THE EFFECT OF HYDROGENOUS ENVIRONMENTS ON THE FRACTURE TOUCHNESS OF POWER PLANT STEELS

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ABSTRACT

The effect of hydrogenous environments on the threshold stress intensity for subcritical crack propagation K_{IH_2} in AISI 4340 type steels and in Cr-Mo pressure vessel steels has been determined. In the 4340 type steels tested in 100% H_2S at room temperature, the K_{IH_2} values were lowered markedly with inceasing yield strength or with increasing temper embrittlement, ultimately reaching limiting values as low as 17 MPa $\sqrt{m}$. At high yield strength levels (1200 MPa), the purity of the steel or the degree of temper embrittlement had no effect on the K_{IH_2}. Conversely when saturation of the grain boundaries by impurities due to severe temper embrittlement had occurred, K_{IH_2} was insensitive to the yield strength. In the case of the 2.25Cr Cr-1 Mo steels, tests at room temperature in 6% H_2S - H_2 mixtures showed that the steel was susceptible to subcritical crack growth resulting in K_{IH_2} values that were about 30% of the baseline K_{IC} values derived from J_{IC} data obtained in air. At 315 and 455°C, however, subcritical crack growth was no longer significant to material performance. A new mechanism of damage was observed resulting in reduced load bearing capability for the specimens compared to that in air.

KEY WORDS

Turbine steel; pressure vessel steel; hydrogen; fracture toughness; temperature; embrittlement; yield strength.

INTRODUCTION

Low alloy steels are widely used in a variety of high-stress applications in electric power plants. In applications requiring a combination of high strength as well as toughness, the AISI 4340 family of steels and the 2.25Cr-1 Mo steels are extensively employed. The former steels are utilized for highly stressed turbine and generator parts, while the later steels are utilized for pressure vessels and high pressure piping. More recently, the 2.25Cr-1Mo steels have also become the candidate steels for use in pressure vessels of coal conversion systems. The service conditions for the steels often involve aggressive environments which can cause entry of hydrogen into the steel and lead to hydrogen assisted subcritical crack propagation. The present study was undertaken with a two-fold objective: (1) To characterize the susceptibility of the 4340 type steels to subcritical crack growth in a hydrogenous environment, as a function of the strength level, alloy content, and grain boundary impurity concentration of the steel, and (2) to characterize the susceptibility of 2.25Cr-1Mo steels to subcritical crack growth in hydrogenous environments at temperatures and pressures typical of coal conversion vessels. Since the two types of steels have been evaluated for different applications and with different objectives in mind, results of this study will be presented in two separate parts, each dealing with a specific steel.

EXPERIMENTAL PROCEDURES

Two types of 4340 steels, designated X and Y, were included for study. Basically, the type X steel contained lower amounts of Ni, Cr, Mo and V, but higher amount of C and Mn relative to the type Y steels. Both types of 4340 steels were produced as "pure" and "impure" 23 kg heats by vacuum induction melting and were forged to bar stock. The "pure" heat contained no impurity additions, while the "impure" heat contained deliberate additions of 300 ppm each of P, Sb and Sn. Specimen blanks from the forged bars were austenitised at 840°C for 1.5 hr, oil quenched and tempered in the range 482 to 593°C to various yield strength levels. Subsequent to tempering, some of the blanks from the impure heat were subjected to an accelerated temper embrittlement treatment consisting of 50 hr at 450°C and 500 hr at 400°C with furnace cooling after each step.

Two grades of 2.25Cr-1Mo steel were evaluated in this program: normalized and tempered ASTM A387, class 2-grade 22 and quenched and tempered ASTM A542, class 3. The steels were procured as 17.8 cm thick plates representing the commercial fabrication practice for Chicago Bridge and Iron, Inc. The A387 plate had been normalized at 954°C and tempered at 690°C. The A542 plate had been austenitised at 954°C, quenched and tempered at 663°C. The chemical compositions and the baseline mechanical properties of the various steels are shown in Table 1 and Table 2, respectively.

TABLE 1 Chemical Composition of Steels

Steel	C	Mn	P	S	Sb	Sn	Cu	Si	Ni	Cr	Mo	V
4340 type X												
Pure	.43	.75	.001	.002	.0002	.0007	Nil	.25	1.96	0.83	0.24	.036
Impure	.42	.73	.031	.002	.032	.023	Nil	.26	2.0	0.83	0.26	.031
4340 type Y												
Pure	.25	.32	.0015	.002	.0002	.0007	Nil	.24	3.41	1.86	.44	.15
Impure	.25	.31	.031	.003	.032	.023	Nil	.20	3.45	1.83	.45	.15
2.25Cr-1Mo												
A387	.12	.42	.013	.02	NA*	NA*	.16	.25	0.14	2.48	1.06	Nil
A542	.12	.47	.01	.017	NA*	NA*	.12	.22	0.22	2.26	0.99	Nil

*Not analyzed.

Charpy impact tests were conducted selectively in air to characterise the Fracture Appearance Transitions Temperatures (FATT).

The environmental susceptibility of 4340 type steels was measured at room temperature in presence of 4 atmospheric pressure H_2S. Test conditions for the 2.25Cr-1Mo steels included temperatures of 25, 315, and 455°C and pressures of 5.5, 10.5 and 24 MPa of a 6% H_2S - H_2 gas mixture.

TABLE 2 Baseline Mechanical Properties of Steels

Steel	Heat Treatment Condition	Yield Strength, MPa	Tensile Strength, MPa	Elongation %	Reduction of Area, %
4340					
Type X	K	869	1007	19	59
	J	1054	1200	16	56
	F	1103	1213	16	56
	G	1124	1227	15	55
	H	1213	1338	14	51
Type Y	A	862	965	19	65
	B	986	1089	18	63
	C	1089	1186	17	58
	D	1172	1303	16	56
	E	1200	1386	16	57
2.25Cr-1Mo	A387	313	521	30	--
	A542	495	608	24	--

The susceptibility of the steels to hydrogen-induced cracking was characterized in terms of the threshold stress intensity for crack propagation K_{IH_2}. Test specimens were compact type specimens of the dimensions 7.25 x 6.08 x 2.54 cm. The test method involved conventional monotonic loading of the precracked specimens at low strain rates (approximate K of 0.002 MPa $\sqrt{m}$/sec) in the H_2-H_2S environment and is essentially similar to the ASTM E-399-72 procedure used for K_{IC} testing in air. The load corresponding to the start of the subcritical crack extension was determined from the point of deviation of the load vs. displacement curve from baseline behavior. The stress instensity level associated with the onset of crack growth was determined from the K_I - calibration given by Wessel (1968).

While the conventional procedures described above were adequate for measuring the K_{IH_2} of the high strength 4340 type steels, the procedures had to be modified for application to the 2.25Cr-1Mo steels, due to the following reasons: The high temperature high pressure corrosive environments involved in the test procedures required the use of a remotely located (70 mm from load line) LVDT system to measure displacement. Since displacement is normally measured at the load line, corrections had to be applied to the measured values of displacement under the present set up. A second complication arose because the deviation of the load-displacement curve from the baseline curve often occurred at load levels above the linear elastic range, indicating the development of large crack tip plastic zones. Plasticity corrections therefore had to be applied to the crack size. The procedures employed for K_{IH_2} determination from nonlinear test records and for normalization of displacements measured remotely from the load line are described and justified in detail elsewhere (McCabe and Landes, 1979) and therefore will not be repeated here. The design of the high pressure H_2S test system is also described in another report (McCabe and Landes 1980b).

Scanning Electron Fractography (SEM) was performed selectively on some specimens and the percentage of intergranular fracture at the point of initial crack growth was estimated.

RESULTS AND DISCUSSION

4340 Type Steels

Results of the 50% Ductile-to-Brittle transition temperatures (FATT) determined by charpy tests are shown in Table 3.

TABLE 3 FATT for 4340 Type Steels

Type	Heat Treatment Condition	FATT, °C Pure Steel	FATT, °C Impure Steel	FATT, °C Impure Steel Deliberately Embrittled	ΔFATT, °C Impure Steel as Heat Treated	ΔFATT, °C Deliberately Embrittled
X	J	-31	35	121	66	152
	F	-76	54	190	130	266
	G	-82	24	204	106	286
Y	A	-51	112	288	163	339
	B	-18	165	343	183	361
	C	10	143	3239	133	319
	D	10	96	307	86	297

The results contained in Table 3 show significant shifts in FATT (ΔFATT) in the impure steels due to temper embrittlement, even in the as heat treated condition. Deliberate step cooling embrittlement treatments resulted in a further increase of the ΔFATT. There appears to be no clear cut correlation between the FATT values and the strength level of the steels. In general, the Type Y steels show a much greater susceptibility to temper embrittlement than the Type X steels, presumably due to the higher content of Ni and Cr in the steels. There is considerable evidence in the literature that both Ni and Cr accentuate the grain boundary segregation by impurity elements and lead to increased susceptibility to temper embrittlement (Low and Colleagues, 1968).

The K_{IH_2} of the steels are found to vary synergistically with the yield strength level as well as the degree of temper embrittlement, as may be seen from Figs. 1 and 2. The yield strength level exerts a marked effect on the K_{IH_2} for the high purity steel but not in the case of the temper embrittled steels. Similarly, temper embrittlement exerts an influence on K_{IH_2} at low yield strength levels, but not at the higher strength levels. At a yield strength of about 1200 MPa, the curves for all the steels converge to a limiting value of about 17 MPa $\sqrt{m}$, regardless of the degree of prior embrittlement. If Figs. 1 and 2 were superimposed on each other it can be seen that plots for steel X (lower alloy content) fall below the corresponding plots for steel Y, in the pure and in the impure conditions, indicating an inherently higher susceptibility to hydrogen attack for the lower alloyed steel. The higher susceptibility may also be the result of microstructural factors. At the high yield strength level of about 1200 MPa however, all the plots in Fig. 1 as well as those in Fig. 2 converge to the limiting K_{IH_2} value of about 17 MPa $\sqrt{m}$, indicating that, even the effects of alloy content and microstructural factors become indistinguishable. The effect of temper embrittlement is pronounced only at the low and intermediate strength levels. The K_{IH_2} decreases rapidly at first with temper embrittlement, but levels off beyond a critical degree of embrittlement. The same behavior is observed in case of the Type X steels.

The convergence of the K_{IH_2} data for "pure" and "impure" steels at high strength levels may be due to the possibility that a small amount of grain boundary segregate even in the so-called "pure" steel, in combination with a high yield strength, may lower the K_{IH_2} markedly. In other words, a large contribution may occur from an interactive mechanism between the effects due to yield strength and impurities, thereby facilitating intergranular fracture in the high strength steel. Alternately it can also be argued that the convergence of K_{IH_2} data at high strength levels, regardless of purity, is due to a large contribution from an interaction effect between yield strength and the H_2S in a synergistic fashion, thereby masking the effect of impurities. In any event, the results of this study are indicative of complex interactive effects between H_2, impurities and yield strength. There is considerable evidence in the literature pointing to the possibility of interactive effects between yield strength, hydrogen and impurities. For instance, both the solubility of hydrogen and the critical crack tip concentration of hydrogen in steels are believed to be affected by the yield strength (Gerberich and Chen, 1973). In addition, temper embrittlement studies indicate that the embrittlement susceptibility (ΔFATT) of steels may increase with increasing yield strength for a given impurity level in the steel (Viswanathan and Joshi, 1975). Interactive effects between impurities and hydrogen are suggested by the observation that the temper embrittling impurities also act as poisons to the recombination reaction of atomic hydrogen (McRight and Staehle, 1973).

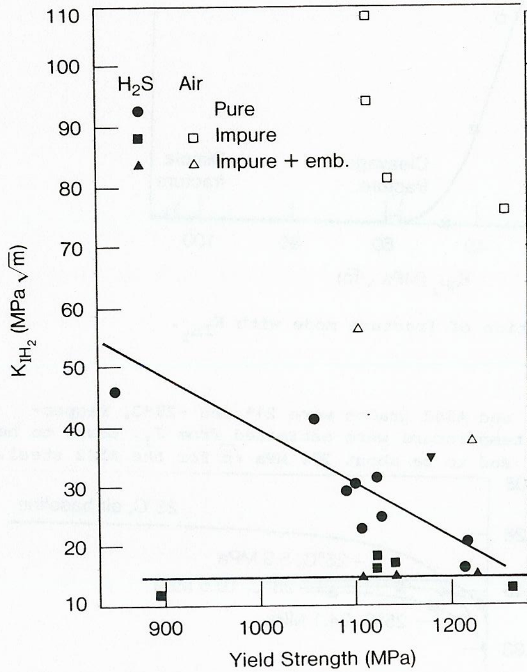

Fig. 1. Effect of yield strength and impurities on K_{IH_2} of 4340 Type X steel.[2]

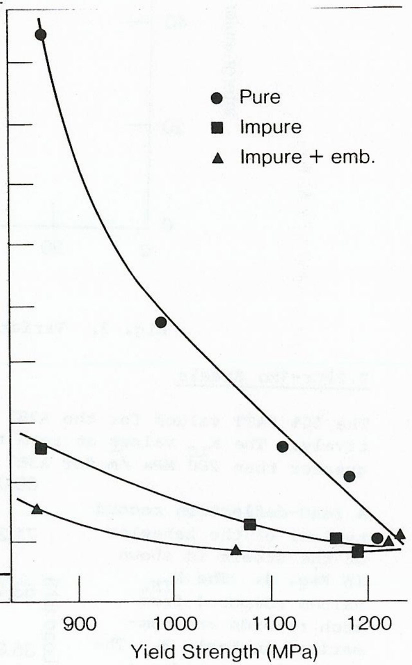

Fig. 2. Effect of yield strength and impurities on K_{IH_2} of 4340 Type Y steel.[2]

Results from the SEM Fractographic investigations are shown in Fig. 3. The mode of fracture is not found to be a function of yield strength or the degree of embritlement or the type of steel, but is a function of the K_{IH_2} resulting from interactive effects between the many variables. Qualitatively, as K_{IH_2} decreases, the fracture mode follows the sequence: dimple → Cleavage → intergranular. At K_{IH_2} below about 50 MPa $\sqrt{m}$ the degree of intergranular fracture increases linearly with decreasing K_{IH_2} regardless of the yield strength-impurity combination that produces a given value of K_{IH_2}.

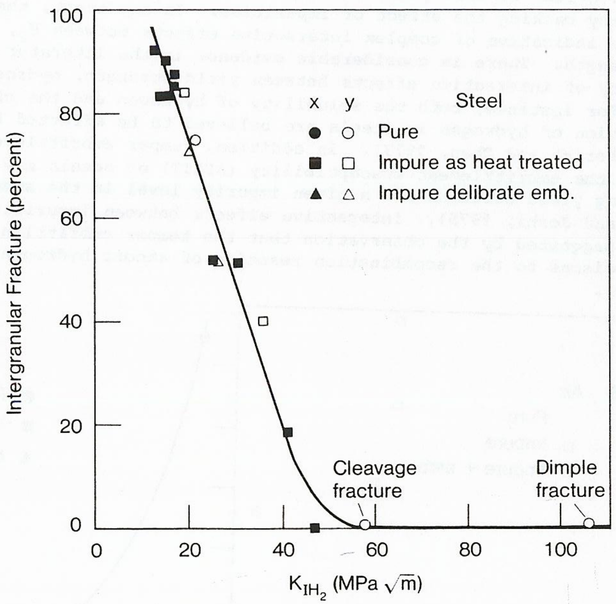

Fig. 3. Variation of fracture mode with K_{IH_2}.

2.25Cr-1Mo Steels

The 50% FATT values for the A387 and A542 grades were 21° and -29°C, respectively. The K_{IC} values at room temperature were estimated from J_{IC} tests to be greater than 280 MPa $\sqrt{m}$ for A387 and to be about 290 MPa $\sqrt{m}$ for the A542 steel.

A load-deflection record typical of the behavior of the steels is shown in Fig. 4. The K_{IH_2} values computed from such records are summarized in Table 3. The table also provides a comparison of the maximum load (P_{max}) reached in the environment and the maximum load reached under baseline conditions (generally air). At room temperature all the specimens displayed hydrogen enhanced

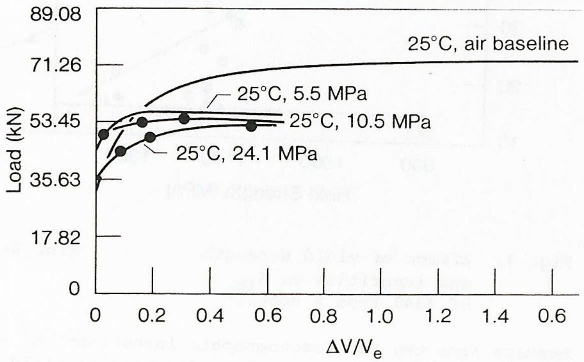

Fig. 4. Typical rising load test record for A542 steel at 25°C.

subcritical crack growth and developed the expected deviation from baseline behavior so that the K_{IH_2} could be easily calculated. Generally the K_{IH_2} values are of the order of 30% of the room temperature K_{IC} values estimated from J_{IC} tests. There is also a trend of decreasing K_{IH_2} with increasing pressure of hydrogen. There is no appreciable difference in the K_{IH_2} values between the two grades of steel, as may be seen from Table 4.

Rising load tests at 315 and 455°C in 6% H_2S-H_2 revealed that the classical rising load concept did not apply well, because deviation of the load-deflection curve from the baseline behavior was often unrelated to subcritical crack growth. Although the load at deviation and the maximum load reached in the environment were always below the corresponding values for the baseline curve in air, posttest examination showed that little crack growth, if any, had in fact occurred. It was therefore assumed that some form of hydrogen induced plasticity was responsible for the observed behavior in the environment. Consequently, a new philosophy was adopted for evaluation of the test records. Comparison of maximum loads (P_{max}) was introduced as a measure of the extent of high temperature environmentally-induced plasticity. During the tests, specimens were taken to a fixed displacement level of 3.81 mm at the LVDT position and the tests were then terminated. The specimens were then pulled open at room temperature and posttest examination was then performed to ascertain the extent of crack growth and the fracture mode. The posttest examination for physical crack growth involved the measurement of crack extensions corresponding to 3.81 mm of LVDT displacement in the rising load test. Crack growth, if any, was measured at mid thickness and at the two outside surfaces and this was handled as a weighted average to take into account tunnelling tendencies. In all the high temperature environmental tests the extent of crack growth Δa_p (see Table 4) was considerably below the total LVDT displacement of about 3.81 mm, indicating that mechanisms other than subcritical crack growth were operative.

A typical rising load test record for the A542 steel tested at 455°C is shown in Fig. 5. The test record for the environmental test is found to be clearly below that of the baseline test conducted in air. Posttest observation, however, showed little subcritical crack growth, see Table 4. The effects of prior exposure and testing at the higher temperatures on the subsequent post test behavior of the

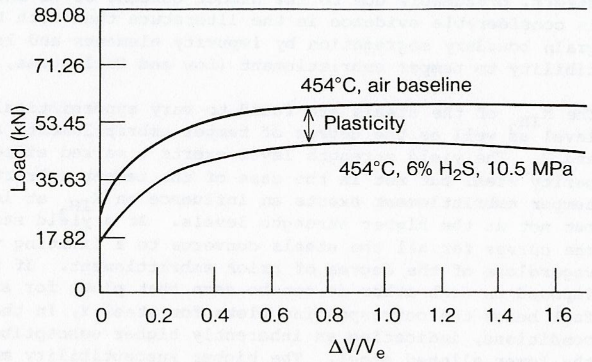

Fig. 5. rising load test record for A542 steel at 454°C

samples at room temperature in air were inconsistent. A review of the data presented in Table 4 shows that the fracture modes at room temperature following prior high temperature exposure were brittle and intergranular in some specimens, but ductile in other specimens. The reduction of the maximum loads achievable in the room temperature test due to prior exposure also vary haphazardly with respect to the baseline. These inconsistencies suggest that the only type of damage to the room temperature properties that may be occuring due to prior exposure and testing at higher temperatures may be the embrittlement due to retained hydrogen. The extent of hydrogen retention would be expected to vary from specimen to specimen depending on the cooling rate, and duration of holding prior to testing at room temperature and would lead to inconsistent results.

Table 4. Results of Rising Load Tests in 6% H_2S-H_2 For 2.25Cr-1Mo Steels

								Post Test Observations			
Steel	T, °C	P, MPa	Specimen No.	K_{IH_2}, MPa $\sqrt{m}$ or plasticity	Pmax Test, KN	Pmax Baseline, KN	Pmax Ratio	Pmax[1] KN	Fracture Mode[2]	Δa_p[3] mm	δTotal[4] mm
A387	25	5.5	13	--	--						
		10.5	8	108	39.20	49.22	.79			3.05	2.87
		24.1	19	50	32.07	49.88	.65			2.03	--
A542	25	5.5	8	105	56.56	73.04	.77			7.36	4.14
		10.5	10	101	54.47	73.04	.75			7.87	5.43
		24.1	16	69	53.45	73.04	.73			6.35	3.15
A387	315	5.5	14	Pl[5]	43.2	45.83	.95	11.14	B	0	3.91
		24.1	23	Pl	41.87	45.83	.92	10.69	B	.38	3.87
A542	315	5.5	9	No effect	64.14	67.7	.95	66.8	D	1.14	2.69
		24.1	5	Pl	55.23	67.7	.82	59.68	D	1.52	3.81
		10.5	20	Pl	46.32	59.7	.78	--	D	1.14	3.81
A387	455	5.5	15	108	31.18	41.18	.76	39.2	B	1.4	3.45
		10.5	18	Pl	30.73	41.18	.75	42.76	B	1.4	3.81
		24.1	21	Pl	33.63	45.97	.73	44.54	D	.25	3.81
A542	455	10.5	20	Pl	46.32	59.68	.78	--	D	1.14	3.81

(1) Maximum load in breaking open. (2) Brittle or ductile mode. (3) physical crack growth in the rising load test. (4) total displacement in the rising load test. (5) Pl denotes plasticity.

The mechanism of the reduction in the load bearing capability of the precracked specimens without being accompanied by subcritical crack growth remains a mystery. For convenience it has been termed hydrogen-induced plasticity in this publication. It is not known if the phenomenon is unique to the rising load test procedure and the environment employed in this study, or if it has any relevance to actual pressure vessel operating conditions. This aspect is being investigated in continuing studies.

SUMMARY

The susceptibility of 4340 type steels to subcritical crack growth in hydrogenous environments is determined by interactive effects between alloy content, yield strength and the degree of prior temper embrittlement. A unique relationship exists between the percentage of intergranular fracture and the K_{IH_2} of the steel, regardless of the strength level-alloy content-temper embrittlement combination producing a given K_{IH_2}. For the case of 2.25Cr-1Mo steel exposure to hydrogenous enviroments results in severe subcritical crack growth at room temperature with an attendant reduction of K_{IH_2}. At elevated temperatures supercritical crack growth is not found to be a major problem; nevertheless, a reduction in the load bearing capability of the specimen occurs presumably due to hydrogen enhanced plasticity.

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