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

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ABSTRACT

A modified test technique has been developed in this program to overcome difficulties in assessing the hydrogen embrittlement susceptibility of low strength 2½ Cr-1 Mo steels. One steel sample was tempered to a range of strength levels and evaluated using the new technique. The results, showing a lower strength level for which hydrogen embrittlement susceptibility can be assessed in a 446 KPa H₂S environment, are presented in this report. A review of the restructuring of the program is also given.

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1. 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 2½ Cr-1 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 pre-cracked 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 an earlier report.⁽¹⁾

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. However, the same technique would produce no cracking in the low strength steels. The restructuring of the program, based upon these considerations, is presented in this report along with test data from specimens of one sample which show the effect of strength level using the revised testing techniques.

2. RESTRUCTURED PROGRAM

The logic flow diagram shown in Fig. 1 gives an overview of the program structure and Table I gives the detailed program tasks of the original program. Most of the Phase I tasks along with the development of the test technique for evaluation of hydrogen embrittlement susceptibility have been completed. In Phase II, the study of the effects of composition based upon 32 laboratory heats, the tempering curves are currently being generated (task 2.1.5 of Table I). Table II shows the tasks associated with the restructured program.

WEC-3.2.3-2 is a new task. The objective is to investigate various methods of evaluating the hydrogen embrittlement susceptibility of the low strength steels (UTS 400-550 MPa) by changing the test procedure, specimen design or environment. This task replaces the study of hydrogen embrittlement susceptibility of low strength steels in the original program (part of 2.3).

WEC-3.2.3-3. This task is identical to 2.4 of the original program. The temper embrittlement susceptibility will be studied at two strength levels.

WEC-3.2.3-4. This task is the same as 2.1.5 and the heat treatment part of 2.2.2 in Table I.

WEC-3.2.3-5. This is the same as 2.1.4 in Table I.

WEC-3.2.3-6. Task 2.4 in Table I has been reduced to a study of the high strength steels only. The task includes a small study of the effect of prior temper embrittlement on hydrogen embrittlement susceptibility.

WEC-3.2.3-7. This task is the same as 2.5 in the original program.

3. STUDY OF THE EFFECT OF STRENGTH LEVEL ON HYDROGEN EMBRITTLEMENT SUSCEPTIBILITY

3.1 Background

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 H₂S environment. This is quite consistent with the findings in earlier investigations.^(2,3) In this small study the objective was to define the effect of strength level on the hydrogen embrittlement susceptibility in one sample of 2¼ Cr-1 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 an earlier report for a more detailed discussion.⁽¹⁾

3.2 Experimental Procedure

The composition of sample no. 74 used in this experiment is given in Table III. The heat treatment history and the tempering conditions used to produce the range of strength levels in the bainitic structure is given in Table IV. The strength level was assessed by conversion from Rockwell B or C hardness readings.⁽⁴⁾

After the heat treated standard 2T-Compact Tension (CT) specimens were machined from the specimen blanks, 0.25 in (6×10^{-3} 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 H₂S.

The incubation time for crack initiation is reduced to a minimum by cyclically loading the specimen in the environment at 0.5 to 1 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_{Isc} 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.

3.3 Results and Discussion

The results of the tests are given in Table V. 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 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 $K_{APP} = 113 \text{ ksi}\sqrt{\text{in}}$ ($124 \text{ MN/m}^{3/2}$).

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).

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.⁽⁵⁾ A similar trend was found by Payer, et al.⁽⁶⁾ for specimens charged with hydrogen. In most of the studies reviewed, the UTS or σ_y is very high compared with the 2½ Cr-1 Mo steels which have been tested in this study. Also, the test techniques did not usually incorporate side grooves. Consequently, exact comparison with this study is not possible. Hicko and Gilmore⁽⁷⁾ used an aqueous environment of ½ wt percent glacial acetic acid with H₂S at one atmosphere and showed that K_{Isc} in low strength 2½ Cr-1 Mo steel could be as low as 48 ksi√in (53 MN/m^{3/2}). The data from an aqueous solution, however, cannot necessarily be directly compared with that from a gaseous environment.

It is concluded that the modified test procedure (based upon one sample only) can be used to assess the hydrogen embrittlement susceptibility of 2½ Cr-1 Mo steels with a UTS greater than 110 ksi√in (121 MN/m^{3/2}). Below this strength level the ranking of various alloy steels will probably have to be carried out either with a different test method or a more aggressive environment. This is reflected in the new task WEC-3.2.3-2 in Section 2 of this report. The next planned step in this task is to use the same experimental test technique and to make the environment more aggressive by adding H₂O water vapor to the H₂S gas.

4. 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.

5. REFERENCES

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PERMANENT RECORD BOOK ENTRIES

Fig. Book 208613, pp. 30-31

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 - Restructured Schedule and Status of the Cr-Mo Steel Optimization Program

Task No.		Comments or Start Date	Projected Completion Date
WEC-3.2.3-2	Establish means of evaluating hydrogen embrittlement susceptibility in low strength Cr-Mo steels.	Started	8.80
WEC-3.2.3-3	Evaluate temper embrittlement susceptibility of Cr-Mo steels at two strength levels.	7.80	12.80
WEC-3.2.3-4	Heat treat 32 Cr-Mo steels, with compositions arranged according to a statistical design, to produce a bainitic structure at two strength levels.	Started	8.80
WEC-3.2.3-5	Establish the chemistry and microstructure of 32 Cr-Mo steels heat treated to produce a bainitic structure.	Started	7.80
WEC-3.2.3-6	Evaluate hydrogen embrittlement susceptibility of 32 higher strength Cr-Mo steels.	8.80	8.81
WEC-3.2.3-7	Produce, via regression analyses, the effect of composition on temper embrittlement and hydrogen embrittlement of Cr-Mo steels.	12.80	8.81

TABLE III - Composition of Sample No. 74

Element	C	Cr	Mo	Mn	Si	Ni	Cu
Wt %	.103	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 IV - 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 +
1275°F - 16 hr

} Simulated post weld heat treatment

(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 ksi = 6.895 MPa

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

Specimen No.	Approximate JTS (ksi)	Estimated K _{Isc} (ksi√in)	Comments
74-3	126	28	Slow crack growth from 42 ksi√in in 54 hr.
74-1	117	34	Catastrophic fracture; specimen completely failed.
74-5	114	52	No failure after 17 hr at 50 ksi√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 x 10⁻² m

1 ksi = 6.895 MPa

1 ksi√in = 1.099 MN/m^{3/2}

1 hr = 3.6 x 10³ s

Key

API	American Petroleum Institute
HAZ	Heat Affected Zone
H ₂ S	Hydrogen Sulphide Gas at 50 psig
T.E.	Temper Embrittlement
H.E.	Hydrogen Embrittlement
Task Numbers Included as Appropriate	

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graph TD
    1.1[1.1 Peak Hardness in HAZ API Production Weldments] --> 1.1.1[1.1.1 Simulated HAZ Strength Level  
RB ~ 97  
API Re-Tempered Plate]
    1.1.1 -- 1.1.2 --> 1.1.3[1.1.3]
    2.1.1[2.1.1 Statistical Design] --> 2.1.2[2.1.2 Cast 32 Heats Variables  
Mo, Cr, C, Mn, Si, P]
    2.1.2 -- 2.1.3 --> 2.1.3[2.1.3 Forge and Temper to Two Strength Levels]
    2.1.2 -- 2.1.5 --> 2.1.4[2.1.4 Statistical Array of 32 Steels at Two Strength Levels:  
Composition and Structure]
    2.1.3 --> 2.1.4
    2.1.4 -- 2.2.1 --> 2.2.1[2.2.1 Temper Embrittled Steels]
    2.1.4 -- 2.2.2 --> 2.3[2.3]
    2.2.1 -- 2.2.1 --> 2.3
    2.2.1 -- 2.2.1, 2.4 --> 2.5[2.5 Effect of Composition and Strength on Temper Embrittlement]
    1.2[1.2 HAZ of Actual Weldments of API Material] -- 1.2.2 --> 1.2.3[1.2.3]
    1.1[1.1 API Plate Material] -- 1.1.2 --> 1.1.3[1.1.3]
    1.2.3 --> 1.1.3
    1.1.3 --> 1.1.3[1.1.3 Evaluate H.E. Susceptibility]
    1.1.3 --> 2.5[2.5 Effect of Composition Strength and T.E. on H.E. Susceptibility]
    2.5 --> 2.3[2.3 Correlation Between Temper Embrittlement and Hydrogen Embrittlement Susceptibilities]
    2.3 --> 2.5[2.5 Composition Optimization of Cr - Mo Steel]
    2.5[2.5 Data from API Temper Embrittlement Program] --> 2.5[2.5 Effect of Composition and Strength on Temper Embrittlement]
  
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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.