The Effect of Impurities and Strength Level on Hydrogen Induced Cracking in a Low Alloy Turbine Steel

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The effect of impurities on the threshold stress intensity for cracking in H_2S (K_{ISCC}) has been investigated at various yield strength levels for a low alloy steel. Results show that the effect of impurities on K_{ISCC} is a function of the yield strength level. At low yield strength levels the K_{ISCC} of the steel is lowered markedly due to additions of impurities. However, at higher yield strength levels the K_{ISCC} data for pure and impure steels converge to a single value. In addition, the effect of yield strength level on K_{ISCC} is a function of the degree of temper embrittlement caused by impurity segregation. For small degrees of temper embrittlement, increasing the yield strength decreases the K_{ISCC} appreciably, while for large degrees of temper embrittlement, K_{ISCC} is relatively insensitive to the yield strength. At K_{ISCC} values below about 50 MPa $\sqrt{m}$, the percentage of intergranular fracture in H_2S is found to be uniquely related to K_{ISCC} regardless of the yield strength-impurity combination by which a given K_{ISCC} is obtained. Results of the study indicate that the K_{ISCC} of steels is affected by impurities, yield strength and H_2S both directly and indirectly via interactive mechanisms.

MANY similarities have been reported in the literature between the phenomena of hydrogen induced cracking and impurity induced temper embrittlement of steels. Temper embrittlement can occur in low alloy steels that are exposed to the temperature range 350 to 540°C and manifests itself as an increase in the ductile-to-brittle transition temperature.[1] In temper embrittlement as well as hydrogen induced cracking of steels, fracture generally occurs along the prior austenite grain boundaries. The susceptibility of steels to both types of embrittlement phenomena generally increases with increasing yield strength. Most importantly, temper embrittlement is caused by grain boundary segregation of certain impurity elements—Sb, P, Sn, S, Se, Ge and Te,[2,3] the same elements that are also known to poison the recombination reactions of atomic hydrogen.[4,5] In view of the many similarities, several recent studies have attempted to examine the possibility of a relationship between the two fracture mechanisms. These studies have shown that prior temper embrittlement can indeed augment fracture tendencies in the presence of hydrogen.[6-8] It is also interesting to note that prior temper embrittlement appears to augment intergranular active path anodic dissolution in boiling caustic solutions.[9-12]

In the present study the effect of deliberate additions of P, Sb, and Sn on the susceptibility of a low alloy steel (similar to 4340) to cracking in a H_2S environment has been investigated as a function of the yield strength of the steel. At each strength level, the threshold stress intensity for cracking, K_{ISCC}, has been determined in the 'pure', 'impure' as well as 'impure and step cooled' conditions.

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EXPERIMENTAL PROCEDURE

Two 23 kg heats of the low alloy steel (similar to 4340) were produced in the 'pure' and 'impure' conditions by vacuum induction melting and were forged to 150 × 6.7 × 2.8 cm 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. The actual analyzed concentrations in parts per million of impurity elements were as follows:

	N	O	S	P	Sb	Sn
Pure	11	31	20	15	2	7
Impure	12	21	30	310	320	230

Specimen blanks were austenitized at 840°C for 1 1/2 h, oil quenched and tempered to various yield strength levels. Details of the tempering treatments and resulting tensile properties are listed in Table I. Subsequent to tempering, one-half of the blanks from the impure heat were subjected to a step-cool temper embrittlement treatment consisting of 50 h at 450°C and 500 h at 400°C, with furnace cooling after each step.

The degree of temper brittlement following heat treatment and step cooling was determined by means of charpy tests in terms of the shift in 50 pct ductile-to-brittle transition temperature (ΔFATT).

Susceptibility to hydrogen induced cracking was characterized in terms of the threshold stress intensity for crack propagation, K_{ISCC}, in a 50 psig H_2S environment. Test specimens were compact type fracture mechanics specimens of the dimensions 7.25 × 6.08 × 2.54 cm. The test technique is essentially identical to the procedure used for K_{IC} fracture toughness testing (ASTM E-399-72) except that a slower rate of loading is normally involved and the specimen is exposed to the environment while being loaded. The fatigue-precracked specimens were subjected to a monotonically increasing stress intensity at the rate of 0.01

Table I. Tempering Treatments and Resulting Tensile Properties of Low Alloy Steel

Condition	Tempering Treatment	Yield Strength, MPa	Ultimate Tensile Strength, MPa	Elongation, Pct	Reduction of Area, Pct
A	565°C-200 h	862	965	19	65
B	565°C-100 h	986	1089	18	63
C	538°C-180 h	1089	1186	17	58
D	538°C-23 h	1172	1303	16	56
E	538°C-33 h	1200	1386	16	57

MPa $\sqrt{m}$/s. The load corresponding to the start of subcritical crack extension was determined from the point of nonlinear deviation on the load-displacement record. The stress intensity level associated with the onset of crack growth was determined from the K_I-calibration given by Wessel for the specimen type used herein.[13] Specimens were tested in duplicate at each strength level. The rising load K_{ISCC} testing procedure used in this study has been discussed in detail elsewhere.[14,15]

Scanning electron microscopy (SEM) was performed selectively on the fracture specimens to determine the amount of intergranular fracture at the point of initial crack growth. A scanning Auger microprobe technique was used to determine the nature and quantity of grain boundary segregates in various step-cooled samples. The procedures used for K_{ISCC} determination, SEM and SAM are identical to those described in a previous study of 4340 steels[16] and therefore are not repeated in this paper.

RESULTS

Results of FATT determinations on the various steels are listed in Table II. Values of ΔFATT as large as 183°C are observed in the as-heat treated condition indicating appreciable temper embrittlement of the steels merely due to heat treatment in the range 538 to 565°C. Additional step cooling results in a further increase in ΔFATT. The total embrittlement appears to increase slightly with yield strength at first and then decrease with further increase in yield strength.*

*It is not implied that grain boundary segregation is a function of yield strength. Rather, the microstructure and ferrite chemistry associated with different yield strengths are believed to influence segregation.

Figure 1 depicts the variation of K_{ISCC} with yield strength for the 'pure' steel and the 'impure' steel with different degrees of prior embrittlement. The impure steel has appreciably lower values of K_{ISCC} compared to the pure steel, especially at the lowest yield strength. While the decrease in K_{ISCC} due to temper embrittlement of the as-heat treated impure steels is marked, further decrease in K_{ISCC} due to step cooling is only marginal. With increasing yield strength, all three curves tend to converge, so that at yield strength above 1200 MPa, the effect of prior temper embrittlement ceases to be significant.

A comparative view of the fracture modes in the 'pure' and 'impure' steels of 862 MPa yield strength is shown in Fig. 2. In the pure steel the fracture mode is predominantly transgranular, while the impure steels in the as-heat treated, as well as in the step cooled condition, contain large amounts of intergranular fracture. The amount of intergranular fracture increased with increasing yield strength, although at any given yield strength below about 1200 MPa, the impure steel in the step-cooled condition contained the largest amount of intergranular fracture. At K_{ISCC} values below about 50 MPa $\sqrt{m}$, a unique relation was observed to exist between the percentage of intergranular fracture and the K_{ISCC} of the sample, as shown in Fig. 3. The amount of intergranular fracture decreases rapidly from 84 to 0 pct as the K_{ISCC} increased from 19 MPa $\sqrt{m}$ to 57 MPa $\sqrt{m}$.

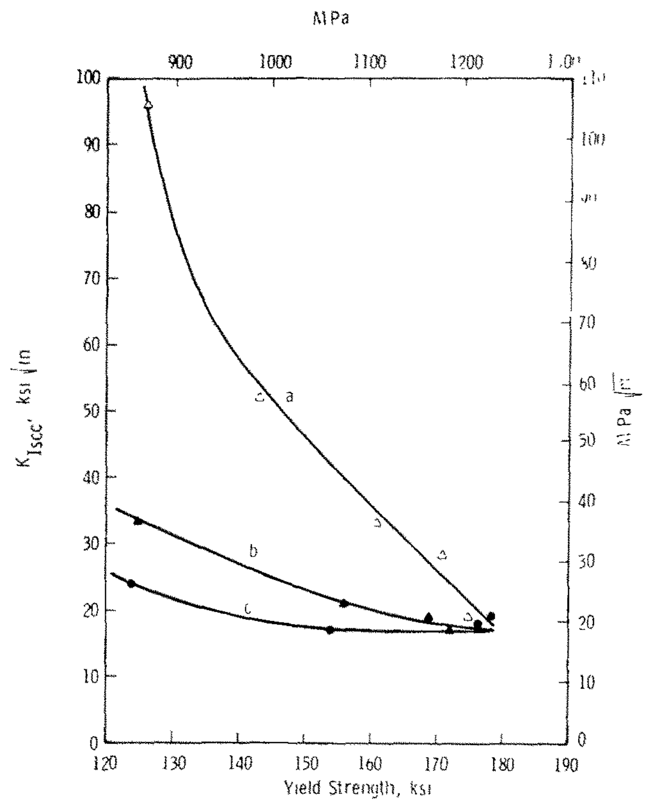


Fig. 1—Decrease of K_{ISCC} with yield strength and prior temper embrittlement. (*a*) Pure steel, (*b*) impure steel as heat treated, (*c*) impure steel, step-cool embrittled.

Results of scanning Auger microprobe (SAM) analysis of the temper embrittled samples are shown in Table III. Analysis at three different regions of intergranular fracture on each sample showed that the results were reproducible to within 10 pct of the reported values. The only elements present in detectably large amounts were P and Ni. The grain boundary segregation of P was relatively insensitive to the variations in yield strength of the steel, whereas the segregation of Ni decreased somewhat with increasing yield strength. Since the relative sensitivities of P

Table II. Fracture Appearance Transition Temperatures of Low Alloy Steel

Condition	FATT of Pure Steel, °C	FATT of Impure Steel, °C	ΔFATT Due to Impurities After Heat Treatment	ΔFATT of Impure Steel in the Embrittled Condition, °C	Total ΔFATT in the Impure Steel After Embrittlement, °C
A	−51 ± 2	112 ± 2	163 ± 4	288 ± 13	339 ± 15
B	−18 ± 2	165 ± 5	183 ± 7	343 ± 2	361 ± 4
C	10 ± 2	143 ± 6	133 ± 8	329 ± 2	319 ± 4
D	10 ± 2	96 ± 2	86 ± 4	307 ± 8	297 ± 10

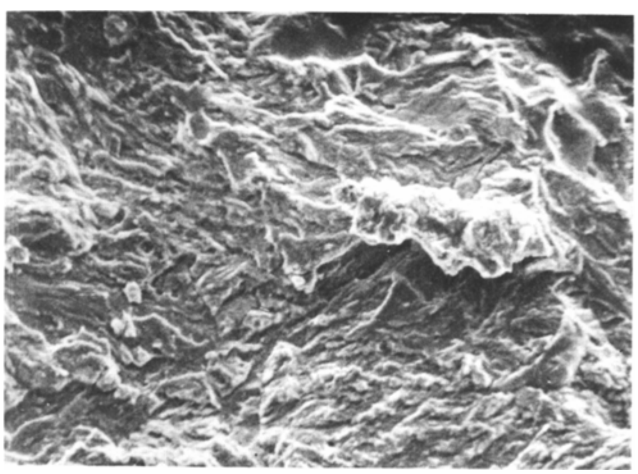
Table III. Peak Height Ratios and Estimated Concentrations of P and Ni Based on SAM Analysis of Step-Cooled Samples

Condition	Location	I_P/I_{Fe}, Pct	Approximate Concentration, Wt Pct	Enrichment Factor	K_{Ni}/K_{Fe}, Pct	Approximate Concentration, Wt Pct	Enrichment Factor
A	Grain boundary	13	3.25	105	17	17	4.25
C	Grain boundary	14	3.5	113	13	13	3.25
D	Grain boundary	14	3.5	113	9	9	2.25
E	Grain boundary	11	2.75	89	10	10	2.50
All samples	Bulk	Not detectable	–	–	4	4	1

and Ni are not precisely known, their exact amount can not be determined. Utilizing the relative sensitivity factors reported in the Handbook of AES[17] approximate concentrations of P and Ni have been estimated and are included in Table III.

DISCUSSION

The influence of prior temper embrittlement (as measured by ΔFATT) on the K_{ISCC} of low alloy steels in hydrogen bearing environments, is pronounced only at low yield strength levels. For a 862 MPa yield strength steel, the K_{ISCC} is reduced appreciably by prior temper embrittlement, but levels off beyond a critical degree of embrittlement, as may be seen from Fig. 4. Alternatively, at high yield strength levels, data for 'pure' and 'impure' steels converge, indicating that the K_{ISCC} is relatively insensitive to ΔFATT as shown by curve (*d*) of Fig. 4. The convergence of K_{ISCC} 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_{ISCC} markedly. In other words, a large contribution may occur from an interactive mechanism between the effects due to yield



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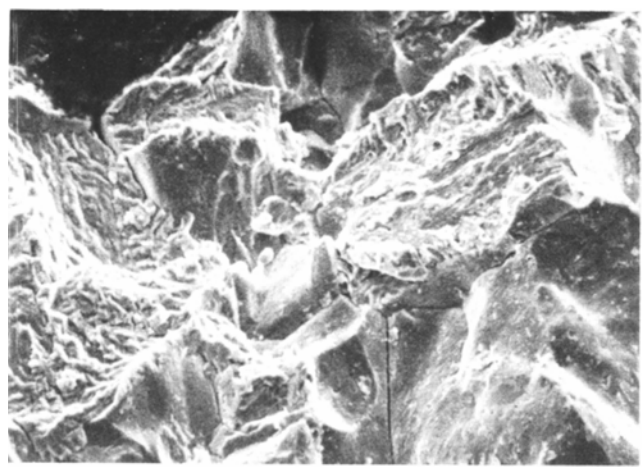

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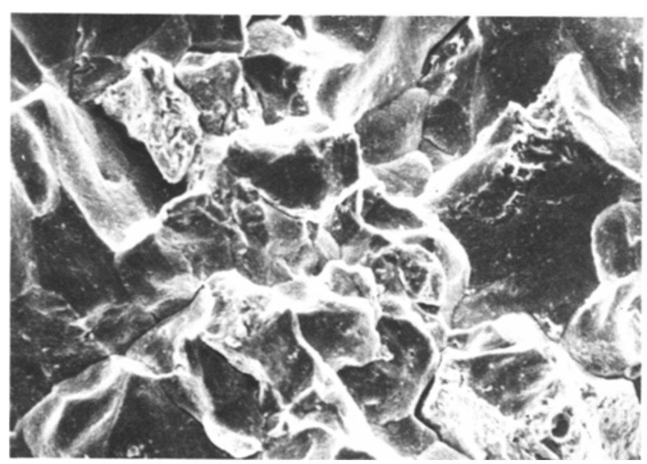

(*c*)

Fig. 2—Effect of prior temper embrittlement on the degree of intergranular fracture in H_2S for condition *A*, yield strength 862 MPa; magnification 480 times. (*a*) Pure steel, ΔFATT = 0°C, K_{ISCC} = 105 MPa $\sqrt{m}$, (*b*) impure steel as heat treated, ΔFATT = 163°C, K_{ISCC} = 36 $\sqrt{m}$, (*c*) impure steel, step-cool embrittled, ΔFATT = 339°C, K_{ISCC} = 26 MPa $\sqrt{m}$.

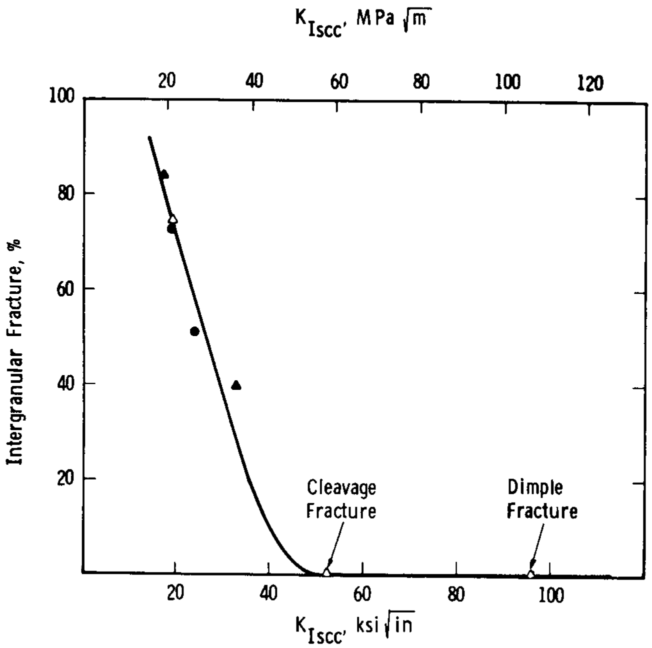

Fig. 3—Variation of the pct of intergranular fracture with K_{ISCC}. The symbols Δ, ▲, and ● denote the pure steel, impure steel as heat treated and the impure steel in the step-cooled conditions, respectively.

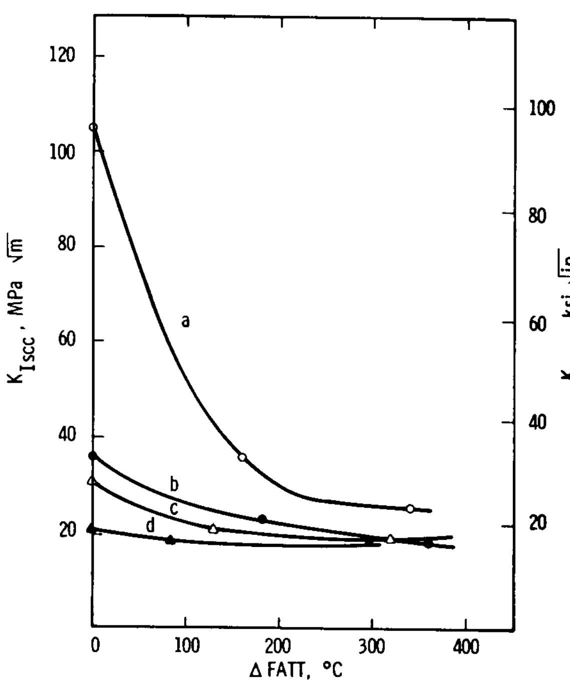

Fig. 4—The effect of prior temper embrittlement on the K_{ISCC} of steels at constant yield strength levels. (*a*) 862 MPa yield, (*b*) 1089 MPa yield, (*c*) 1172 MPa yield, (*d*) 1200 MPa yield.

strength and impurities, thereby facilitating intergranular fracture in the high strength steels. This implies that the K_{ISCC} at high strength levels (curve (*d*), Fig. 4) may vary with ΔFATT in the same fashion as the low strength steels (curve (*a*), Fig. 4), but that we may only be observing the plateau region in our experiments.

It can also be argued that the convergence of K_{ISCC} 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 environment. In other words, the high yield strength level would accentuate the effect due to H_2S in a synergistic fashion, thereby masking the effect of impurities.

Evidence is not lacking 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.[18] 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.[19] Interactive affects 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.[4,5]

Although results of the present study clearly show that interactive mechanisms between yield strength, impurities and H_2S are indeed operative in determining the K_{ISCC} and the overall fracture mechanism, the individual contributions due to the various interactions cannot be resolved. It can nevertheless be concluded that improving the purity does not appear to be a viable means of improving the hydrogen cracking resistance of commercial grade low alloy high strength steels. This conclusion is also confirmed by our earlier study using 4340 steel.[16]

Results of this study also show that the mode of fracture is a function of the K_{ISCC} of the steel and not the yield strength. Qualitatively, as K_{ISCC} decreases, the fracture mode follows the sequence: dimple → cleavage → intergranular. At K_{ISCC} below about 50 MPa $\sqrt{m}$ the degree of intergranular fracture increases linearly with decreasing K_{ISCC} regardless of the yield strength-impurity combination that produces a given value of K_{ISCC}.

CONCLUSIONS

1) Prior temper embrittlement causes a reduction in the K_{ISCC} in H_2S of low alloy steels. The effect is appreciable for small degrees of embrittlement but tends to level off with further embrittlement.

2) The effect of temper embrittlement on K_{ISCC} is pronounced at low and intermediate yield strength levels. At yield strengths in excess of 1200 MPa, K_{ISCC} for all the steels converge to the same value regardless of purity or degree of prior temper embrittlement.

3) The amount of intergranular fracture is uniquely related to the K_{ISCC}, regardless of the strength level-impurity combination leading to a given K_{ISCC}.

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