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STUDY TO OPTIMIZE Cr-Mo STEELS TO RESIST HYDROGEN AND TEMPER EMBRITTLEMENT

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ABSTRACT

Hydrogen sulfide environmental tests on a 2-1/4 Cr-1 Mo sample are presented. The present emphasis is on modifying a testing technique for low yield strength steels (by ∿100 ksi) in which (i) plane stress-plane strain and (ii) incubation time problems are severe. It is demonstrated that the plane stress zones pin the crack and that these zones can be eliminated by side grooving the specimen. The incubation time is reduced by pre-fatiguing in the environment. The reasons for using an arrest stress intensity value, from a simulated bolt load test (K_{arr}), rather than a crack onset K, from a rising load test (K_o) for an assessment of hydrogen embrittlement susceptibility are given. It is shown in this sample that a smooth sided 3T specimen has a K_o ∿150 ksi $in^{1/2}$ whereas a side grooved 2T specimen has a K_{arr} ∿ 20 ksi $in^{1/2}$.

1. Introduction

In the first and second combined reports(1) of this program the technical structure was outlined and the measurements of the peak hardnesses in the heat affected zone (HAZ) were given. A discussion of the effect of the plane-stress zone in a compact tension specimen on the hydrogen cracking characteristics was also presented.

One of the primary difficulties in the assessment of the plane-strain hydrogen cracking susceptibility of the low yield strength steels ($\sigma_y \sim$ 60-100 ksi; 414-689 MPa) stems from the plane-stress component on the sides of the crack front in compact tension specimens. A second difficulty is associated with the incubation time required prior to crack propagation in some steels. This report presents the initial data derived from specimens of commercial 2-1/4Cr-1Mo steel which have been re-tempered to a strength level comparable with that of the peak hardness in the HAZ. The primary emphasis has been in establishing experimental techniques to minimize the plane-stress and incubation time problems.

2. Discussion of the Approach to Hydrogen Environment Testing in Low Strength Steels

There are many standard methods of testing steels in an environment: two are the rising load test and the bolt loaded test on air fatigue pre-cracked specimens. It has been observed(2) that the arrest value of the stress intensity K, (K_{arr}) in the bolt loaded test is significantly lower than the peak value of K, (K_o) measured in a rising load test. Furthermore, if a rising load test is stopped after cracking has started and if the specimen is then held at a constant displacement, the crack will continue to propagate at continuously decreasing K-values. The reason for $K_o > K_{arr}$ has been described in terms of the incubation time required for crack initiation(2). The incubation time can be expressed as an inverse function of the applied K, of the form(2)

$$t_{io} = -\ln\left[\frac{K_o - K_{arr}}{K_{Ic} - K_{arr}}\right]$$

where t_{io} is a time constant.

A similar expression may be fitted to the relationship between the applied K and time to failure, t_f, which includes t_i as well as a component due to crack growth rate. See for example the data of Sheinker(3) analysed by Johnson and Shaw(2).

As a consequence of K_{or} depending upon t_{io} and implicitly upon the rate of loading (or $\dot{K}$) in a rising load test, we do not regard it as a viable material constant for the proposed screening tests in this program. On the other hand K_{arr} is free from the incubation time factor and can be more reliably used to characterize the hydrogen embrittlement resistance of the range of steels to be tested.

In early tests on compact tension specimens (C.T.) it was found that the crack front was tunneled with a greater crack advance in the center plane-strain region than in the plane stress regions on either side. After the crack arrest it was difficult to ascribe a value to K_{arrest} in the plane strain region. This problem was outlined in the previous report(1). The approach we have therefore taken has been to deeply side groove the C.T. specimens in order to eliminate the plane-stress effect and thereby essentially obtain straight crack fronts at arrest, from which a valid K_{arr} may be obtained.

The incubation time is then 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 FeS 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 to the region of maximum triaxial tensile stress, (d) hydrogen accumulation in the triaxially 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 eliminate t_i to the greatest extent we therefore pre-fatigue cracked specimens in the H_2S environment. Since we are no longer concerned with measurements of K_{or} the maximum fatigue stress level is <u>not</u> 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

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

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 the last pre-fatigue displacement. This is essentially a simulated bolt loaded test in which the load drop at constant displacement can be monitored. Typically in 2-1/4Cr-1Mo 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 - 2.6×10^5s)

3. Hydrogen Sulphide Testing Equipment

An overview of the equipment used for the DOE test program is shown in Fig. 1. The chamber is designed to test 2T and 3T compact tension specimens in an environment of 50 psig H_2S. The maximum load capacity is 100 kips.(45.3 Mg). The control assembly is capable of giving

a) A large range of loading rates from 20 lbs/min (15 kg/s)(minimum)
b) Constant displacement rate or constant loading rate tests
c) Cyclic loading at 1/2 Hz or less in displacement or load control
d) Time-load and time displacement strip charts.
e) Load displacement curves
f) Automatic compliance measurements as a test proceeds.

The rising load or fatigue tests are performed with a servo-hydraulic machine with control from either a load cell mounted on the main tie rod to the specimen or by an LVDT which monitors the displacement on the front face of the C.T. specimen. The LVDT is located outside the chamber with the control rods sealed by an O-ring to prevent exposure of the wiring to H_2S.

4. Experimental Results and Discussion

i) Background

In this report we present the data generated from three C.T. specimens (1T, 2T and 3T) taken from one steel sample. The sample is 2-1/4Cr-1Mo plate donated to the program by the American Petroleum Institute and is designated as No54. It was re-austenized and cooled to produce a bainitic structure and subsequently tempered to a Rockwell C hardness of order 19. This is equivalent to a U.T.S. level of order 110 ksi (758 MPa). The heat treatments and sample analytical chemistry are given in Table I.

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 2-1/4 Cr-1Mo plate.(1)(5) 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 made later in the program.

Throughout the text values for K at various stages of crack growth will be given. These values are <u>estimates</u> 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.(6) (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.(6)

c) For a given crack length in a side-grooved specimen K is estimated by replacing the specimen thickness B by an effective specimen

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Throughout this section please convert
1 hr = $3.6\ 10^{3}$ x
1 in = $2.54\ 10^{-2}$ M
1 ksi in$^{1/2}$ = 1.099 MN/m$^{3/2}$

thickness B_{eff}, which is the geometric mean of the overall thickness and the crack plane thickness.

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

ii) The 3T-CT Test: Sample No54H

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 environment at a maximum K of 77 ksi$\sqrt{in}$ to produce approximately .17 ins 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 $in^{1/2}$. 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 hrs 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 $in^{1/2}$. The crack continued to grow at decreasing loads as the displacement was increased. The test was stopped at K of order 155 ksi $in^{1/2}$ at which point the crack hand grown .09 in. The specimen was then re-loaded to a K of order 159 ksi $in^{1/2}$ and held at $\dot{v} = 0$ for 53 hrs. In this period the load dropped continuously. The constant displacement test was ended to take a compliance check at K of order 143 ksi $in^{1/2}$ 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 hrs and from K = 143 to 125 ksi in$^{1/2}$ in 71 hrs. At this point the tests were concluded, even though the crack was still growing, and the specimen was pulled apart in air. Fig. 2 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.

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.

iii) The 2T-CT -0.25 Side Groove Test: Sample No54H

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$^{1/2}$. It was then loaded to a K of 105 ksi in$^{1/2}$ and held at constant displacement. After 70 hrs 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$^{1/2}$. A plot of the crack length as a function of time was almost linear giving $\dot{a} = 22.10^{-3}$ in/hr. Similarly $\dot{K}$ was almost constant at -1.3 ksi in$^{1/2}$/hr. The photograph of the fracture surface shows that the crack has a straight front indicating that the entire test was under the plain-strain conditions. It should be noted however that the fatigue crack front was not straight but had a "reverse-tunnel" shape. (Fig. 3).

iv) The 1T-CT-0.25 Side Groove Test: Sample 54H

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 $in^{1/2}$ for 39 hrs and after cyclicly cracking again at $K = 48$ ksi $in^{1/2}$ for 20 hrs. No static displacement crack growth took place in either test. The final environmental cyclic loading K_{max} was 63 ksi $in^{1/2}$. The specimen was then loaded to 69 ksi $in^{1/2}$ and held in constant displacement. After 17 hrs the crack had extended to an applied K of order 50 ksi $in^{1/2}$. The specimen was unloaded and pulled apart in air. The fracture surface, Fig. 4, 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 $\dot{a} = 15.10^{-3}$ in/hr and $\dot{K} = -1.1$ ksi $in^{1/2}$/hr. The 1T data compares reasonably well with the 2T-specimen data bearing in mind that reliable calibrations for compliance and K values are not available for the deeply side grooved 1T specimens.

v) Discussion

The original intent of this program was to assess the hydrogen assistance of a range of alloy steels around the 2-1/4Cr-1Mo composition by evaluating K_o. In section 2 the reasons for abandoning K_o and instead using K_{arr} as a measure of hydrogen resistance was outlined. The details given in parts (ii) to (iv) of this section have provided the background of the experimental approach we have evolved for the most rapid determination of a K_{arr} value.

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 $in^{1/2}$ was reached. After over 140 hrs of constant displacement testing the experiment was terminated, without crack arrest, at $K \sim 125$ ksi $in^{1/2}$. 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 $in^{1/2}$/hr were very slow.

In comparison, the 2T specimen with 0.25 in side grooves started cracking readily at 105 ksi $in^{1/2}$ and cracked at a rate $\dot{a} = 22 \times 10^{-3}$ in/hr and $\dot{K} = -1.3$ ksi $in^{1/2}$/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 $in^{1/2}$. In comparison the 1T test was started at an estimated K of order 60 ksi $in^{1/2}$, though earlier attempts to start the constant displacement crack growth at K = 43 and 48 ksi $in^{1/2}$ 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 $in^{1/2}$ (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.(7) 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.

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.(8) Alternatively hydrogen is accumulated at the tip of the crack and is swept along with its associated stress field.

5. Acknowledgements

We are grateful to R. J. Smykal who conducted the tests and also helped develop the apparatus with L. J. Ceschini as the laboratory supervisor.

6. References

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2) E. W. Johnson and B. J. Shaw; Final Report U.S. Navy Contract N00600-77-C-0991 April (1979).

3) A. A. Sheinker; Technical Report to ONR Contract N00014-C-0365 Jan. (1978).

4) E. W. Johnson and B. J. Shaw; Final Report to ONR Contract N00014-77-C-0372. Aug. (1979).

5) R. K. Nanstad and D. A. Canonico. ORNL Contract -5238 Dec (1976).

6) A. Saxena and S. J. Hudak Jr. Int. Jnl Fract. 14 (5) 453 (1978).

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

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

Table I. Heat Treatment and Analytical Chemistry of Sample 54

Heat Treatment on 6 in thick plate

i) 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

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 = $3.6 \cdot 10^3$ s

$t°C = (t°F - 32)/1.8$

Table II. Resume of data from specimen 54H-3T. See text for details. The units of K are ksi $in^{1/2}$ throughout, and are derived solely from compliance data and load-time curves.

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 hrs	No crack growth
	ii) K = 124 for 16 hrs	No crack growth
	iii) K = 130 for 65 hrs	No crack growth
	iv) K = 133 for 175 hrs	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 hrs Unload at K = 143	Crack growth rate $\dot{a}$ approx. 5.5×10^{-3} in/hr$^{(\#1)}$ $\dot{K}$ approx- 0.3 ksi $in^{1/2}$/hr
6	Reload to K = 143 and hold at constant displacement 20 hrs Unload at K = 140 for compliance data	Crack growth rate $\dot{a}$ approx. 5.0×10^{-3} in hr$^{(\#2)}$ $\dot{K}$ approx -0.15 ksi $in^{1/2}$/hr
7	Growth at constant displacement continued from K = 143 to K = 125 in 71 hrs. Test ended - crack still growing.	Crack growth rate $\dot{a}$ approx. 6.0×10^{-3} in/hr$^{(\#3)}$ $\dot{K}$ approx. -.25 ksi $in^{1/2}$/hr

Total testing time approx. 20 days.

(#1) $\dot{a}$ at specimen center 6.8×10^{-3} in/hr
(#2) $\dot{a}$ at specimen center 7.5×10^{-3} in/hr
(#3) $\dot{a}$ at specimen center 4.2×10^{-3} in/hr
derived from actual crack lengths at specimen center.

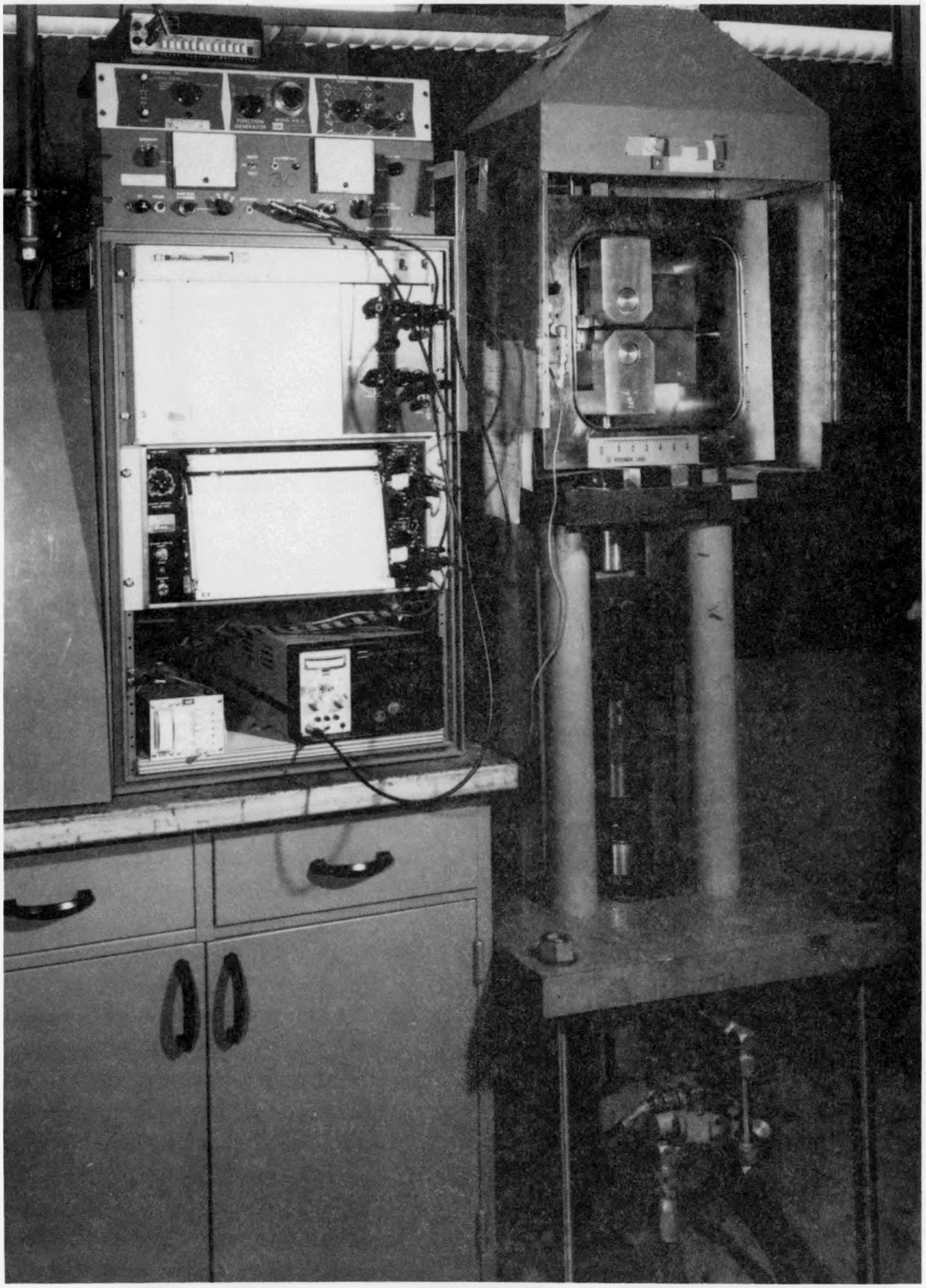

Fig. 1. Test stand developed for 3T and 2T compact tension experiments in 50 psig H_2S. A 3T CT specimen is installed in the chamber on the right above the hydraulic ram. Function generators and recording equipment are on the left.

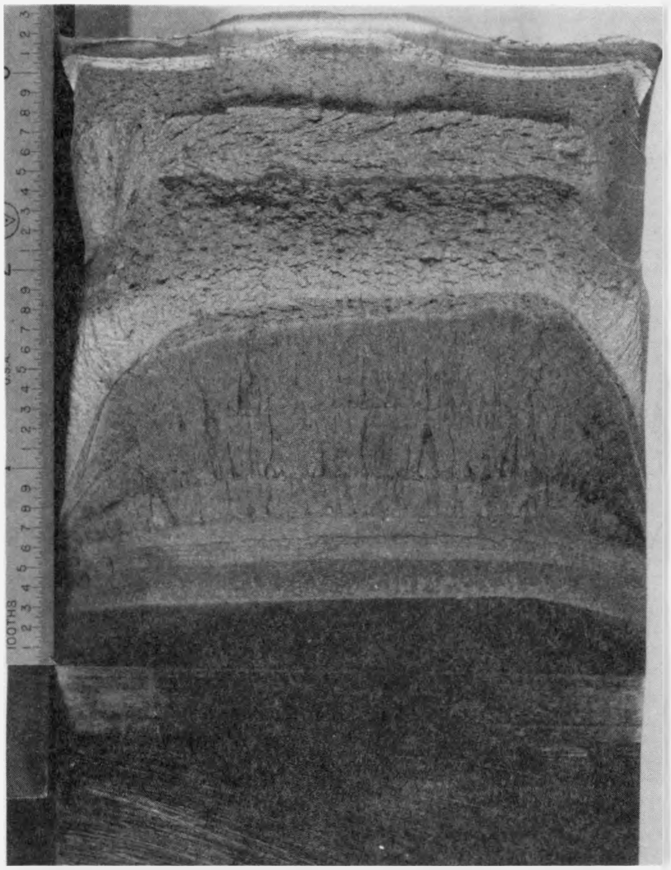

Fig. 2. Fracture surface of 3T compact tension specimen 54-H tested in 50 psig H_2S. This was a smooth sided specimen which exhibited the effect of the plane-stress zones on either side. The crack front pinning in the plane-stress zones is very striking.

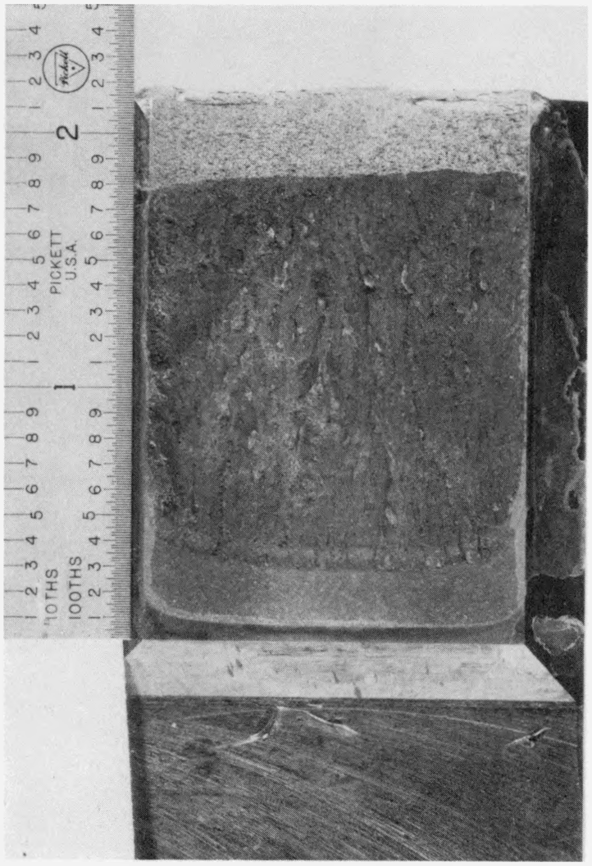

Fig. 3. Fracture surface of deeply side grooved 2T compact tension specimen 54H tested in 50 psig H_2S. This specimen exhibits little or no effect from plane-stress on either side of the crack front

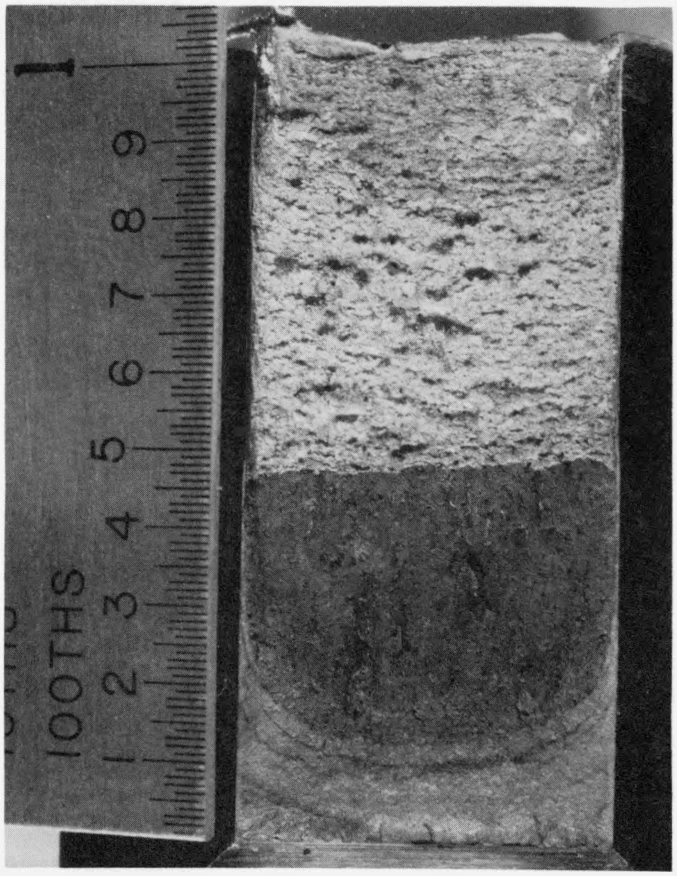

Fig. 4. Fracture surface of deeply side grooved 1T compact tension specimen 54H tested in 50 psig H_2S. The constant displacement test was terminated prior to crack arrest in order to assess the crack front configuration. There is no evidence of plane stress pinning on the sides of the crack front.