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

Embrittlement of Cr-Mo Steels in H_2S Plus H_2O Vapor
Environment

B. J. Shaw

November 28, 1980

MASTER

Quarterly Report No. 8
(May 15 to August 15, 1980)

Contract No. DE-AC05-78-R13513

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

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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 $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ 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 a 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 H_2S environment (K_{Isc}). 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.

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 stress intensity can be substantially lower if side grooves are incorporated. Incubation time effects were reduced by fatigue pre-cracking 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_{ISCC} 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 $2\frac{1}{2}Cr - 1Mo$ steel is immune to cracking in the H_2S environment provided by a tank of commercial high purity H_2S .

Quarterly Report No. 7
November , 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.

DISCUSSION OF CURRENT ACTIVITIES

Tests in $H_2S + H_2O$ Vapor Environment

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 $2\frac{1}{2}Cr-1Mo$ and $1\frac{1}{2}Cr-\frac{1}{2}Mo$ 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 $2\frac{1}{2}Cr-1Mo$ 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.

Experimental Procedure

After the chamber containing the specimen had been evacuated at ~20 Pa, distilled water was drawn into a connecting tube. The H_2S 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 top 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.

The modified test procedure, described in detail in Reports 3 and 4 of this series, was also used in this series of tests. The procedure employs pre-cracking by cyclic loading at 1 Hz in the H₂S environment to induce an unoxidized sharp crack. The method is designed primarily to reduce the incubation time to a minimum. Once the crack is propagating under cyclic loading, the stress intensity is raised slightly and the specimen held at a constant displacement. This is achieved by LVDT displacement control of the servohydraulic system which loads the specimen. The simulated bolt load test (i.e. constant displacement) is then monitored for load drop, which indicates crack growth. By measuring the compliance of the specimen (i.e. by unloading to measure v/P , where v is displacement and P is load), crack growth can also be assessed. When the load no longer decreases, the crack has arrested and a measure of K_{Isc} is obtained from the actual crack length and the final applied load. The side grooves in the specimens were introduced to eliminate plane-stress pinning of the crack, which is a severe problem in low strength steels.

Results

The analytical chemistries and strength levels of the samples tested are given in Table 1.

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 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. 1. Based

Table 1

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

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

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

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

Fig. 1 Fracture surface of specimen 55L, a 2T compact tension specimen with 0.125 in. side grooves. The scale is in inches.

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. 2, 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. ($3.1 \times 10^{-3} \text{ m}$) 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 $1.8 \times 10^{-3} \text{ m}$) 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. 3.

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. ($6.3 \times 10^{-3} \text{ m}$) 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 $44 \text{ ksi in.}^{\frac{1}{2}} (48.5 \text{ MPa m}^{\frac{1}{2}})$. Unfortunately, the test was run in a period of an unusually large number of electrical storms, which created the occasional excursion in the power supply which, in turn, caused the servohydraulic pumps to shut down. In all there were four such failures. At each point the crack was started again at a load very slightly above the final load prior to the power failure. 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. 4.

The second specimen test was interrupted by only one power failure. 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 4 shows the fracture surface.

The third run was interrupted by an instrument failure which resulted in an overload. The fracture surface, Fig. 5, is of particular

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

Fig. 3 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. 4 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.

55H - No. 3

55H - No. 4

Fig. 5 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.

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 pre-cracked 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. 5.

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 (Ref. 1). 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. 6.

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 ($45\text{--}75 \text{ ksi}$ or $300\text{--}500 \text{ MPa}$) samples which had been given a

Fig. 6 Fracture surface of specimen 77L, a 1T-CT specimen with 0.125 in. side grooves. The scale is in inches.

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} in a salt water environment of a 4340 steel tempered to 180 ksi (1240 MPa) was measured. 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. 5). 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 determined. Crack advance along the side grooves is consistent with the theoretical work of deLorenzi and Shih,² 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 $1\frac{1}{4}\text{Cr}-\frac{1}{2}\text{Mo}$ 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 advanced 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.²

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