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

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ABSTRACT

This report gives the results of tests designed to measure the threshold stress intensity (K_{Isc}) in H_2S of the peak hardness zone in the HAZ of welds in $2\frac{1}{4}$ Cr-1 Mo 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 K_{Isc} could be significantly below $80 \text{ ksi}\sqrt{\text{in}}$ but the absolute value could not be determined from the current tests. Details of the forging process and the status of the program are also presented.

TABLE OF CONTENTS

	<u>Page</u>
1. OBJECTIVES OF PROGRAM	1
2. STATUS OF PROGRAM	3
3. HEAT AFFECTED ZONE STUDY (HAZ).	4
4. FORGING OF LABORATORY HEATS	8
5. ACKNOWLEDGMENTS	9
6. REFERENCES.	10

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1. OBJECTIVES OF PROGRAM

This program is designed to assess the hydrogen embrittlement susceptibility and temper embrittlement susceptibility of Cr-Mo steels. In Phase I of the program, the hydrogen embrittlement susceptibility of commercial 2½ Cr-1 Mo steels is studied. This phase has two components: (a) the hydrogen embrittlement susceptibility of plate or forged steel, and (b) the susceptibility of the peak hardness zone in the heat affected zone (HAZ) in a weld. Since only a small amount of weld material was available, plate steel was heat treated to a strength level comparable with that of the peak hardness in the HAZ for simulation tests. Phase II of the program is a study of the effect of alloying elements in the Cr-Mo steel, using a set of 32 laboratory steels with compositions arranged according to a statistical design. The alloying variables in this set are Mo, Cr, Mn, Si, C and P. The steels are to be assessed for hydrogen embrittlement and temper embrittlement at two strength levels, one corresponding to typical strength levels used commercially and the second corresponding to the peak hardness in the HAZ. The hydrogen embrittlement data generated in Phase II will be compared with that of Phase I. The temper embrittlement data will be compared with data from the American Petroleum Institute (API) program on temper embrittlement of commercial 2½ Cr-1 Mo steels. The main emphasis is on

the evaluation of the effect of the alloying elements on the two modes of embrittlement. A small effort will be expended on synergistic effects, i.e. the effect of prior temper embrittlement on hydrogen embrittlement.

The results of the program will allow for a determination of the optimum Cr-Mo steel compositions for resistance to hydrogen and temper embrittlement.

2. STATUS OF PROGRAM

The logic flow diagram for the program is given in Fig. 1, and the objectives are given in Table I. In Phase I of the program (1.1.1 to 1.1.3) the main emphasis was on the evaluation of hydrogen embrittlement susceptibility of API commercial steels. Very early in this part of the program it became evident that the proposed test technique, the fatigue pre-cracked Charpy rising load test in H_2S , was not a viable means of assessing the threshold stress intensity (K_{Isc}) in the environment. Moreover, it was not a reasonable method for approximately estimating K_{Isc} for relative screening purposes. This was discussed in detail in the first annual report.⁽¹⁾ A new issue in the program was therefore to evolve a means of assessing the hydrogen embrittlement characteristics of the Cr-Mo steel. The method for testing the steels heat treated to a strength level comparable with that of the HAZ (Rockwell B hardness ~97) has been established. Thus objective 1.1.3 in Table II is essentially completed. Since the lower strength steels showed resistance to hydrogen embrittlement in our current test using commercial high purity H_2S , a secondary study has been initiated to evaluate the effect of strength level (Table III).

In Phase II of the program the forging of the 32 laboratory steels has been completed and the tempering conditions (time, temperature) for two strength levels are being evaluated.

3. HEAT AFFECTED ZONE STUDY (HAZ)

3.1 Introduction

The primary objective of this part of the program, identified as 1.2 in the logic flow diagram, 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 IV.

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).

3.2 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. 2). 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 because of size limitations of the instrument. A typical hardness profile, using Knoop measurements, is shown in Fig. 3.

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 H_2S . The modified test procedure, which has been described in detail in an earlier report,⁽¹⁾ was employed to assess the hydrogen embrittlement susceptibility of the PHZ. This procedure employs pre-cracking by cyclic loading at 1 Hz in the H_2S 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.

3.3 Results and Discussion

(a) H_2S Environmental Tests

Tests on the PHZ of specimen no. 62 were carried out by the above procedure. Whereas crack advance could be obtained under cyclic loading, 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_{arrest} of the order of $85 \text{ ksi}\sqrt{\text{in}}$ ($93.5 \text{ MN/m}^{3/2}$).

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 4 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 5 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. 3.

The test underlines one of the difficulties in testing the PHZ adjacent to a weld. Clearly there is a 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 earlier tests in this study⁽¹⁾ on simulated HAZ (higher strength level) $2\frac{1}{4}$ Cr - 1Mo steel, the K_{arrest} of a smooth-sided 3T-CT was compared with that of a side-grooved 2T-CT. The difference in K_{arrest} ($110 \text{ MN/m}^{3/2}$ versus $22 \text{ MN/m}^{3/2}$ 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_{arrest} for the PHZ in this sample should be less than half of the original estimate, even though an actual measurement could not be obtained.

Sample no. 25 was tested in the same way as no. 62, with essentially identical results, except that the measured K_{arrest} 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 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. This specimen was not broken open since an attempt will be made at a later date to locate a smaller compact tension specimen around the tip of the present crack in the 2T-WOL.

(b) Charpy Impact Tests

The locations of specimens taken from samples 25, 62 and 63 are shown in Fig. 6. The data from the Charpy impact curves is given in Table VI. 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.

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 VI). The evidence therefore suggests that the component of the HAZ most susceptible to hydrogen embrittlement could lie outside the PHZ.

4. FORGING OF LABORATORY HEATS

The cast heats were 12 in* long tapered square ingots with side dimensions of approximately 5 in at the top and 4 in at the bottom. The hot tops were removed prior to forging leaving approximately 10 in long ingots. The forging temperature was between 1100 and 1200°C. In the first stage of forging the ingots were reduced from a 4 to 5 in side dimension to 3.5 in. The 17-18 in length ingot was then sectioned into 3 pieces. Two pieces from the bottom, 5.5 in long, were upset in the second stage of forging to produce pieces 2.25 in thick by 5.5 in square. These pieces are large enough to make a 2T-Compact Tension (C·T) specimen. The remaining piece, 6-7 in long by 3.5 by 3.5 in, was forged from one side to produce a "pancake" approximately 1.125 in thick by 6 by 9 in. It is planned to take 1T-CT specimens and Charpy specimens from these pieces.

Since problems were encountered in the initial stages of making these heats, due to the use of larger than normal moulds for the apparatus, a redundant heat was employed for a trial run on the forging routine. The cross sections of the forged material showed a uniform structure throughout (Fig. 7). The 32 heats for the main part of the program were therefore identically forged. The forging was done at Butler Forge, Butler, PA.

* 1 in = 2.54×10^{-2} m.

5. ACKNOWLEDGMENTS

Metallography and hardness measurements were taken by R. J. Burland. The environmental tests were conducted by R. J. Smykal under the general supervision of L. Ceschini. The interest and critical comments of Dr. J. M. Wells are gratefully acknowledged.

6. REFERENCES

1. B. J. Shaw and E. W. Johnson, "Study to Optimize Cr-Mo Steels to Resist Hydrogen and Temper Embrittlement," DOE Contract ET-78-C-01-3050, First Annual Report, Dec. 1979.

PERMANENT RECORD BOOK ENTRIES

Fig. Book No. 208613, pp. 27-28

TABLE I - List of Primary Tasks, Schedule and Status of the Cr-Mo Steel Optimization Program

		Comments or Start Date	Projected Completion Date
Phase I	Evaluation of API Commercial Material	Started	9.80
Task 1.1	Evaluation of Simulated HAZ Commercial Material	Started	9.80
Item 1.1.1	Material Characterization and Heat Treatment	Finished	6.79*
1.1.2	Machining of Test Specimens	Finished	5.79
1.1.3	Evaluation of Hydrogen Embrittlement Susceptibility	Table II	6.81*
1.1.4	Evaluation of Temper Embrittlement Susceptibility	11.79	4.80*
1.1.5	Correlation, Analysis and Topical Report	3.80	6.80
Task 1.2	Evaluation of Actual HAZ Commercial Material	Started	9.80
Item 1.2.1	Material Selection and Characterization	Finished	8.79*
1.2.2	Machining of Test Specimens	Finished	7.79*
1.2.3	Evaluation of Hydrogen Embrittlement Susceptibility	Finished	3.80
1.2.4	Fractography and Hardness Evaluation	Continuing	6.80
1.2.5	Correlation, Analysis and Topical Report	4.80	9.80*
Phase II	Evaluation of Laboratory Statistical Compositions	Started	9.81
Task 2.1	Procurement of Statistical Composition Material	Started	12.79
Item 2.1.1	Design of Statistical Composition Material	Finished	10.78
2.1.2	Casting of Laboratory Alloys	Finished	5.79*
2.1.3	Processing of Laboratory Alloys	Finished	8.79*
2.1.4	Materials Characterization	11.79*	4.80*
2.1.5	Development of Hardness and HT Schedules	Started 6.79	4.80*
Task 2.2	Specimen Preparation	12.79*	6.80*
Item 2.2.1	Machining of Specimens	10.79	6.80*
2.2.2	Specimen HT and Precracking	3.80	9.80
Task 2.3	Evaluation of Hydrogen Embrittlement Susceptibility	7.80	6.81
Task 2.4	Evaluation of Temper Embrittlement Susceptibility	7.80	6.81
Task 2.5	Statistical and Summary Analysis and Final Report	7.81	9.81

* Revised dates.

TABLE II - Modification Task for 1.1.3 in Phase I

	Comments or Start Date	Projected Completion Date
Task 1.1.3(a) Long Term Bolt Loaded Tests on Low Strength Steels		
(i) Machine specimens	Finished	---
(ii) Air pre-fatigue crack speci- mens and shim load (equivalent to bolt load)	Finished	---
(iii) Periodical inspection for crack advance	Continuing	6.81
Task 1.1.3(b) Evaluation of Testing Pro- cedures to Assess Hydrogen Embrittlement Resistance		
(i) Modification of compact tension specimens to elimi- nate plant stress zones	Finished	---
(ii) Modification of testing procedure to reduce incuba- tion time and measure crack arrest stress inten- sity	Finished	---

TABLE III - Additional Tasks Introduced in Phase I, Item 1.1.3

	Comments or Start Date	Projected Completion Date
Task 1.3 Effect of Strength Level on Hydro- gen Embrittlement Resistance		
1.3.1 Selection of Material	Finished	---
1.3.2 Heat Treatments for Strength Levels	Continuing	3.80
1.3.3 Evaluation of Hydrogen Embrittle- ment Characteristics	10.78	4.80
1.3.4 Analysis and Topical Report		7.80

TABLE IV - Post Weld Heat Treatments of Weld Samples

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

Conversions: 1 hr = 3.6×10^3 s.

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

TABLE V - 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.

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

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

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

Fig. 2 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. 3 500 gm Knoop hardness as a function of distance from fusion line showing the peak hardness in the heat affected zone of the plate.

Actual Size

2T-WOL with 0.25 in side grooves

Fig. 4 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.

x4

Fig. 5 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.

$x \frac{1}{2}$

$x \frac{1}{2}$

$x \frac{1}{2}$

Fig. 6 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.

x200

Fig. 7 Typical structure found throughout the cross section of a trial forged sample blank. This sample has not been heat treated after forging.