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AN EVALUATION OF HYDROGEN EMBRITTLEMENT IN Cr–Mo PRESSURE VESSEL STEELS

Topical Report No. 1

By
B. J. Shaw
E. W. Johnson

August 24, 1980

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Westinghouse Electric Corporation
Research and Development Center
Pittsburgh, Pennsylvania

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Abstract

Commercial 2¼ Cr-1 Mo low strength steel specimens have been tested to measure their susceptibility to hydrogen embrittlement in an environment of H_2S at 50 psig. It was found that two factors, viz. i) the plane stress zones on the crack front in compact tension specimens and ii) incubation time effects, seriously confounded measurements on these steels when tested by conventional rising load experiments. Because of the incubation time effect, K_{or} (the stress intensity at which cracking starts in a rising load test) is a loading rate dependent variable and is usually significantly greater than the arrest stress intensity, K_{arr} in a bolt loaded test. K_{arr} must therefore be used as a measure of hydrogen resistance. The incubation time has been significantly reduced by cyclicly loading in the environment to initiate the crack and K_{arr} has been measured by holding the specimen in constant displacement immediately after crack initiation. The plane stress problem has been eliminated by deeply side grooving the compact tension (CT) specimens.

As an example of the importance of these effects a 3T CT smooth sided specimen was compared with a side grooved 2T CT specimen of the same steel. Whereas the K_{or} value for the smooth 3T was approximately 150 ksi $in^{\frac{1}{2}}$ the K_{arr} value for the side notched 2T was approximately 20 ksi $in^{\frac{1}{2}}$. A study of the effect of strength level is included.

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Introduction

Hydrogen embrittlement of low alloy steels can be divided into three broad categories: high strength steels, with yield strengths (σ_y) of order 175 ksi or 1200 MPa which are prone to cracking in pure hydrogen gas; intermediate strength steels (σ_y ~120 ksi or 850 MPa) which are less susceptible to fracture in hydrogen gas but crack readily in H_2S gas; and low strength steels (σ_y ~70 ksi or 500 MPa) which will only crack in hydrogen charged aqueous solutions. These three categories have been delineated in earlier papers (1,2).

In this paper we report the methods developed to assess the hydrogen embrittlement susceptibility of low strength 2¼ Cr-1 Mo steels in commercially pure H_2S gas. The area explored lies in the range in which the propensity to cracking is limited and consequently the experimental technique had to be carefully refined. The experiments were designed to measure the threshold stress intensity (K_{th}) which is also commonly designated K_{Iscc} where scc is sub-critical cracking. Since our experiments measured the stress intensity at which the crack apparently arrested, we use both the terms K_{arr} and K_{Iscc} for our results.

The most important factors recognized in obtaining K_{arr} were the influence of incubation time and the role of the plane stress zones present on either side of the compact tension (CT) specimens used in the tests. Since the incubation time for crack initiation is usually large in low strength steels, it was not possible to estimate K_{Iscc} from a simple rising load test. The rising load method yields a satisfactory value of K_{Iscc} if the incubation time is very short and is sometimes referred to as the "apparent K_{Iscc}" (3). A detailed discussion of the influence of incubation time in the rising load test is presented elsewhere (4).

The effect of the plane stress zones is essentially that of pinning the crack on either side of the CT specimen. The conventional bolt loaded CT specimen, for example, would have a "tunneled" crack front, in which the center of the crack in plane strain has advanced much further than the sides. This effect is discussed by Gerberich (5). The evaluation of K_{Iscc} from a specimen with a tunneled crack configuration is extremely difficult.

The experiments presented here incorporate various methods for overcoming these difficulties and may be regarded as a hybrid of the more standard techniques. The measured K_{arr} values in many instances are surprisingly small. However, from the point of view of the industrial

designer, it should be pointed out that the mechanical history of the specimen tested in the laboratory is unlikely to be found in normal commercial applications.

Discussion of the Experimental Technique for Testing Low Strength Steels in H_2S

One of the objectives of this study was to evaluate K_{Iscc} as rapidly as possible. Whereas this is a relatively easy task in high strength steels, which have small incubation times and very small plane stress zones, it is increasingly difficult as the yield stress is decreased. The constant displacement or bolt load test described by Novak and Rolfe (6) has been demonstrated to yield a K_{arr} which is identical to K_{th} measured in constant load tests. After an incubation time t_i (in this test), the crack grows at decreasing K values until arrest occurs at K_{arr}. There are difficulties in using this test for low strength steels. First, the incubation time is usually very long and hence one is tempted to start at an applied K very much greater than K_{arr}. However, if K is too great compared with K_{arr}, the crack approaches the back face of the specimen on arrest. The experiment cannot then yield a valid K_{arr}, since the plastic zone size may be comparable with the remaining ligament. A second problem lies in the excessively large plane stress zone r_y produced in low strength steels. An approximate value for r_y is given by (7) $r_y = \frac{1}{2\pi}\frac{K^2}{\sigma_y{}^2}$, where K is the applied stress intensity and σ_y is the yield stress. It will be shown below that plane stress zones effectively pin the crack and lead to considerable overestimates of K_{arr}.

The two primary problems, plane stress zone pinning and incubation time, were reduced as follows.

Plane Stress Zone Elimination

In the first test described below on a 3T CT specimen, it was found that the plane stress zone was 0.5 in or 12 mm maximum (Fig. 1). It was decided therefore to incorporate side grooves on specimens with a depth approximately half of the maximum plane stress pinning zone. The result of this specimen modification can be seen in Fig. 2; the crack front is reasonably straight, thus implying to a first approximation that the entire crack front is in plane strain.

Estimates of the stress intensity K in a side grooved specimen are not as precise as those for a conventional smooth sided specimen. The simplest

approach for an estimate of K (8) is to assign an effective thickness to the specimen, B_{eff}, which is the geometric mean of the overall thickness, B, and the crack plane thickness, B_N, or $B_{eff} = (B \times B_N)^{\frac{1}{2}}$. This estimate for B_{eff} was used by Novak and Rolfe (6). Pollock (9) in later work concluded that the effect of side groove depth for B/B_N in the range 1.1 to 2.9 on the crack growth rate in stress corrosion tests was not significant.

Throughout the text values for K at various stages of crack growth will be given. These values are estimates based upon the following methods: (a) If the compliance of the specimen is measured at any stage an estimate of the crack length is obtained from methods given by Saxena and Hudak (10). [This applies for both grooved and ungrooved specimens.] (b) For a given crack length, either measured or estimated in an ungrooved specimen, K can be evaluated directly from the load P (10). (c) For a given crack length in a side grooved specimen K is estimated by replacing the specimen thickness B by an effective specimen thickness B_{eff}.

Wherever possible the crack length at any given stage is taken directly from the specimen fracture surface.

Reduction of the Incubation Time (t_i)

Once the plane stress problem is removed, the incubation time is the primary obstacle to evaluating K_{arr}, since we require to evaluate K_{arr} as rapidly as possible. There are probably a large number of factors, with varying degrees of importance contributing to t_i. These include (a) hydrogen sulfide reaction with a surface oxide film near the crack tip, (b) H_2S reaction with the fresh metal surface in the crack tip vicinity, (c) hydrogen entry into the metal and diffusion or transport to a critical crack tip location, (d) hydrogen accumulation in the critically stressed region until a concentration sufficient for internal crack nucleation is attained, (e) nucleation of the internal crack and growth at a rate determined by the rate of supply of hydrogen in the previously described processes, and finally (f) breakthrough of the internal crack to join the existing crack.

Of these the surface oxide film at the crack tip after air pre-fatigue cracking is probably one of the most important factors. Fractographic evidence to support (e) and (f) has been found in an HY 180 steel tested in hydrogen (4) in which it was also observed that the crack circumvented the plastic zone at the tip of the pre-fatigue crack. Thus it is inferred that the work hardened region at the tip of the crack can also act as a crack inhibitor.

In order to minimize incubation time effects we therefore fatigue pre-cracked specimens in the H_2S environment. Since we are no longer concerned with measurements of K_{or} the maximum fatigue stress level is not a consideration as it would specifically be for measurements of K_{Ic} (i.e. K_{or} measured in air). The procedure developed for crack initiation test was to cyclicly load the specimen in the environment at 0.5 Hz, by increasing K_{max} values* in steps until crack growth was clearly discernible by a change in the specimen compliance. Each step was conducted at a constant maximum displacement so that crack growth was exhibited by a decreasing maximum load. A decreasing K_{max} with crack advance is automatically brought about by this method.

Immediately after the environmental cyclic loading crack growth started, unoxidized metal was exposed and the specimen could be tested to evaluate K_{arr} without an excessive incubation time. The method used to arrive at K_{arr} was simply to hold the specimen at a constant displacement $v(\dot{v} = 0)$, starting at a displacement slightly higher than that associated with the last K_{max}. This is essentially a simulated bolt loaded test in which the load drop at constant displacement can be monitored. Typically in 2¼ Cr-1 Mo specimens, tempered to an ultimate strength level of order 105 ksi (724 MPa), the time for the crack to grow to K_{arr} is 2 to 3 days (1.7×10^5 - 2.6×10^5 s).

Experimental Test Assembly

Stainless steel chambers were designed to test 1T, 2T and 3T compact tension (CT) specimens in an environment of 446 KPa commercial high purity H_2S. The load or displacement applied to the specimen was controlled by a function generator. The loading was performed by a servohydraulic machine with continuous feedback control based upon the output either from the load cell on the tie rod to the specimen or from an LVDT, which measured displacement on the front face of the CT specimen. Both the LVDT and the load cell were located outside the chamber to prevent degradation by the H_2S gas. Prior to each test the chamber was evacuated at ~20 Pa for 16 to 20 hr.

*K_{max} is the upper K associated with the cyclic loading.

Experimental Results

Preliminary Tests: Sample No54H

In this section we present the data generated from three CT specimens (1T, 2T and 3T) taken from one steel sample. The sample is 2¼ Cr-1 Mo plate donated to the program by the American Petroleum Institute and is designated as No54. It was re-austenitized and cooled to produce a bainitic structure and subsequently tempered to a Rockwell C hardness of order 19.5. This is equivalent to a U.T.S. level of order 108 ksi (758 MPa). The heat treatments and sample analytical chemistry are given in Table I.

Table I. Heat Treatment and Analytical Chemistry of Sample 54

Heat Treatment of 6-in thick plate:

As received	1750°F - 8 hr	- water quench
	1290°F - 8 hr	- water quench
Second Heat Treatment		
pre-heat	900°F - 15 hr +	
	1700°F - 3 hr	
Repeated water dip quench*		
to	900°F - 1 hr	- air cool
temper	1100°F - 9 hr	- air cool

*Not less than 700°F; Rockwell Hardness R_C 19.5; Equivalent UTS 108 ksi

Analytical Chemistry

Element	C	Cr	Mo	Mn	Si	Ni	Cu
Weight percent	.125	2.19	.93	.47	.47	.13	.09
Element	**P**	**S**	**Sn**	**Sb**	**O**	**N**	**As**
Parts per million	143	42	106	21	51	142	249

Conversions: 1 hr = 3.6×10^3 s

$t°C = (t°F - 32)/1.8$

1 ksi = 6.895 MPa

The hardness of this sample is the same order of magnitude as the peak hardness found in the heat affected zones (HAZ) around welds in 2¼ Cr-1 Mo plate [1]. The re-tempered steel was intended to simulate the HAZ in plate material recognizing at the same time that the structure would not be comparable with that found in an actual HAZ. Comparison with data from an actual HAZ will be published elsewhere.

Sample No54H, 3T CT Smooth Sided Specimen. The 3T specimen was machined according to the ASTM E399 specifications. It was machined without side notches since it was large enough to have at least 60% of the crack front in a plane strain condition. Complete details of the experiments on this specimen are given so as to provide the background for the final test technique.

The specimen was cyclicly loaded at 0.5 Hz in 50 psig H_2S (446 KPa) environment at a maximum K of 77 ksi$\sqrt{in}$ to produce approximately .17 in of crack growth. It was then loaded and held at constant displacement ($\dot{v} = 0$) in four stages of increasing applied K = 102, 124, 130 and 133 ksi $in^{\frac{1}{2}}$. At each stage the compliance check indicated no crack growth had taken place. In the final stage of this set of experiments the specimen was held at a K of 133 ksi$\sqrt{in}$ for 175 hr or just over one week.

In order to be sure that the crack tip had not blunted in these experiments, the specimen was cyclicly loaded again at a maximum K of 130 ksi$\sqrt{in}$. It was then reloaded at a constant displacement rate until crack growth started at a K of approximately 148 ksi $in^{\frac{1}{2}}$. The crack continued to grow at decreasing loads as the displacement was increased. The test was stopped at K of order 155 ksi $in^{\frac{1}{2}}$ at which point the crack had grown .09 in. The specimen was then reloaded to a K of order 159 ksi $in^{\frac{1}{2}}$ and held at $\dot{v} = 0$ for 53 hr. In this period the load dropped continuously. The constant displacement test was ended to take a compliance check at K of order 143 ksi $in^{\frac{1}{2}}$ in which time the crack had grown 0.23 in. This represents a crack growth rate of 5.5×10^{-3} in/hr.

Two similar tests were conducted from K = 143 to 140 in 20 hr and from K = 143 to 125 ksi $in^{\frac{1}{2}}$ in 71 hr. At this point the tests were concluded, even though the crack was still growing, and the specimen was pulled apart in air. Figure 1 shows the fracture surface upon which the various test stages are reasonably clearly delineated. Measurements of the crack length on the specimen did not correlate well with the crack lengths derived from the compliance data. In fact the compliance estimates of the crack length were almost exactly the average of the maximum (center) and minimum (side) crack lengths and not the average crack length across the crack front.

Throughout this section please convert:
1 hr = 3.6×10^3 s
1 in = 2.54×10^2 m
1 ksi $in^{\frac{1}{2}}$ = 1.099 MPa $m^{\frac{1}{2}}$

A review of the data is given in Table II. This one test, which consumed more than 20 days active testing time, showed that there was a significant plane-stress component of approximately 0.5 in on each side, and that crack growth rate was very slow. The second test, on the 2T CT specimen, was therefore modified in an attempt to eliminate the plane stress component by introducing a 0.25 in side groove on the specimen sides.

Table II. Resume of Data from Specimen 54H-3T*

Test Step	Test	Comment
1	Cyclic loading at 0.5 Hz in H_2S K_{max} = 77	Crack growth
2	Constant displacement	
	i) K = 102 for 10 hr	No crack growth
	ii) K = 124 for 16 hr	No crack growth
	iii) K = 130 for 65 hr	No crack growth
	iv) K = 133 for 175 hr	No crack growth
3	Cyclic loading at 0.5 Hz in H_2S K_{max} = 130	Crack growth
4	Slow constant rising displacement rate. Test stopped at K = 156	Crack growth at K = 148
5	Reload to K = 159 and hold at constant displacement 53 hr. Unload at K = 143	Crack growth rate å approx. 5.5×10^{-3} in/hr (#1) $\dot{K}$ approx. 0.3 ksi $in^{\frac{1}{2}}$/hr
6	Reload to K = 143 and hold at constant displacement 20 hr. Unload at K = 140 for compliance data	Crack growth rate å approx. 5.0×10^{-3} in/hr (#2) $\dot{K}$ approx. 0.15 ksi $in^{\frac{1}{2}}$/hr
7	Growth at constant displacement continued from K = 143 to K = 125 in 71 hr. Test ended - crack still growing.	Crack growth rate å approx. 6.0×10^{-3} in/hr (#3) $\dot{K}$ approx. .25 ksi $in^{\frac{1}{2}}$/hr
	Total testing time approx. 20 days	
(#1) å at specimen center 6.8×10^{-3} in/hr (#2) å at specimen center 7.5×10^{-3} in/hr (#3) å at specimen center 4.2×10^{-3} in/hr		Derived from actual crack lengths at specimen center.

*See text for details. The units of K are ksi $in^{\frac{1}{2}}$ throughout, and are derived solely from compliance data and load-time curves.

Sample No54H, 2T CT 0.25 Side Groove Test. The standard 2T CT specimen was modified by the introduction of a 0.25 in side groove on the specimen side. The specimen was cyclicly loaded at 0.5 Hz to a final K_{max} of 48 ksi $in^{\frac{1}{2}}$. It was then loaded to a K of 105 ksi $in^{\frac{1}{2}}$ and held at constant displacement. After

70 hr the crack had extended to 0.35 in from the back of the specimen and had a K estimated between 20 and 25 ksi $in^{\frac{1}{2}}$. A plot of the crack length as a function of time was almost linear giving $\dot{a} = 22 \times 10^{-3}$ in/hr. Similarly $\dot{K}$ was almost constant at -1.3 ksi $in^{\frac{1}{2}}$/hr. The photograph of the fracture surface shows that the crack has a straight front indicating that the entire test was under the plane-strain conditions. It should be noted however that the fatigue crack front was not straight but had a "reverse-tunnel" shape (Fig. 2).

Sample 54H, 1T CR 0.25 Side Groove Test. The standard 1T CT specimen was modified by machining a 0.25 in side-groove on the sides. Since the rationale for the side grooves was to eliminate the plane-stress component, which in this sample was of order 0.5 in (i.e. a total of 1 inch in the entire crack front) and since also the side grooves represented such a radical modification to the conventional CT specimen, the test on the 1T specimen was limited to assess its applicability to obtaining valid data. The specimen cracked by cyclic loading in the 50 psig H_2S environment and held at constant displacement at K = 43 ksi $in^{\frac{1}{2}}$ for 39 hr and after cyclicly cracking again at K = 48 ksi $in^{\frac{1}{2}}$ for 20 hr. No static displacement crack growth took place in either test. The final environment cyclic loading K_{max} was 63 ksi $in^{\frac{1}{2}}$. The specimen was then loaded to 69 ksi $in^{\frac{1}{2}}$ and held in constant displacement. After 17 hr the crack had extended to an applied K of order 50 ksi $in^{\frac{1}{2}}$. The specimen was unloaded and pulled apart in air. The fracture surface, Fig. 3, shows that the crack front is straight, indicating that plane-strain conditions prevailed. The compliance measurements gave accurate estimates of the crack length in both the 2T and the 1T specimen. For the test period in the 1T specimen $\dot{a} = 15 \times 10^{-3}$ in/hr and $\dot{K}$ = -1.1 ksi $in^{\frac{1}{2}}$/hr. The 1T data compares reasonably well with the 2T-specimen data bearing in mind the method used to assess the compliance and K values for the deeply side grooved 1T specimens.

Tests on Samples 55H and 77H

The heat treatments and chemistries of samples 55 and 77 are given in Tables III and IV. These samples were tempered to approximately the same strength level as No54H.

In this section the data of tests very similar to those of 54H 2T are recorded with less fine detail. Changes or modifications in the test procedure are noted.

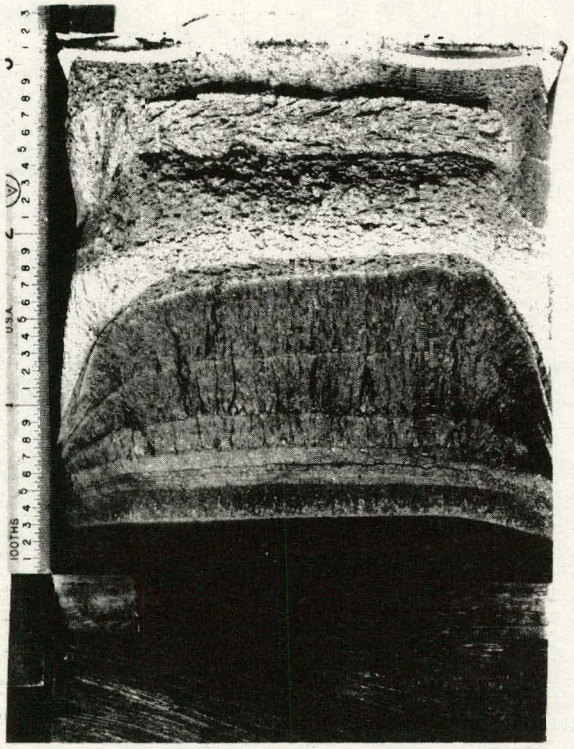

Fig. 1 - Fracture surface of 3T compact tension specimen 54H tested in 50 psig H_2S. This was a smooth sided specimen which exhibited the effect of the plane-stress zones on either side. The crack front pinning in the plane-stress zones is very striking.

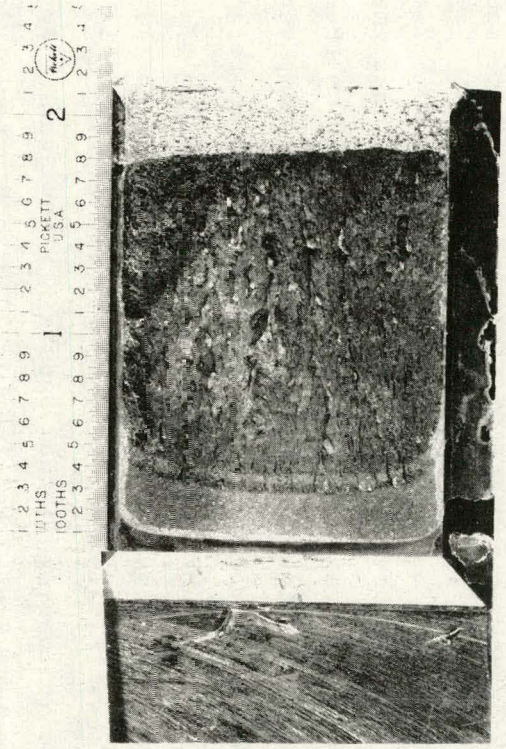

Fig. 2 - Fracture surface of deeply side grooved 2T compact tension specimen 54H tested in 50 psig H_2S. This specimen exhibits little or no effect from plane-stress on either side of the crack front.

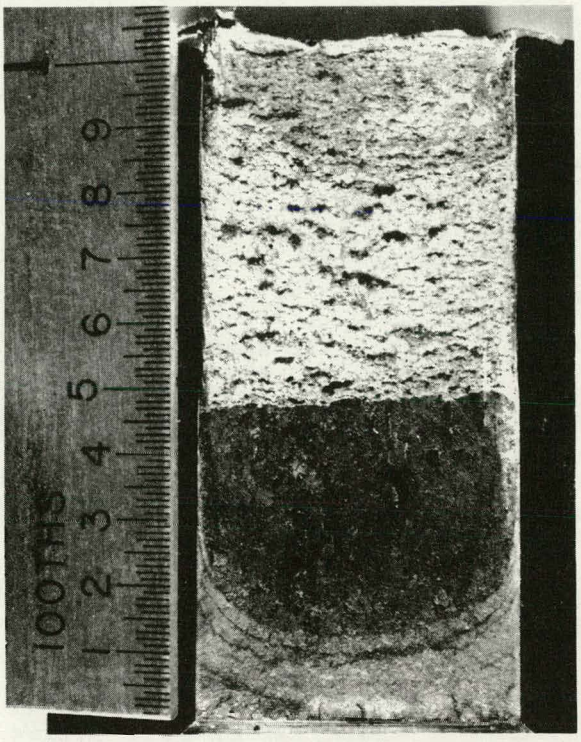

Fig. 3 - Fracture surface of deeply side grooved 1T compact tension specimen 54H tested in 50 psig H_2S. The constant displacement test was terminated prior to crack arrest in order to assess the crack front configuration. There is no evidence of plane stress pinning on the sides of the crack front.

Sample No55H, 3T CT 0.25 in Side Grooved Specimen. This standard 3T CT specimen had 0.25 in side grooves. After cracking by cyclic loading in the 50 psig H_2S environment, the specimen was subjected to simulated bolt load conditions or constant displacement control. The same test at increasing K values was repeated but in no instance did crack growth take place. The specimen finally failed catastrophically at a stress intensity of 134 ksi$\sqrt{in}$. The arrest value of K could not be measured.

Sample No55H, 2T CT 0.25 in Side Grooved Specimen. This specimen was cracked by cyclic loading in the environment after finding no crack growth in constant displacement at K = 50 ksi$\sqrt{in}$ the cyclic load cracking was continued up to a K_{max} = 75 ksi$\sqrt{in}$. At this point, at the peak of one load cycle the crack advanced dynamically, and arrested at K = 66 ksi$\sqrt{in}$, producing 0.6 in crack growth. All further attempts to make the crack grow in constant displacement were unsuccessful.

Table III. Heat Treatment and Analytical Chemistry of Sample 55 (2¼ Cr-1 Mo Steel)

Heat Treatment on 6-in thick plate:

As received 1750°F - 8 hr - air cool
1290°F - 8 hr - water quench
Second Heat Treatment
pre-heat 900°F - 15 hr +
1700°F - 3 hr
Repeated water dip quench*
to 900°F - 1 hr - air cool
temper 1100°F - 9 hr - air cool

*Not less than 750°F; Rockwell Hardness R_C 20; Equivalent UTS 110 ksi

Analytical Chemistry

Element	C	Cr	Mo	Mn	Si	Ni	Cu
Weight percent	.126	2.23	.97	.45	.39	.16	.10
Element	P	S	Sn	Sb	O	N	As
Parts per million	130	52	112	20	35	145	307

Conversions: 1 hr = 3.6×10^3 s
t°C = (t°F - 32)/1.8
1 ksi = 6.895 MPa

Table IV. Heat Treatment and Analytical Chemistry of Sample 77 (1¼ Cr-½ Mo Steel)

Heat Treatment on 5½-in thick forging:

As received 1675°F - 5½ hr - air cool
1240°F - 5½ hr - air cool
Second Heat Treatment
pre-heat 900°F - 15 hr +
1700°F - 3 hr
Repeated water dip quench*
to 900°F - 1 hr - air cool
temper 1100°F - 9 hr - air cool

*Not less than 750°F; Rockwell Hardness R_C 22; Equivalent UTS 115 ksi

Analytical Chemistry

Element	C	Cr	Mo	Mn	Si	Ni	Cu
Weight percent	.140	1.34	.45	.51	.60	.18	.17
Element	P	S	Sn	Sb	O	N	As
Parts per million	108	173	145	22	23	78	90

Conversions: 1 hr = 3.6×10^3 s
t°C = (t°F - 32)/1.8
1 ksi = 6.895 MPa

Sample No55H, 1T CT 0.25 in Side Grooved Specimen. After cracking by cyclic loading to K_{max} = 50 ksi$\sqrt{in}$ the stress intensity was increased to 64 ksi$\sqrt{in}$. The specimen was then held in constant displacement control and the crack advanced slowly to a K_{arr} = 44 ksi$\sqrt{in}$ in 34 hr.

Sample No77H, 3T CT 0.25 in Side Grooved Specimen. This specimen was cracked by cyclic loading in the environment. Numerous small dynamic crack advances, represented by audible clicks and slight load decreases, were observed in the constant displacement loading cycles. No crack growth took place in constant displacement tests. The test was then modified to give constant displacement for 1 hr followed by an unload and reload cycle for a periodic compliance check. A number of small crack advances were observed within the 1 hr hold periods. The stress intensities for these events ranged from 20 to 30 ksi$\sqrt{in}$.

After the environmental test, the specimen was exposed to air for 4 hr and loaded to failure at a rate $\dot{K}$ = 1.2 ksi$\sqrt{in}$/min. Failure in air took place at a stress intensity of approximately 112 ksi$\sqrt{in}$ after a very small amount of plastic deformation.

Sample No77H, 2T CT 0.25 Side Grooved Specimen. This specimen failed catastrophically during initial loading in the environment at K_{or} = 53 ksi in.

Sample No77H, 1T CT 0.25 Side Grooved Specimen. After cracking by cyclic loading in the environment, three tests were run on the same specimen. Crack arrest took place in each test at K_{arrest} = 29, 25.5 and 24 ksi$\sqrt{in}$, respectively. A small amount of discontinuous cracking was observed in the second test at K = 35 ksi$\sqrt{in}$. After the environmental test, the specimen was loaded in air at a constant displacement rate $\dot{K}$ = 1.5 ksi$\sqrt{in}$/min. The specimen underwent gross plastic deformation and did not crack at a stress intensity of approximately 80 ksi$\sqrt{in}$. At this point the test was ended. Plastic deformation set in at approximately 50 ksi$\sqrt{in}$. The specimen appearance was similar to that shown in Fig. 3.

Sample No74, Effect of Strength Level. The effect of strength level, using the same test technique, was carried out on sample No74. The heat treatments and analytical chemistry are given in Table V.

The results of the tests are given in Table VI. The highest strength specimen, which was untempered, cracked slowly from a maximum applied stress intensity K_{or} of 42 ksi$\sqrt{in}$ to crack arrest at K_{arr} = 28 ksi$\sqrt{in}$. The three specimens with UTS in the intermediate range of this series cracked catastrophically. One of the three, 74-5, was held at constant displacement for 17 hr

Table V. Heat Treatment History and Final Strength Levels of Specimens of Sample No. 74

(a) Heat Treatment Prior to Receipt

1750°F - 3 hr + water quench
1225°F - 4.5 hr + air cool
1100°F - 15 hr + }
1200°F - 30 hr + } Simulated post weld heat treatment
1275°F - 16 hr }

(b) Heat Treatment to Form Bainite

900°F - 15 hr +
1700°F - 3 hr +
Repeated water dip quench to 900°F (not less than 700°F)
900°F - 1 hr - air cool

(c) Tempering Conditions and Strength Levels

Specimen No.	Temperature °F	Time hr	Rockwell Hardness	Equivalent UTS (ksi)
74-3	Untempered	-	C27	126
74-1	1100	4	C22	117
74-5	1100	6	B99	114
74-4	1100	12	B97.5	109
74-2	1100	16	B97	106

Conversions: 1 hr = 3.6×10^3 s
$t°C = (t°F - 32)/1.8$
1 ksi = 6.895 MPa

(d) Composition of Sample No. 74

Element	C	Cr	Mo	Mn	Si	Ni	Cu
Weight percent	.103	2.28	1.00	.41	.21	.15	.15
Element	**P**	**Sn**	**Sb**	**As**	**O**	**N**	**S**
Parts per million	70	150	30	100	60	70	160

Table VI. Results of H_2S Environment Tests on Sample No. 74

Specimen No.	Approximate UTS (ksi)	Estimated K_{Iscc} (ksi$\sqrt{in}$)	Comments
74-3	126	28	Slow crack growth from 42 ksi$\sqrt{in}$ in 54 hr.
74-1	117	34	Catastrophic fracture; specimen completely failed.
74-5	114	52	No failure after 17 hr at 50 ksi$\sqrt{in}$. Catastrophic at 52.
74-4	109	42	Catastrophic fracture.
74-2	106	113	Very small crack growth (.05 in) in 28 hr.

Conversions: 1 in = 2.54×10^{-2} m
1 ksi = 6.895 MPa
1 ksi$\sqrt{in}$ = 1.099 MN/$m^{3/2}$
1 hr = 3.6×10^3 s

at an applied stress intensity (K_{APP}) of 50 ksi$\sqrt{in}$ without any indication of cracking. A slight increase in K_{APP} to 52 ksi$\sqrt{in}$ resulted in an immediate catastrophic failure. In comparison, the lowest strength specimen of the set exhibited a very small amount of crack growth at K_{APP} = 113 ksi$\sqrt{in}$.

These results indicate that, for this one sample of steel, there is a fairly sharp transition from a susceptibility to hydrogen embrittlement to relatively high resistance. This transition corresponds to the UTS range 106-109 ksi.

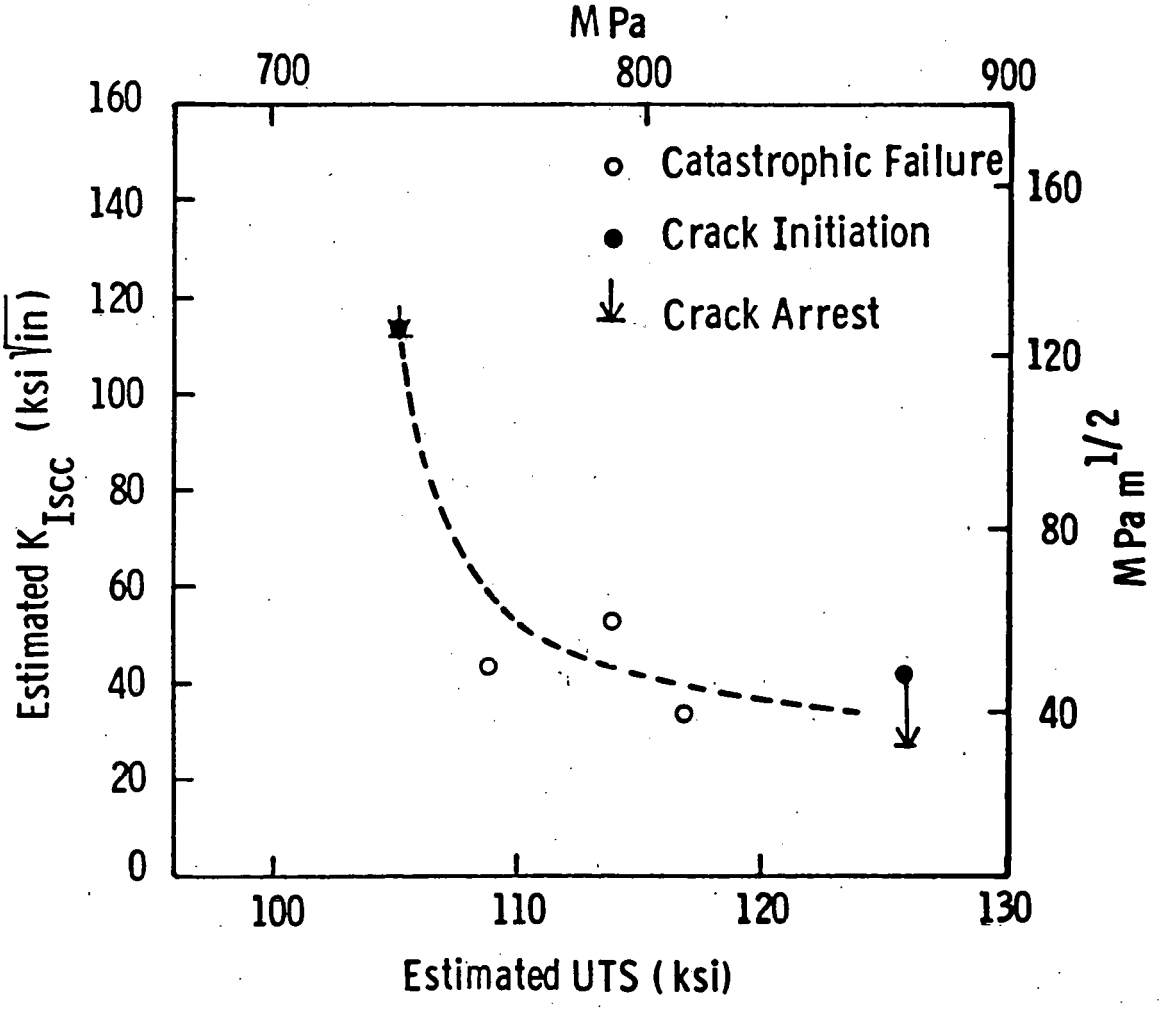

Fig. 4 - K_{Iscc} as a function of the ultimate tensile strength for sample No. 74. The K_{Iscc} was estimated from tests in 50 psig H_2S on 2T CT side grooved specimens and the UTS from the Rockwell Hardness measurements.

Discussion

The details given in the Experimental Results Section have provided the background of the experimental approach we have evolved for the most rapid determination of a K_{arr} value.

In the course of some of the experiments attempts to reduce the time requirement to reach K_{arr} by load shedding (i.e. a reduction of the applied K by reducing the displacement) proved unsuccessful. A reduction of 5% or more in the displacement resulted in an immediate arrest of the crack, at K values well above the finally measured K_{arrest}. Small reductions of about 1% did not cause crack arrest but at the same time did not significantly lessen the total time to arrest. The possible influence of test interruptions on crack-growth inhibition have been explained in part by the ensuing change in the crack hydrogen concentration (12).

The tedious test on the smooth sided 3T specimen served to emphasize the importance of the plane-stress zone. It did not prove possible to make the crack start under static loading until a stress intensity of order 148 ksi $in^{\frac{1}{2}}$ was reached. After over 140 hr of constant displacement testing the experiment was terminated, without crack arrest, at $K \sim 125$ ksi $in^{\frac{1}{2}}$. The estimated crack growth $\dot{a}$ of order 5.5×10^{-3} in/hr and the rate of decrease of the stress intensity, $\dot{K} \sim -.25$ ksi $in^{\frac{1}{2}}$/hr were very slow.

In comparison, the 2T specimen with 0.25 in side grooves started cracking readily at 105 ksi $in^{\frac{1}{2}}$ and cracked at a rate $\dot{a} = 22 \times 10^{-3}$ in/hr and $\dot{K} = -1.3$ ksi $in^{\frac{1}{2}}$/hr, which is significantly faster than the 3T specimen. Thus the important role of the plane stress zones is in pinning the crack on the specimen sides and inhibiting crack growth.

The crack advance to the back of the 2T specimen was undesirable and was a result of starting the constant displacement test at 105 ksi $in^{\frac{1}{2}}$. In comparison the 1T test was started at an estimated K of order 60 ksi $in^{\frac{1}{2}}$, though earlier attempts to start the constant displacement crack growth at $K = 43$ and 48 ksi $in^{\frac{1}{2}}$ failed. Our approach, of course, is to start the crack at the lowest possible K in order to reduce the time to reach K_{arr}.

It is important to note that the crack can advance at K = 20 to 25 ksi $in^{\frac{1}{2}}$ (from the 2T test) and therefore evidence of a required incubation time was revealed in the 1T test. Presumably this incubation time is associated with the time required for hydrogen to accumulate in the maximum stress zone ahead of the tip of the (unoxidized) crack (13). Apart from pre-charging the specimen with hydrogen, a variable not included in this program, it may not be possible to eliminate this component of incubation time.

Marked differences in behavior during the cyclic loading stage were found in that dynamic or catastrophic cracking occurred in larger specimens of 55H and 77H but not 54H. This phenomenon was not exhibited by the

smaller specimens which failed by continuous slow crack growth. The three samples had approximately the same strength level, as defined by R_B or R_C measurements. However, the yield strength, work hardening rate and ductile brittle transition temperature have not yet been determined. These factors could be significant in our understanding of the data.

The fact that the crack, once it has started to grow, can propagate at stress intensities well below that at which it would not propagate in many hours before it had started to grow, may provide evidence for dislocation sweeping of hydrogen (14). Alternatively hydrogen is accumulated at the tip of the crack and is swept along with its associated stress field.

The results of the tests on the first three samples are comparable with those of No. 74, shown in Fig. 4. Most investigations of the effect of yield strength or UTS on the threshold stress intensity show the same trend, though not necessarily as sharp a transition. A substantial review of collected data showing this trend is given by Gerberich (15). A similar trend was found by Payer, et al. (16) for specimens charged with hydrogen. In most of the studies reviewed, the UTS or σ_y is very high compared with the 2¼ Cr-1 Mo steels which have been tested in this study. Also, the test techniques did not usually incorporate side grooves. Consequently, exact comparison with this study is not possible. Hicko and Gilmore (17) used side grooved specimens in an aqueous environment of ½ wt percent glacial acetic acid with H_2S at one atmosphere and showed that K_{Iscc} in low strength 2¼ Cr-1 Mo steel could be as low as 48 ksi$\sqrt{in}$ (53 MN/m$^{3/2}$). The data from an aqueous solution, however, cannot necessarily be directly compared with that from a gaseous environment.

Conclusion

It has been shown that for low strength 2¼ Cr-1 Mo steels the plane stress zones in a conventional compact tension specimen serve to pin the crack front and thereby make the measurement of the threshold stress intensity in H_2S very difficult. The introduction of side grooves on the specimen substantially reduces this effect. The incubation time for crack initiation can be reduced by starting the crack with cyclic loading in the environment. The time required to reach crack arrest in a constant displacement test cannot be reduced by load shedding. Load shedding greater than one percent of the applied load appears to arrest the crack. The effect of strength level on K_{Iscc} has been determined, using the modified test approach. Based upon the samples evaluated in this study it appears that hydrogen embrittlement in H_2S is a sensitive function of the strength level and that the steel is relatively immune if the UTS is below 100 ksi (690 MPa).

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References

1. H. Okada, NACE-5 International Corrosion Conference Series, p. 124 (1973).

2. M. O. Speidel and P. M. Fount, ibid., p. 57.

3. W. G. Clark, Jr. and J. D. Landes, ASTM STP 610, p. 108 (1976).

4. E. W. Johnson and B. J. Shaw, submitted for publication to Met. Trans. Also Final Report U.S. Navy Contract N00014-77-C-0372 (1979).

5. W. W. Gerberich and Y. T. Chen, Met. Trans. A, p. 271 (1975).

6. S. R. Novak and S. T. Rolfe, Corrosion 26, p. 121 (1970).

7. D. Broek, Elementary Engineering Fracture Mechanics, Noordhoff (1974).

8. C. N. Freed and J. M. Krafft, Mater. 1, p. 770 (1966).

9. W. J. Pollock, Materials Note 121, Australian Dept. of Defense, Aero. Res. Labs (1979).

10. A. Saxena and S. J. Hudak, Jr., Int. Jnl. Fract. 14, p. 453 (1978).

11. R. K. Nanstad and D. A. Canonico, ORNL-5238, Dec. (1976).

12. S. J. Hudak and R. P. Wei, 5th Int. Conf. on Structural Mechanics in Reactor Technology, West Berlin, Germany, Aug. (1979).

13. P. Doig and G. T. Jones, Met. Trans. A, 7, p. 1993 (1977).

14. J. K. Tien, "Effect of Hydrogen on Behavior of Materials," Proc. Int. Conf., Jackson Lake Lodge, p. 609 (1975).

15. W. W. Gerberich, "Hydrogen in Metals," ASM Conf., Seven Springs, p. 115 (1973).

16. J. H. Payer, et al., Corrosion 32, p. 52 (1976).

17. G. S. Hicko and C. M. Gilmore, ASTM STP 645, p. 351 (1978).

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