

Since hydrogen entry is believed to occur at or near the crack tip region, it is reasonable to assume that the surfaces created by the fracture process (as observed in fractography) would, by their physical and chemical nature, strongly influence both the kinetics and thermodynamics of the permeation process. On this basis, the mode of fracture may explain the difference in heat of adsorption, and therefore the
pressure dependence of crack velocity, observed in Regions I and II. The fractographic results, for the case of a first power hydrogen pressure dependence of crack velocity, show either a ductile, transgranular fracture or a mixed mode fracture, with secondary cracking. Higher pressure dependencies \( (P_H^{3/2} - P_H^2) \) were observed in the case of an intergranular fracture mode (along prior austenite grain boundaries). Therefore, the key issue is the effect of such fracture modes on the heat of adsorption for hydrogen on steel.

The original investigation by Porter and Tompkins (68) has described hydrogen chemisorption on iron using the assumption that all sites on the iron surface do not possess the same adsorption potential. The non-uniformity of a metal surface, with regard to binding energy for gas adatoms, has also been used to describe the decrease of the heat of adsorption with increasing surface coverage (148,149). Such Temkin behavior is exhibited by hydrogen on iron (69). As suggested in the literature (148), the heat of adsorption is
expected to be greater at unsaturated surface sites, such as those at the edges of crystals. Such high binding energy sites would be more prevalent in the heterogeneous and rough fracture surface observed in Region II, as opposed to the relatively smooth, intergranular fractures of Region I. It is then postulated that, at high stress intensity values, the heat of chemisorption of hydrogen is greater. It must be noted that either an increase of the initial heat of adsorption or a decrease in fractional surface coverage could produce the same effect on the kinetic equation for permeation. However, in the absence of experimental measurement of these parameters for the fracture surfaces of Regions I and II, the result can only be attributed to the heat of adsorption, per se.

A second consideration in the pressure dependence transition between Region I and Region II crack growth is the chemistry of prior austenite grain boundaries, as contributing to a lower heat of adsorption for hydrogen in Region I slow crack growth. Prior work
with low alloy high strength steels (150) has shown a correlation between temper embrittlement, involving fracture along prior austenite grain boundaries, and the presence of impurity elements (P, As, Sb, N, Si, and Sn) in the steel. Studies by Trapnell (151) of the initial heat of chemisorption of hydrogen on transition metals has shown the following order:

\[ \text{Ta} > \text{W} > \text{Cr} > \text{Fe} > \text{Ni} > \text{Rh} > \text{Cu, Au} \]

On this basis, the presence of elements from groups V or VI of the Periodic Table could result in a lower heat of adsorption of hydrogen on the grain boundary surface, as opposed to a transgranular surface. The result would then be a lower heat of adsorption for a Region I cracking process, than for a slow crack growth process at a Region II stress intensity value. It is believed (150) that the grain boundary segregation in steels occurs during prior austenitization, in which case the chemical effect would be present with or without the temper embrittle-
ment phenomenon. In addition, the required amount of impurity to affect chemisorption is expected to be less than one monolayer, whereas the amount required for temper embrittlement to occur is, as yet, undefined.

The lower heat of hydrogen chemisorption, due to impurity segregation at prior austenite grain boundaries is in agreement with recent studies by Hondros et al (152). Using Auger electron spectroscopy techniques, the authors found that a 0.5 monolayer coverage by sulfur existed on the intergranular fracture surface of an iron-sulfur alloy. The sulfur concentration (in the alloy) was 44 atom ppm. In the present study, the investigated steels contained 40 ppm (D6AC), and 90 ppm (AISI 4335V). Therefore, grain boundary segregation of sulfur, as affecting hydrogen chemisorption on grain boundary surfaces, is a reasonable explanation for the results of the present study.

The significant effect of fractographic considerations is that, in a qualitative manner, the
fracture mode can explain the application of the Sawicki permeation model to the results of both the present study and the original Sawicki investigation (4).

4.8 Experimental Problems Encountered in Gaseous Environment Testing

During each test in Cl₂, HCl, or HBr gas, a corrosion attack of the Speedi-Vac gauge occurred, to the extent that each new gauge malfunctioned after a single test. Similarly, a corrosion attack of both the tool steel specimen grips and the specimen itself was observed after each test. On exposure of the test system to air for several weeks (after a 48 hour bake-out cycle), severe corrosion of all non-stainless steel parts, and mild corrosion of the Type 304 stainless steel chamber, was observed. For these reasons, the halogen and halide gas environment testing was not extensive.

In the testing of H₂/O₂ gas mixtures, as crack growth environments, the total pressure in the test
chamber, after backfilling, was found to decrease with time. This was particularly observed at the high oxygen pressure (4.7 torr). Since the vacuum gauge (Alphatron) sensitivity for oxygen gas is 5 times greater than for hydrogen, the removal of 5 vol% oxygen results in a significant reduction in the apparent total pressure (approximately 25%). When the system was backfilled to 4.7 torr 0₂, the gauge reading was 5.45. After the addition of 104 torr H₂, the gauge reading was 28.0. Within five minutes after the start of the test, the gauge reading had reduced to 20.5. Using the experimentally determined gauge sensitivities of 1.17 and 0.22 for oxygen and hydrogen respectively, the final pressure reading agrees (within experimental error) with that expected in the consumption of all oxygen (and twice as much hydrogen) to form a phase whose vapor pressure is quite small ( < 0.5 torr). The valve to the vacuum pumps was checked for leakage, and none was found. No cryogenic traps were directly open to the system during any H₂/O₂ or H₂/H₂O tests. Since the obvious product,
H₂O, has a vapor pressure of 24 torr at 25°C, and a nominal gauge sensitivity comparable to that for oxygen, the result suggests that: (1) water is formed in the H₂/O₂ gaseous mixture, and (2) the water vapor is condensed on a cold surface in the test system, possibly near the chevron baffle trap.

During the H₂S environment testing, it was observed that the toxic gas was retained by the mechanical pump oil for at least one week. Therefore, for safety reasons, the pumping system cannot be exhausted directly into the laboratory. The use of flexible tubing (4" diameter) between the mechanical pump and the laboratory exhaust fan (2000 cfm) provided a satisfactory solution to the exhaust problem.

A study of the effect of temperature on crack growth kinetics, although included in other investigations (2,4,89), was not possible in the present study. Attempts were made to vary specimen temperature, using either: (1) nichrome wire heating
elements in the vacuum chamber, or (2) heating tapes (external) on the vacuum chamber. Temperatures were monitored with chromel-alumel thermocouples, resistance welded to the specimen, and in contact with the inner chamber wall. However, for several reasons, the study was discontinued. The non-continuous trapping system (12 hours maximum) did not permit both a preliminary bake-out and the attainment of steady state high temperature conditions in the system (with trapping throughout). Such a study also requires isothermal conditions (gas, specimen, and test chamber), such that heat transfer and thermal expansion (or contraction) of the specimen or loading rods do not occur upon admission of the test gas. Such conditions could not be achieved. Since a typical test involved a displacement of 0.001", the error due a temperature change of the stainless steel loading rods may be estimated. A value of $9 \times 10^{-6}$ in/in/°C is taken as the thermal expansivity of 18-8 stainless steel (153). At least fifteen inches of such stainless
steel loading rod was present in the vacuum chamber. For a 1°C temperature change of the rods, the displacement corresponds to a 13.5% error, on the basis of a 0.001" test displacement. The use of an LVDT device across the specimen grips (inside the vacuum chamber) was the original approach to minimizing the temperature effect. However, the LVDT output voltage was found to change slowly (for several hours) upon either evacuation or backfilling of the test chamber. Two new hermetically-sealed LVDT devices were used, and exhibited the same effect.

Following several bake-out cycles (specimen always absent), diffusion pump oil was found on the specimen loading rods. Since the rods were not externally heated throughout the bake-out cycle, the observation indicated oil condensation on the cooler rods (as opposed to the chamber wall). It was felt that the use of external heating tapes to attain high temperatures would thus result in contamination
of the specimen by oil. The use of internal nichrome heating elements resulted in at least a $5^\circ$C temperature difference across the constant $K_I$ zone of the specimen. On the basis of the experimental difficulties, the attempts to vary temperature were discontinued.
CONCLUSIONS

On the basis of the results obtained in the present study, it is concluded that:

(1) For the same steel, gas pressure, and applied stress intensity, the gaseous species HCl, HBr, Cl₂, or H₂S promote environmentally-assisted slow crack growth at velocities at least one order of magnitude greater than those observed in pure molecular hydrogen gas.

(2) Regions of strong and weak dependence of crack velocity on both applied stress intensity and gas pressure occur in molecular hydrogen and molecular hydrogen sulfide gas environments.

(3) For the case of high strength steel, crack velocities are 2.1 to 2.8 times slower in gaseous deuterium than in gaseous hydrogen, for the same gas pressure and applied stress intensity.
(4) The presence of hydrogen is not required for slow crack growth in a high strength steel exposed to a gaseous environment.

(5) The addition of 2.1 vol% hydrogen sulfide to a molecular hydrogen gas environment increases the observed crack velocity in high strength steel by two orders of magnitude.

(6) Both water vapor and oxygen gas additions, at levels of less than 5 vol%, retard the crack growth kinetics in molecular hydrogen gas environments (1 atmosphere pressure) by one order of magnitude or more.

(7) Methane or ammonia gases, at room temperature, are notably less severe crack growth environments than pure molecular hydrogen gas.

(8) The cracking behavior of high strength steel in molecular hydrogen gas environments is consistent with the Sawicki model for hydrogen permeation-controlled slow crack growth.
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