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CONTRACT WEC 3.2.3 STUDY TO OPTIMIZE Cr-Mo STEELS
TO RESIST HYDROGEN AND TEMPER EMBRITTLEMENT

Review of Susceptibility of Commercial Cr-Mo
Steels to Hydrogen Embrittlement

January 20, 1981

MASTER

Quarterly Report No. 9
Second Annual Report (January 1 - December 31, 1980)

Contract No. DE-AC05 78ET13513

U.S. Department of Energy
Division of Coal Conversion

DOE Project Manager: Mr. E. E. Hoffman
(W) Program Manager: Dr. Bevil J. Shaw

Effective Date of Contract: August 17, 1978

Contract Expiration Date: August 16, 1981

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WEC 3.2.3 — STUDY TO OPTIMIZE Cr-Mo STEELS TO RESIST
HYDROGEN AND TEMPER EMBRITTLEMENT

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ABSTRACT

The hydrogen embrittlement susceptibility of commercial $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steels has been investigated, using H_2S as the primary environment. After it was found that low strength steels, which had been given a post weld heat treatment, were immune to the test techniques developed, the effect of strength level was studied to establish a lower limit for embrittlement. Similar tests on the peak hardness zone in the heat affected zone of a weld showed that the crack preferred to move to the far heat affected zone where the strength level was below the lower limit established above. It is suggested that residual stresses may account for the anomaly, although other factors such as structural change could be important. In order to assess the low strength steels, the environment was changed to include saturated water vapor in the H_2S . It was found that the low strength steels could be readily tested in this environment, thus providing a means of ranking Cr-Mo steels for hydrogen embrittlement susceptibility. Tests on one steel were included to show that the variability in the data using the $\text{H}_2\text{S} + \text{H}_2\text{O}$ environment was small enough to make the screening test results significant.

WEC 3.2.3 — STUDY TO OPTIMIZE Cr-Mo STEELS TO RESIST
HYDROGEN AND TEMPER EMBRITTLEMENT

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INTRODUCTION

The primary objective of this program is to evaluate a range of Cr-Mo steels in order to assess the role of compositional variables on the susceptibility to hydrogen and temper embrittlement. The program is divided into two phases.

Phase I is designed to establish the hydrogen embrittlement susceptibility of commercial 2½Cr - 1Mo steels provided by the American Petroleum Industry. This phase consists of two parts. The first part is to assess the hydrogen embrittlement characteristics of the steels at conventional strength levels (Ultimate Tensile Strength, UTS, in the range 60-80 ksi or 400-550 MPa). The second part is to measure the hydrogen embrittlement susceptibility of the peak hardness zone (PHZ) in the heat affected zone (HAZ) adjacent to the weld. Since few large weld samples were available, tests were also to be conducted on plate material heat treated to a higher strength level corresponding to that of the PHZ. This corresponds to an UTS of the order 100-110 ksi or 690-760 MPa.

Phase II consists of an evaluation of 32 laboratory heats with compositions arranged according to a statistical design and tempered in a bainitic condition to two strength levels, corresponding to the ranges used in Phase I. The primary evaluations are for temper embrittlement and hydrogen embrittlement. Comparison of the data generated from the laboratory heats can be made with commercial samples from Phase I of the

program for hydrogen embrittlement and with an independent API program for temper embrittlement. Based upon the data to be generated in Phase II, it is anticipated that compositional areas with high or low susceptibility to either form of embrittlement may be identified.

The original intention was to use a simple rising load test on fatigue precracked Charpy specimens for the hydrogen embrittlement study. However, because the yield strength of this class of steel is so low, a study of the effect of specimen size on the validity of the data was included in Phase I. Consequently, tests were carried out on 1T, 2T and 3T Compact Tension (CT) specimens for comparison.

As a result of this study, it became clear that the inexpensive Charpy test would not yield reliable data. Moreover, the rising load test on a standard CT specimen would not necessarily give the value of the threshold stress intensity in the H₂S environment (K_{ISCC}). Two factors of considerable importance, i.e. the incubation time and plane-stress pinning of the crack, had to be considered in some detail. A review of the effects is given in Quarterly Report #4.

Since the revision of the test technique necessitated the use of larger specimens and a more complex test procedure, the scope of the program (but not the primary objectives) had to be revised. To date, it appears that the method for evaluating the hydrogen embrittlement susceptibility of the higher strength steels (690-760 MPa) is resolved.

The same technique that would satisfactorily produce cracking in the steels tempered to a higher strength level was totally unsuccessful for steels of a lower strength level. In order to obtain a screening test for the low strength steels, it was decided to introduce a more potent environment. This report gives the results of tests on both high and low strength steels subjected to the same (mechanical) test procedure using hydrogen sulfide gas saturated with water vapor for the environment. The modified environment appears to be quite satisfactory in that it provides a means of embrittling steels over the entire strength level range required.

The original program structure is shown in Fig. 1. All the tasks have been completed except the final part of Phase II. This consists of the actual tests for temper embrittlement and hydrogen embrittlement susceptibility data and the regression analyses to give the optimum Cr-Mo steel composition for resistance to embrittlement. The current program schedule and status for 1981 is given in Table 1.

RESULTS FROM PRIOR QUARTERS

Combined Quarterly Report Nos. 1 and 2
May 7, 1979

This report gives

- i) The original structure and objectives of the program.
- ii) The formal statistical matrix to be used in Phase II of the program.
- iii) The levels of the alloying elements in the 32 steels of the statistical design compared with the ASTM A387 specification limits.
- iv) The experimental determination of the peak hardness in the heat affected zone (HAZ) via microhardness measurements.
- v) Considerations of the test requirements for hydrogen embrittlement measurements in low strength steels.

Quarterly Report No. 3
August 23, 1979

The report gives the data from one sample $2\frac{1}{4}\text{Cr} - 1\text{Mo}$ steel which had been re-heat treated to a strength level comparable with that of the peak hardness zone of the HAZ. A standard 3T compact tension (CT) specimen tested in 50 psig (446 KPa) H_2S was compared with side grooved 2T and 1T CT specimens. It was shown that the plane stress zones inhibit crack advance in the 3T specimen and that estimates of the threshold

FIGURE 1 LOGIC FLOW DIAGRAM FOR THE OPTIMIZATION OF Cr-Mo STEEL COMPOSITION

TABLE 1 - Schedule and Status of the Cr-Mo Steel Optimization Program

Task No.		Comments or Start Date	Projected Completion Date
WEC-3.2.3-1	Establish means of evaluating hydrogen embrittlement susceptibility in low strength Cr-Mo steels.	Finished	
WEC-3.2.3-2	Evaluate temper embrittlement susceptibility of Cr-Mo steels at two strength levels.	Started	6-81
WEC-3.2.3-3	Heat treat 32 Cr-Mo steels, with compositions arranged according to a statistical design, to produce a bainitic structure at two strength levels.	Finished	
WEC-3.2.3-4	Establish the chemistry and microstructure of 32 Cr-Mo steels heat treated to produce a bainitic structure.	Finished	
WEC-3.2.3-5	Evaluate hydrogen embrittlement susceptibility of 32 higher strength Cr-Mo steels.	Started	8-81
WEC-3.2.3-6	Produce, via regression analyses, the effect of composition on temper embrittlement and hydrogen embrittlement of Cr-Mo steels.	5-81	8-81

stress intensity can be substantially lower if side grooves are incorporated. Incubation time effects were reduced by fatigue precracking the specimens in the environment.

Quarterly Report No. 4 (First Annual Report)
December 17, 1979

The first annual report gives a review of the status of the program and an outline of the most significant tests performed in H_2S to date. A description of the new testing procedure developed to evaluate hydrogen embrittlement susceptibility is presented. The report lists estimates of the crack arrest stress intensities measured on commercial steels which have been re-heat treated to strength levels comparable with that of the peak hardness zone in the HAZ.

Quarterly Report No. 5
July 23, 1980

This report gives the results of tests designed to measure the threshold stress intensity in H_2S of the peak hardness zone in the HAZ of welds in $2\frac{1}{2}Cr - 1Mo$ plate. Difficulty was encountered because of a variability in the location of the peak hardness zone relative to the weld-base interface. There are indications that the K_{arr} could be significantly below $80 \text{ ksi in.}^{\frac{1}{2}}$ ($88 \text{ MPa m}^{\frac{1}{2}}$) but the absolute values could not be determined from the current tests. Details of the forging process for heats produced for Phase II of the program are given.

Quarterly Report No. 6
July 28, 1980

Because of difficulties encountered in the testing of low strength steels in commercially pure H_2S , a modification to the program was incorporated to study the effect of strength level on hydrogen embrittlement susceptibility. The report presents the results of this study on one

steel in which it was found that there appears to be a strength level limit, approximately 100 ksi (690 MPa) below which the $2\frac{1}{4}\text{Cr} - 1\text{Mo}$ steel is immune to cracking in the H_2S environment provided by a tank of commercial high purity H_2S .

Quarterly Report No. 7
October 20, 1980

In Phase II of the study, 32 heats with compositions based upon a statistical design have been cast and forged. The analytical chemistry of the heats is reported and found to be very close to the original aim compositions. The initial stage of the heat treatment, transformation to a bainitic structure, is described. High percentages of ferrite were found in some of the samples. The occurrence of ferrite is discussed briefly in terms of the levels of alloying elements.

Quarterly Report No. 8
November 20, 1980

In the first annual report of this series (Report No. 4), the modified test method developed to assess the hydrogen embrittlement susceptibility in H_2S was described. It was found that the $2\frac{1}{4}\text{Cr} - 1\text{Mo}$ and $1\frac{1}{4}\text{Cr} - \frac{1}{2}\text{Mo}$ steels with conventional post weld heat treated (PWHT) strength levels (UTS in the range 60-80 ksi or 400-550 MPa) were essentially immune to the test method using 50 psig (446 KPa) commercially pure H_2S as the environment. An evaluation of the effect of yield strength (Report No. 6) showed that, for one sample of $2\frac{1}{4}\text{Cr} - 1\text{Mo}$ steel, there was a lower limit below which failure could not be induced. In this section a series of tests using a new environment of H_2S and water vapor is reported.

DISCUSSION OF CURRENT ACTIVITIES

The second phase of the program has been started. This phase consists of the investigation of the effect of compositional variables (Mo, Cr, Mn, Si, C and P) on the susceptibility of the steels to temper and hydrogen embrittlement. The statistically designed set of 32 heats have been tempered to two strength levels. Unembrittled Charpy specimens and blanks to be temper embrittled are currently being machined from both strength levels. Concurrently 1T-compact tension specimens are being machined from the high strength steels. The first two hydrogen sulfide-saturated water vapor environment tests on these steels have been started.

REVIEW OF PROGRAM IN 1980

Background

Early in this DOE program the intention was to rank Cr-Mo steels for susceptibility to hydrogen resistance by using a rising load test on fatigue precracked Charpy specimens in a H₂S environment. It was concluded that the rising load test may not yield reliable information, even for screening purposes, because of the incubation time effects in the low strength Cr-Mo steels. Also the Charpy specimen was not necessarily large enough to circumvent the problem of plane stress zones which are, compared with the plane-strain zone, relatively insensitive to hydrogen embrittlement. A series of tests on 3T-CT (compact tension) specimens compared with 2T-CT and 1T-CT side-grooved specimens were conducted in order to establish a viable method of assessing the hydrogen-embrittlement susceptibility of the steels. In essence, the specimen design and test procedure were modified as follows:

- i) Reduce the plane-stress effect by incorporating side grooves in the CT specimens.

ii) Reduce the incubation time effect by cyclically loading (~0.5 Hz) in the environment.

iii) Having started crack growth by (ii), raise the load slightly and hold the specimen in constant displacement until crack arrest has taken place. Crack growth is indicated by increasing compliance and crack arrest by a zero change in compliance in one to two days.

iv) The hydrogen embrittlement susceptibility is measured by the stress intensity in the arrest condition (K_{arr} or K_{arrest}). The value of K_{arr} is probably close to K_{ISCC} measured in a very long term bolt loaded specimen.

The complete background to these tests was recently presented as a paper by Shaw and Johnson.^{1,2} This report reviews results derived from commercial Cr-Mo steels using the above techniques. In particular, the effect of strength level in nominally dry H_2S from a high purity commercial source is presented. Since a lower strength level was found below which the Cr-Mo steels exhibited extreme resistance to cracking in dry H_2S , and since there was interest in assessing the lower strength level steels typical of the post weld heat treated (PWHT) condition, a new environment of H_2S with saturated H_2O vapor was evaluated.

Tests on the heat affected zone (HAZ) adjacent to a weld in H_2S were not easy to perform, due to the variability in the peak hardness zone location in the HAZ. Nevertheless the data indicated that the HAZ could have less resistance to hydrogen embrittlement than the typical base plate material.

The Effect of Strength Level on Hydrogen Embrittlement Susceptibility in One Cr-Mo Steel

In Phase I of this program it was found that the lower strength steels (UTS ~ 400-550 MPa) exhibited extreme resistance to cracking in the H_2S environment. This is quite consistent with the findings in earlier investigations.^{3,4} In this small study the objective was to

define the effect of strength level on the hydrogen embrittlement susceptibility in one sample of $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steel. This, in turn, would provide an indication of the lowest strength level at which our current test procedure might be used. A very brief outline of the test procedure is included here and the reader is referred to earlier papers for a more detailed discussion.^{1,2}

Experimental Procedure

The composition of sample no. 74 used in this experiment is given in Table 2. The heat treatment history and the tempering conditions used to produce the range of strength levels in the bainitic structure is given in Table 3. The strength level was assessed by conversion from Rockwell B or C hardness readings.

After the heat treated standard 2T-Compact Tension (CT) specimens were machined from the specimen blanks, 0.25 in. ($6 \times 10^{-3}\text{m}$) deep side grooves were incorporated on the sides of each specimen in order to reduce to a minimum the effects of plane stress. The specimens were tested in 50 psig (446 KPa) of commercial high purity H_2S .

The incubation time for crack initiation is reduced to a minimum by cyclically loading the specimen in the environment in the range 0.1 to 0.5 Hz. Once the crack is propagating under cyclic loading, the load is raised slightly over the maximum cyclic load and the specimen is held in constant displacement. This is achieved by LVDT displacement control of the servohydraulic system which loads the specimen. The test at this point is a simulated bolt load test in which the load drop due to crack growth can be monitored. When the load no longer decreases, the crack has arrested and a measure of K_{arr} may be obtained. The value of K depends upon the load and the crack length. The latter may be measured directly after the specimen is broken open or indirectly from the compliance of the specimen (i.e. v/P where v is the displacement and P is the load). The compliance method is less accurate than the direct measurement, but is useful since it enables one to perform more than one test on a specimen if the crack length is short enough.

TABLE 2 - Composition of Sample No. 74

Element	C	Cr	Mo	Mn	Si	Ni	Cu
Wt %	1.03	2.28	1.00	.41	.21	.15	.15
Element	P	Sn	Sb	As	O	N	S
Wt %	.007	.015	.003	.010	.006	.007	.016

TABLE 3 - 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 hrs	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

$$t^{\circ}\text{C} = (t^{\circ}\text{F} - 32) / 1.8$$

$$1 \text{ ksi} = 6.895 \text{ MPa}$$

Results and Discussion

The results of the tests are given in Table 4. The highest strength specimen, which was untempered, cracked slowly from a maximum applied stress intensity K_{or} of $42 \text{ ksi}\sqrt{\text{in.}}$ to crack arrest at $K_{arr} = 28 \text{ ksi}\sqrt{\text{in.}}$ ($46 \text{ to } 31 \text{ MN/m}^{3/2}$). 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 at an applied stress intensity (K_{APP}) of $50 \text{ ksi}\sqrt{\text{in.}}$ ($55 \text{ MN/m}^{3/2}$) without any indication of cracking. A slight increase in K_{APP} to $52 \text{ ksi}\sqrt{\text{in.}}$ ($57 \text{ MN/m}^{3/2}$) resulted in an immediate catastrophic failure. In comparison, the lowest strength specimen of the set exhibited a very small amount of crack growth at $K_{or} = 113 \text{ ksi}\sqrt{\text{in.}}$ ($124 \text{ MN/m}^{3/2}$).

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 (730-750 MPa). (Fig. 2)

Most investigations of the effect of yield strength (σ_y) or UTS on the threshold stress intensity show the same trend, though not necessarily quite as sharp a transition. A substantial review of collected data showing this trend is given by Gerberich.⁶ A similar trend was found by Payer, et al.⁷ for specimens charged with hydrogen. In most of the studies reviewed, the UTS or σ_y is very high compared with the $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steels which have been tested in this study. Also, the test techniques did not usually incorporate side grooves. Consequently, exact comparisons with this study is not possible. Hicko and Gilmore⁸ used an aqueous environment of $\frac{1}{2}$ wt percent glacial acetic acid with H_2S at one atmosphere and showed that K_{ISCC} in low strength $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steel could be as low as $48 \text{ ksi}\sqrt{\text{in.}}$ ($53 \text{ MN/m}^{3/2}$). The data from an aqueous solution, however, cannot necessarily be directly compared with that from a gaseous environment.

TABLE 4 - Results of H₂S Environment Tests on Sample No. 74

Specimen No.	Approximate UTS (ksi)	Estimated K_{arr} (ksi $\sqrt{\text{in.}}$)	Comments
74-3	126	28	Slow crack growth from 42 ksi $\sqrt{\text{in.}}$ in 54 hr.
74-1	117	34	Catastrophic failure; specimen completely failed.
74-5	114	52	No failure after 17 hr at 50 ksi $\sqrt{\text{in.}}$. 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 $\sqrt{\text{in.}}$ = 1.099 MN/m^{3/2}

1 hr = 3.6×10^3 s

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

It is concluded that the modified test procedure (based upon one sample only) can be used to assess the hydrogen embrittlement susceptibility of 2½Cr - 1Mo steels with a UTS greater than 110 ksi in. (121 MN/m^{3/2}). For steels with lower strength levels a more potent environment, H₂S + H₂O vapor, was used. Tests with this environment are presented in the next section.

EMBRITTLEMENT OF Cr-Mo STEELS IN H₂S PLUS H₂O VAPOR ENVIRONMENT

Experimental

Exactly the same test procedure as presented above was used except that the environment was modified to include saturated water vapor. After the chamber had been evacuated at ~20 Pa, distilled water was drawn into a connecting tube. The H₂S was then introduced into the chamber via the tube containing water. Sufficient water was introduced to ensure that a small puddle would be formed at the bottom of the chamber. Inspection of the specimen immediately after a test showed that water was condensed at the tip of the crack and also on the walls of the chamber. All of the tests were performed in 50 psig (446 KPa) H₂S saturated with water vapor.

Results

The analytical chemistries and strength levels of the samples tested are given in Table 5.

Specimen No. 55L 2T-CT

This specimen had a conventional compact tension design with 0.125 in. (3.1×10^{-3} m) side grooves. After producing a crack by cyclic loading in the environment, the applied stress intensity was increased to 88 ksi m^{1/2} (97 MPa m^{1/2}) and the specimen was held in constant displacement. After 26 days of slowly decreasing load representing

TABLE 5 - Analytical Chemistry and Strength Levels
of $2\frac{1}{4}\text{Cr} - 1\text{Mo}$ and $1\frac{1}{4}\text{Cr} - \frac{1}{2}\text{Mo}$ Specimens Tested

No.	Element in wt %						
	C	Cr	Mo	Mn	Si	Ni	Cu
55	.126	2.23	.97	.45	.39	.16	.10
77	.140	1.34	.45	.51	.60	.18	.17

No.	Element in parts per million						
	P	S	Sn	Sb	O	N	As
55	130	52	112	20	35	145	307
77	108	173	145	22	23	78	90

No.	Ultimate Tensile Strength UTS (ksi)	Structure
55L	82	Ferrite-Pearlite
55H	110	Bainite
77L	76	Ferrite-Pearlite

crack growth, the load remained unchanged, thus indicating an approach to crack arrest. In this time the crack grew approximately 0.8 in. (2.0×10^{-2} m). The fracture surface is shown in Fig. 3. Based upon the final average crack length and the arrest load, the stress intensity at arrest was $K_{arr} = 49 \text{ ksi in.}^{\frac{1}{2}}$ ($54 \text{ MPa m}^{\frac{1}{2}}$). The crack growth rate as a function of K , shown in Fig. 4, exhibits the three stages normally found in crack growth rate tests.

Specimen 77L 2T-CT

This specimen was machined as a standard 2T-CT with 0.125 in. (3.1×10^{-3} m) side groove modification. The test was conducted in the same way as for 55L 2T-CT above. The initial applied stress intensity at the constant displacement stage was approximately $68 \text{ ksi in.}^{\frac{1}{2}}$ ($75 \text{ MPa m}^{\frac{1}{2}}$) and after a very small amount of crack growth (.07 in. or 1.8×10^{-3} m) the crack arrested at $65 \text{ ksi in.}^{\frac{1}{2}}$ ($71.5 \text{ MPa m}^{\frac{1}{2}}$) after 3 days. The fracture surface is shown in Fig. 5.

1T-CT Specimens from 55H

A set of four specimens were made from the same steel sample in order to assess the experimental scatter in the results using the new testing technique. This steel sample had previously been tested in commercial H_2S without water vapor (Quarterly Report No. 4). The specimens were a standard 1T-CT design with 0.25 in. (6.3×10^{-3} m) side grooves.

Using the same procedure as above, the first specimen (55H 1T-1) was held at constant displacement at an initial stress intensity of $44 \text{ ksi in.}^{\frac{1}{2}}$ ($48.5 \text{ MPa m}^{\frac{1}{2}}$). The crack arrested in the final run at approximately $17 \text{ ksi in.}^{\frac{1}{2}}$ ($19 \text{ MPa m}^{\frac{1}{2}}$). The fracture surface is shown in Fig. 6.

In the second specimen test the initial stress intensity was $45 \text{ ksi in.}^{\frac{1}{2}}$ ($49.5 \text{ MPa m}^{\frac{1}{2}}$) and the crack arrested at $24 \text{ ksi in.}^{\frac{1}{2}}$ ($26 \text{ MPa m}^{\frac{1}{2}}$). Figure 6 shows the fracture surface.

Fig. 3 Fracture surface of specimen 55L, a 2T compact tension specimen with 0.125 in. side grooves. The scale is in inches.

Fig. 4 Crack growth rate as a function of the applied stress intensity for a low strength $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steel tested in 446 KPa $\text{H}_2\text{S} + \text{H}_2\text{O}$ vapor at 25°C .

Fig. 5 Fracture surface of specimen 77L, a 2T compact tension specimen with 0.125 in. side grooves. The scale is in inches.

55H - No. 1

55H - No. 2

Fig. 6 Fracture surfaces of specimens 55H - No. 1 and No. 2, both of which were 1T-CT specimens with 0.25 in. side grooves. The scale is in inches.

The third run was interrupted by an instrument failure which resulted in an overload. The fracture surface, Fig. 7, is of particular interest since it shows the profile of the advancing crack. It also gives evidence, on the right-hand side, that the crack advances preferentially along the side grooves at the higher applied stress intensities.

The last specimen of the series was precracked by fatigue in air prior to the cyclic loading stage in the environment. The initial applied K at constant displacement was $30 \text{ ksi in.}^{\frac{1}{2}}$ ($33 \text{ MPa m}^{\frac{1}{2}}$) and the crack arrested at $23 \text{ ksi in.}^{\frac{1}{2}}$ ($25 \text{ MPa m}^{\frac{1}{2}}$). The fracture surface is shown in Fig. 7.

Specimen 77L 1T-CT

Specimen No. 77L 1T was a standard 1T-CT with 0.125 in. ($3.1 \times 10^{-3} \text{ m}$) side grooves. The specimen had previously been wedge load tested in 50 psig (446 KPa) commercial H_2S . The applied stress intensity was $42 \text{ ksi in.}^{\frac{1}{2}}$ ($46 \text{ MPa m}^{\frac{1}{2}}$) and after 8000 hours the specimen exhibited no evidence of cracking. This was later confirmed by inspection of the fracture surface. Prior to the $\text{H}_2\text{S} + \text{H}_2\text{O}$ experiment, the specimen was fatigue cracked in air. After cyclic load cracking in the environment, the simulated bolt load test was started at a stress intensity of $59 \text{ ksi in.}^{\frac{1}{2}}$ ($65 \text{ MPa m}^{\frac{1}{2}}$). The stress intensity at crack arrest was $48 \text{ ksi in.}^{\frac{1}{2}}$ ($53 \text{ MPa m}^{\frac{1}{2}}$).

After the main experiment the specimen was exposed to air for 6 hours. It was then subjected to a rising load test using an increasing stress intensity of $6 \text{ ksi in.}^{\frac{1}{2}}/\text{min}$ ($11 \text{ KPa m}^{\frac{1}{2}}/\text{s}$). This is equivalent to a standard K_{Ic} test except that the loading rate was slower than the recommended range in ASTM E399.⁹ The specimen broke catastrophically at $K \sim 63 \text{ ksi in.}^{\frac{1}{2}}$ ($69 \text{ MPa m}^{\frac{1}{2}}$). The fracture surface is shown in Fig. 8.

55H - No. 3

55H - No. 4

Fig. 7 Fracture surfaces of specimens 55H - No. 3 and No. 4, both of which were 1T-CT specimens with 0.25 in. side grooves. The scale is in inches.

Fig. 8 Fracture surface of specimen 77L, a 1T-CT specimen with 0.125 in. side grooves. The scale is in inches.

Discussion

In previous tests the environment was H_2S of the highest commercially available purity. In this environment it proved impossible, by our current techniques, to induce hydrogen embrittlement in low yield strength (45-75 ksi or 300-500 MPa) samples which had been given a post weld heat treatment. The introduction of saturated water vapor in the H_2S has clearly served to give conditions in which the lower strength steels can be embrittled.

Earlier in this program sample 55H was tested in H_2S . The side grooved 1T-CT specimen had a crack arrest stress intensity, $K_{arr} = 44 \text{ ksi in.}^{\frac{1}{2}}$ ($48 \text{ MPa m}^{\frac{1}{2}}$). In comparison, the arrest values in three identical specimens tested in $H_2S + H_2O$ vapor were 17, 24 and 23 $\text{ksi in.}^{\frac{1}{2}}$. The average value for the set of three tests was 21 $\text{ksi in.}^{\frac{1}{2}}$ ($23 \text{ MPa m}^{\frac{1}{2}}$) which is approximately half the K_{arr} value measured in H_2S .

The experiment in $H_2S + H_2O$ vapor on 55H was incorporated in the program in order to assess the experimental scatter in the results. The results indicate that the scatter is in the range of $\pm 20\%$, bearing in mind that there is insufficient data for an accurate determination of the standard deviation. Recently, in an extensive program involving 17 laboratories,* K_{Isc} of a 4340 steel tempered to 180 ksi (1240 MPa) was measured in a salt water environment using the bolt load test. The results to date are not published, however, in a private communication, S. R. Novac of U.S. Steel Research indicated that the experimental scatter in his tests was similar to that found in this study.

The fracture surfaces of the 55H 1T-CT specimens exhibit preferred growth along the side grooves. This is particularly evident in specimen No. 3 which was stopped prior to the crack reaching arrest (Fig. 7). In comparison, the same specimen (i.e. a 1T-CT with 0.25 in. side grooves) tested in H_2S had a straight crack front with no evidence of crack growth from the side grooves (Report No. 4). Fortunately, in the $H_2S + H_2O$ vapor environment, the crack front became reasonably straight by the time the crack had arrested and hence values of K_{arr} could be

* ASTM Committee E24-04-02

determined. Crack advance along the side grooves is consistent with the theoretical work of deLorenzi and Shih,¹⁰ who show that the stress intensity at the side groove is greater than that found in the center of the crack. They also report that the energy release of a side grooved specimen is almost the same as that of a specimen in pure plane strain, thus confirming that the use of side grooves in the current tests will yield reasonable data in hydrogen embrittlement.

In comparison with 55H, the same steel tempered to a lower strength level, 55L, had a higher $K_{arr} = 49 \text{ ksi in.}^{\frac{1}{2}}$ ($54 \text{ MPa m}^{\frac{1}{2}}$). This is consistent with the general trend of lower strength steels having a greater resistance to hydrogen embrittlement. Sample 77 is a $1\frac{1}{2}\text{Cr} - \frac{1}{2}\text{Mo}$ steel from which two specimens (a 1T and a 2T-CT) were made. The K_{arr} from the two specimens was 48 and 65 $\text{ksi in.}^{\frac{1}{2}}$, respectively (53 and $71.5 \text{ MPa m}^{\frac{1}{2}}$). These values are within 15% of the average value of $56 \text{ ksi in.}^{\frac{1}{2}}$ ($62 \text{ MPa m}^{\frac{1}{2}}$). Clearly 77L offers more resistance to hydrogen embrittlement than 55L, and this could be due to either a compositional effect or the slight difference in strength level.

In conclusion to this discussion, it appears that the $\text{H}_2\text{S} + \text{H}_2\text{O}$ vapor environment tests yield data which is within the normal experimental scatter and serves to reasonably differentiate between the hydrogen resistance of candidate steel samples. A potential problem stemming from the deep side grooves, which promote advance crack growth in the higher strength steels, can be overcome by reducing the side grooves to 25%. This is the optimum side groove depth recommended by deLorenzi and Shih.¹⁰

HEAT AFFECTED ZONE STUDY (HAZ)

Introduction

The primary objective of this part of the program, identified as 1.2 in the logic flow diagram (Fig. 1), was to characterize the hydrogen embrittlement susceptibility of the HAZ in three commercial samples of

Cr-Mo steel. Three large welds were selected from the American Petroleum Institute (API) stock. These samples, identified as 25, 62 and 63, were large enough to make 2T-WOL specimens with the notches of the specimens lying in the plane of the peak hardness zone of the HAZ. The type of weld and the post-weld heat treatments are listed in Table 6.

In a second series of tests Charpy impact curves were generated to establish the Fracture Appearance Transition Temperature (FATT) and the 40 ft-lb Transition Temperature (40 ft-lb TT) for the HAZ peak hardness zone and the unaffected plate. Similar tests were also performed on sample 62 in a temper embrittled condition (875°F for 1000 hr).

Experimental Procedure

The samples were macroetched in order to reveal the location and orientation of the welds. Specimen blanks were then cut, polished and etched in 2% Nital to reveal the weld interfaces and HAZ (Fig. 9). The peak hardness zone in the HAZ was identified by taking diamond pyramid microhardness measurements on each sample across the weld interface. Knoop hardness measurements were not taken on CT specimens because of size limitations of the instrument. A typical hardness profile, using Knoop measurement on Charpy specimens, is shown in Fig. 10. See Table 7 for comparison of hardnesses in the HAZ and base metal.

The location and orientation of the peak hardness zone (PHZ) was scribed on each sample blank and the tip of the notch of the machined 2T-WOL specimens was located in the plane of the PHZ. Side grooves, 0.25 in. deep, were machined on each specimen to eliminate plane stress zones and also to confine the crack to the PHZ. The notches in the Charpy impact specimens were similarly located. Charpy specimens were not side-grooved. The 2T-WOL side-grooved specimens were tested in 50 psig (446 KPa) of commercial high purity H₂S, using the same procedure as discussed above.

TABLE 6 - Post Weld Treatments of Weld Samples

Sample No.	
25	<p>2½Cr - 1Mo Submerged Arc Weld</p> <p>1100°F - 8 hr 1200°F - 15 hr 1275°F - 7 hr Cool 50°F/hr</p>
62	<p>2½Cr - 1Mo Submerged Arc Weld</p> <p>1274°F - 24 hr - Furnace Cool</p>
63	<p>2½Cr - 1Mo Shielded Metal Arc Weld</p> <p>1274°F - 24 hr - Furnace Cool</p>

Conversions: 1 hr = 3.6 x 10³ s.

$$t^{\circ}\text{C} = (t^{\circ}\text{F} - 32)/1.8$$

TABLE 7 - Comparison of the Peak Hardness in the HAZ with the Base Metal Hardness beyond the HAZ

API Sample No.	Peak Hardness in HAZ			Base Metal		
	Measured Diamond Pyramid Hardness	Equivalent R_B	Equivalent UTS, ksi	Measured Diamond Pyramid Hardness	Equivalent R_B	Equivalent UTS, ksi
25	222	95	101	150	79	71
62	227	96	103	160	82	75
63	214	94	100	190	90	89

R_B — Rockwell B Hardness Value

UTS — Ultimate Tensile Strength

HAZ — Heat Affected Zone

1 ksi — 6.895 MPa

$\times \frac{1}{2}$

Fig. 9 The section of sample no. 62 after macroetching in 2% Nital. The notch of the 2T-WOL specimen machined from this section was placed in the peak hardness zone on the left of the weld.

Fig. 10 500 gm Knoop hardness as a function of distance from fusion line showing the peak hardness in the heat affected zone of the plate.

Results and Discussion

H₂S Environmental Tests

Whereas crack advance could be obtained under cyclic loading in specimen no. 62, little or no crack advance was obtained under constant displacement until the crack was approximately 0.5 in. (1.3×10^{-2} m) long. At this point the crack grew in the constant displacement condition to an estimated K_{arr} of the order of $85 \text{ ksi}\sqrt{\text{in.}}$ ($93.5 \text{ MN/m}^{\frac{3}{2}}$).

After breaking the specimen open, it was found that the crack had advanced out of the PHZ into the plate (or away from the weld). Figure 11 shows an overview of the fracture surface in which shear lines can be seen on the sides of the specimen due to the central part of the crack growing out of the side groove plane. Figure 12 is a cross-sectional view of the center of the cracked specimen. It can be seen that the crack moved away from the plane of the notch by approximately .025 in. (6×10^{-4} m). This distance is comparable with the distance of the PHZ from the weld fusion line shown in Fig. 10.

The test underlines one of the difficulties in testing the PHZ adjacent to a weld. Clearly there is some variability in the location of the PHZ relative to the weld interface. Consequently, the location of the crack notch and side grooves may be correct for the initial crack only. Unfortunately, if the side grooves are not incorporated in the specimen design, the test data is confounded by plane-stress pinning of the crack. In this test, however, the crack grew away from the PHZ into the far HAZ.

In earlier tests in this study^{1,2} on simulated HAZ (higher strength level) 2½Cr - 1Mo steel, the K_{arr} of a smooth-sided 3T-CT was compared with that of a side-grooved 2T-CT. The difference in K_{arr} ($110 \text{ MN/m}^{\frac{3}{2}}$ versus $22 \text{ MN/m}^{\frac{3}{2}}$ for the latter) is due to the plane stress pinning in the 3T-CT. It is clear that the out-of-plane crack advance in the PHZ test of specimen 62 resulted in side pinning of the crack. Conservatively then, the K_{arr} for the PHZ or far HAZ in this sample should be less than half of the original estimate, even though an actual measurement could not be obtained.

Actual Size

2T-WOL with 0.25 in side grooves

Fig. 11 Overview of the fracture surface of sample no. 62 tested in H_2S . The shear lips due to the crack advancing out of the side groove plane can be seen on either side. Note that the last test ended at the 0.6 in. position and that the remainder of the fracture surface was produced by fatigue cracking and overload in air.

x4

Fig. 12 A cross section of the center of fracture surface of sample no. 62. This shows that the crack has advanced from the notch on the left away from the fusion zone.

Sample no. 25 was tested in the same way as no. 62, with essentially identical results, except that the measured K_{arr} was of the order $60 \text{ ksi}\sqrt{\text{in.}}$ ($66 \text{ MN/m}^{3/2}$). Again, the actual threshold stress intensity for the PHZ or far HAZ should be considerably less.

Sample no. 63 exhibited the same kind of load-displacement behavior as nos. 62 and 25. Consequently, it was assumed, since there was increasing resistance to cracking as the crack propagated, that the crack was growing out of the side groove plane.

Charpy Impact Tests

The locations of specimens taken from samples 25, 62 and 63 are shown in Fig. 13. The data from the Charpy impact curves is given in Table 8. In all four sets of data it is clear that the transition temperature in the PHZ is less than that of the base plate. After temper embrittlement of sample 63, the HAZ showed a greater shift ($\Delta FATT$) than the base plate. The impact energy at room temperature is listed since this could have some bearing on the crack path. For example, sample no. 25 has a significantly lower impact energy in the base plate than in the HAZ. Consequently, a crack in the HAZ might be expected to shift out of the HAZ into a lower energy path in the plate. This factor is not significant in samples 62 and 63.

Interpretation of H_2S Data

The variability in the location of the PHZ in the HAZ was discussed above. Even taking this into account the crack advanced further from the approximate PHZ area than would be anticipated in specimen 62. The room temperature impact energy of the plate in this specimen was comparable or greater than that of the HAZ, hence the crack would not be expected to advance into the plate as it might in specimen 25 (Table 8). The evidence therefore indicates that the component of the HAZ most susceptible to hydrogen embrittlement could lie outside the PHZ.

x $\frac{1}{2}$

x $\frac{1}{2}$

x $\frac{1}{2}$

Fig. 13 The location of the Charpy blanks taken from samples 25, 62 and 63. The notch locations were located in the peak hardness zone of the HAZ after the Charpy blanks had been machined and ground to size.

TABLE 8 - Fracture Appearance Transition Temperatures and 40 ft-lb Transition Temperatures from the Peak Hardness Zone of the HAZ and Base Plate of Samples 25, 62 and 63

Sample No.	Location	FATT °F	40 ft-lb TT °F	Room Temperature Impact Energy ft-lbs
25	Plate	150	130	10
	HAZ	30	0	70
62	Plate	30	5	100
	HAZ	0	-5	85
63	Plate	10	5	100
	HAZ	-30	-75	100
63*	Plate	30	0	90
	HAZ	10	-40	95

*Temper embrittled at 875°F for 1000 hr.

Conversions: $t^{\circ}\text{C} = (t^{\circ}\text{F} - 32)/1.8$.

The peak hardness data given in Table 7 shows that the maximum strength lies in the range 100-103 ksi (700 MPa). Comparison with the effect of strength level, Table 4 and Fig. 2, would suggest that the susceptibility of the HAZ to hydrogen embrittlement should be quite small, and that the lower yield stress base steel should be essentially immune (that is as measured by the "dry" H₂S test employed in this series). There are a number of factors which can be of importance in the apparently conflicting evidence. The first is the role of composition and structure which could modify the hydrogen embrittlement susceptibility. The second is the influence of residual stresses around the weld, which could modify the (local) stress intensity at the tip of the crack. Lastly, there is the possible influence of grain boundary decohesion brought about in the PWHT.

Canonico¹¹ recently reviewed the stress relief cracking phenomenon (reheat cracks or stress relief cracking) in certain pressure vessel steels and discussed the formation of microcracks on grain boundaries in the HAZ. Whereas it appears that the microcracks formed do not seriously impair the toughness qualities of the steel (within the HAZ), the effect of microcracks on hydrogen embrittlement was not discussed and is therefore a matter of interesting speculation. Since the cracks in our tests moved out of the HAZ, stress relief cracking is probably not an important factor.

Both the steels tested early in the DoE program and the welds tested in this part of the program were given a PWHT (Table 6). Consequently the base metal outside the HAZ of the welds was comparable with the low strength steels tested in the first phase of the program. It is tentatively concluded therefore that, apart from specimen no. 25, which had a low room temperature impact energy, composition and structure should not be important factors in the differences in the hydrogen embrittlement characteristics.

The final consideration is the role of residual stresses after the PWHT. Whereas in early work¹² it was felt that residual stresses were essentially eliminated in the PWHT, more detailed research in the

last few years indicate that there is a substantial reduction on stress relief but nevertheless small residual stresses can remain. A number of related papers appear in the Welding Institute Conference of 1977 and of particular relevance is the article by Gott.¹³ She shows the maximum residual stresses (perpendicular to the weld interface) was approximately 1 cm from the interface in A533B Class 1 steel. Grotke et al.¹⁴ show the same effect after two different stress relief times in essentially the same class of steel (Fig. 14).

Even though the maximum residual stresses pertinent to the hydrogen embrittlement test situation are relatively small (~7 ksi or 50 MPa), there is clearly a probability of a (residual) stress gradient which would shift an advancing crack out of the selected PHZ plane. In discussion of the phenomenon with Grotke,¹⁵ he pointed out that the residual stress measurements are relatively gross, and that small localized zones of higher residual stress would pass without detection.

To conclude this section, it is worth commenting that research of the properties of the HAZ is difficult because of the complex thermal history and structural variability in a very small zone. The results of the tests were based upon the premise that the PHZ in the HAZ would be the "weak-link" in hydrogen embrittlement susceptibility. The premise is not necessarily incorrect if the effect of residual stresses overrides the effect of higher strength level. However, since the crack moved into the far heat affected zone in each test, clearly future research of this area should be addressed to this zone.

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Fig. 14 Coordinate residual stresses on a nozzle cut-out surface prior to and after final stress relief. σ_x is perpendicular to and σ_z parallel to the weld-base metal interface in an 11-in. thick (280 mm) A533 steel plate (from G. E. Grotke et al.¹³).

REFERENCES

1. B. J. Shaw and E. W. Johnson, Third Int. Conf. on Hydrogen Embrittlement of Materials, Jackson Hole, 1980, to be published.
2. B. J. Shaw and E. W. Johnson, Topical Report No. 1, DoE Contract DE-AC05-78OR13513 (Aug. 1980).
3. H. Okada, "Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys," NACE Conference-5, Unieuk-Firminy, France, p. 124, (1973).
4. T. P. Groenevald, Symposium on Pipe Line Research, E (1969).
5. SAE-ASM-ASTM, Hardness Conversions, ASTM E48.
6. W. W. Gerberich, Hydrogen in Metals, ASM Conference, Seven Springs, 115 (1973).
7. J. H. Payer, et al., Corrosion 32, 52 (1976).
8. G. S. Hicko and C. M. Gilmore, ASTM, STP 645, 351 (1978).
9. 1980 Annual Book of ASTM Standards, Part 10, E399, Section 8 (ASTM Philadelphia, PA).
10. H. G. deLorenzi and C. F. Shih, "3D Elastic-Plastic Investigation of Fracture Parameters in Side Grooved Compact Specimens," General Electric Report No. 80CRD211 (Sept. 1980).
11. D. A. Canonico, Welding Res. Supp. 127-S, May (1979).
12. G. Sachs and K. R. VanHorn, "Practical Metallurgy," ASM Publication (1940).
13. K. E. Gott, Int. Conf. of the Welding Institute on "Residual Stresses in Welded Construction and Their Effects," London (1977).
14. G. E. Grotke, et al., Westinghouse Research Center, Report No. 73-1D4-WELST-R2 (1973).
15. C. E. Crotke, private communication (1981).