IMPURITY EFFECTS ON SUSTAINED LOAD CRACKING OF 2 1/4Cr-1Mo STEEL AT HIGH TEMPERATURE

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Crack initiation and propagation studies have been conducted on commercial purity, high purity, and phosphorus doped versions of 2 1/4Cr-1Mo steel in various as-quenched conditions in the temperature range 773-923K in vacuo. The austenitising treatments were varied to control the amount of sulphur in solid solution available for segregation. Auger surface analyses indicated that the stress field of a notch or crack assists segregation of elemental sulphur to grain boundary regions. The calculated "apparent" activation energy for crack growth is compared to available data on the diffusing species responsible for embrittlement. Tests conducted in air exhibited increased crack growth rates.

INTRODUCTION

The fracture properties of quenched-and-tempered alloy steels are affected strongly by the segregation of trace impurity elements (e.g. P,Sn,Sb,S) to microstructural sites, such as the prior austenite grain boundaries or carbide/matrix interfaces. Work by Yu and McMahon (1) was concerned with situations in which the segregation had occurred prior to subsequent fracture at low temperatures, so that the segregant levels had been "frozen-in" before fracture. Recent work by Hippsley et al. (2-4) and McMahon et al. (5) has shown that as-quenched microstructures of low alloy steels may fail by "low ductility intergranular fracture" (LDIGF) when subjected to stress at elevated temperatures. The practical implications of such testing relates to stress relief cracking in the coarse grained heat affected zone (HAZ) of thick section weldments during post-weld heat treatment, where cracking occurs under the influence of residual stresses and the stress relieving temperature.

The present work investigates effects of segregation on cracking over the temperature range 773-923K in 2 1/4Cr-1Mo steels tested under sustained load conditions. The alloys and heat treatments employed in the present work are summarized in Tables 1 and 2.

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TABLE 1 Bulk Analyses of Steels (Wt.%)

	C	Mn	Si	S	P	Cr	Mo	Sb	Sn
C.P.	0.15	0.43	0.35	0.014	0.010	2.30	1.10	0.003	0.020
P.D.	0.14	0.66	0.01	0.006	0.031	2.16	1.12	0.001	0.001
H.P.	0.14	0.63	0.03	0.005	0.001	2.15	1.10	0.001	0.003

TABLE 2 Heat Treatments

Condition 1	1573/0Q	Condition 3	1573/1223/0Q
Condition 2	1573/573/0Q	Condition 4	1223/0Q
		Condition 5	1223/923/0Q

EXPERIMENTAL

Crack initiation studies were conducted on single- or double-notched bend bars of the design used previously (6). All bend bars were notched to a depth of a = w/4 (where w=width) prior to heat treatment and were notch ground, using small cuts, to the final dimensions. Additional blunt-notched bars containing ρ = 1.0mm and flank angle $\theta = 90^{o}$ were machined. Tensile properties obtained in air at 500^{o}C at initial strain rates of 5 x 10^{-4}/sec. are described by Lewandowski et al. (7,8).

The bend bars were tested in four-point bending under sustained load using a Mand servohydraulic test machine fitted with a high temperature vacuum chamber operating at a total pressure of 0.3 nbar. Test temperatures were achieved using quartz lamps as a heat source. Loads were chosen such that the maximum longitudinal stress ahead of the notch (i.e. σ_{max}), which can be calculated using the elastic/plastic stress analyses of Griffiths and Owen (9) and Wall and Foreman (10) was approximately constant for the various heat treatment/alloy combinations. The specimens were held under constant load at 773K until the plot of crosshead displacement vs. time indicated that cracking had initiated. Additional details are supplied by Lewandowski et al. (7).

Bend specimens which fractured under load at 773K were examined in a Cambridge Instruments Camscan 4 Scanning Electron Microscope (SEM). Bend specimens unloaded prior to catastrophic fracture, as well as specimens unloaded after short times at 773K were sectioned to attempt to locate initiation sites ahead of the notch. The double-notched specimens were particularly useful in this respect: at a stage when one of the notches first exhibited macrocracking which extended to the notch root, the "second" notch root surface was free of cracks. Sectioning this "second" notch should then reveal any microcracks present ahead of the notch root. Longitudinal sections containing both notches were made at the specimen midplane, as well as at one of the quarter-thickness locations, providing three sections for

examination. The notch root regions were metallographically prepared and etched in 2% nital. Auger specimens were machined from the highly stressed notch root region as well as in the specimen bulk (7).

Crack growth tests were carried out using SEN bend specimens of thickness B = 10 mm and depth w = 20 mm, containing a central "V" notch of depth a = w/4 with root radius ρ = 0.1 mm and flank angle 45^{o}. The bend specimens were tested in four-point bending in the high temperature vacuum chamber described earlier. Additional tests were conducted in air. Crack growth in these tests was monitored by the D.C. potential drop technique. The present tests were conducted under load control, such that crack growth resulted in an increasing stress intensity, K. Auger specimens were also machined from the tip of propagating cracks in order to examine the solute chemistry near the crack tip. Additional details regarding the crack growth tests are provided by Lewandowski et al. (11).

RESULTS

Crack Initiation

The different heat treatments and purity levels of steel produced markedly different results in the crack initiation tests conducted at 773K. Only the C.P. steel, conditions 1,2 or 3 cracked within 24 hours. No cracking was observed in any heat treatments of the H.P. or P.D. steels that were loaded to equivalent levels of stress. Cracking in the C.P. specimens also varied according to heat treatment. Conditions 1 and 2 cracked within 2 hours, while condition 3 (1573/1223K) cracked after 12 hours and failed completely after 18 hours. No cracking was observed in C.P. specimens, conditions 4 or 5, for specimens held under load at 773K for up to 100 hours.

Isolated cracks ahead of the notch were observed after sectioning and polishing the "second" notch in failed C.P. double-notched specimens (Fig. 1). The cracks were intergranular with respect to the prior austenite grain boundaries. Fracturing the specimen shown in Fig. 1 at 77K revealed that the intergranular cracks did not link with the notch surface. Fig. 2 clearly shows an intergranular region ahead of the notch, with the remainder of the specimen exhibiting cleavage. High resolution Auger analyses conducted on specimens machined to contain the highly stressed notch root revealed that intergranular regions contained both S and P. However, only P was observed on intergranular regions analysed in specimens machined from the bulk (i.e. lowly stressed regions). Additional details of the surface analyses are provided elsewhere (7).

Crack Propagation

Figures 3 and 4 summarise crack growth data obtained on C.P. and P.D. alloys tested in vacuum, under conditions of rising stress

intensity, K. Crack growth rates increased with either increasing test temperature or increasing K. The C.P. alloy, condition 2 (i.e. 1573/573), exhibited faster cracking rates than did either condition 3 (i.e. 1573/1223) or condition 4 (1223/OQ). The C.P. alloy, condition 2, similarly exhibited faster crack growth rates than did the P.D. alloy, condition 2 (c.f. Figure 3,4) over the range of K's and temperatures tested. Figure 5 shows the effect of test environment at 873K on crack growth in the P.D. alloy, condition 2. Crack growth rates in air at 873K were about two times faster than those obtained under vacuum, while a P.D. specimen, condition 1 (1573/WQ) similarly exhibited faster growth rates than the P.D. condition 2 specimen.

Figure 6 shows that LDIGF was the predominant fracture mode exhibited by specimens heat-treated to either condition 1 (1573/WQ) or condition 2 (1573/573), while voiding was observed on IG facets at high K levels, as Fig. 7 shows. The C.P. specimen, condition 4 (1223/OQ) exhibited predominantly ductile fracture at all K levels, although isolated regions of LDIGF were observed.

P.D. specimens, condition 2, exhibited fractography similar to that observed for the C.P. specimens. The P.D. sample tested in air at 873K appeared to exhibit LDIGF although oxidation may have obscured fine details of the fracture surface.

LDIGF facets contained in Auger specimens machined from the highly stressed crack tip (7,11) exhibited both S and P, while IG facets well ahead of the highly stressed crack tip and in regions well removed from the crack exhibited only P, at levels similar to those found in crack tip regions. Additional surface analyses by Laser Ionisation Mass Analysis (LIMA) confirmed the presence of S (and P) on LDIGF facets near the crack tip while revealing only P in bulk (i.e. lowly stressed) regions (7,11).

DISCUSSION

The susceptibility to sustained load crack initiation at 773K increases with the amount of sulphur available to segregate. This may be deduced from the behaviour of alloys of different purities and from the effects of heat-treatment. Compare the results for the C.P. alloy (0.01P, 0.014S) in the 1573/573K treatment (condition 2) with those for the P.D. alloy (0.013P, but only 0.006S) or the H.P. alloy (0.001P, .005S), after similar heat-treatment. The alloys containing high S cracked within 2.5h, but the low S alloys did not crack when subjected to the same tensile stress below the notch (1100MPa), even when held at 773K for approximately an order-of-magnitude longer (7). From the P levels in the C.P. and P.D. alloys, it may be concluded that P is not the element principally responsible for the short-term cracking observed. The resultant fracture in the CP alloy exhibits smooth intergranular facets typical of LDIGF, and an enchanced S level was detected on these facets by AES and LIMA (7,11). It should be noted that P was also detected on these facets.

The effects of austenitising treatment on crack initiation in the C.P. alloy also indicates that S is primarily responsible for LDIGF crack initiation. At 1573K, the solid solubilities of both S and P in austenite are much greater than at 1223K (Figures for the Fe-0.43 Mn-S ternary system are 37 ppm S at 1573K; 0.8ppm S at 1223K according to Turkdogan (12). A fast quench from 1573K will therefore retain a substantial amount of S or P in supersaturated solid solution, but a slow quench (or a hold at 1223K) will enable these elements to come out of solution. Heat-treatments 1 and 2 (Table 2) therefore give rise to a high supersaturation of elemental S (or P), whereas heat-treatment 3 produces sulphide precipitates (many of which are present at or near grain boundaries) and additional P segregation. The prior austenite grain size is constant for these three heat-treatments. Heat-treatment 4, at 1223K, has a much finer austenite grain size, so that, in addition to the fact that little sulphur has been taken into solution, the amount of grain boundary area per unit volume is increased, and the "degree of coverage" of grain-boundary by a given amount of impurity element per unit volume is decreased.

Consider now the results for these various heat-treatments. Conditions 1 and 2 which were designed to produce a large amount of "free" S (or P) gave rise to cracking within 2.5h. Condition 3, on the other hand, which "ties up" S as sulphide (even at grain boundaries) did not give rise to any signs of cracking in a period less than 12h. Condition 4, for which sulphides do not dissolve and for which the prior austenite grain size is small, did not exhibit any cracking after 24h at 773k. These observations are wholly consistent with those made above for the C.P., P.D. and H.P. alloys in indicating a) that S rather than P is the principal element responsible for LDIGF, b) that the S must be "available", presumably in elemental form, from supersaturated solid solution. Again, AES and LIMA indicated that S (and P) was present on LDIGF facets for conditions 1 and 2, and LIMA indicated the presence of S on LDIGF facets for condition 3 (7).

In addition to the present tests indicating that S is primarily responsible for LDIGF, it is also clear that the stress field of a notch assists segregation of S to the prior austenite grain boundaries. The Auger results (7) which clearly showed S (and P) on LDIGF facets ahead of the highly stressed notch, but only P in bulk (i.e. lowly stressed) regions strongly suggests that the stress field of a blunt notch assists S segregation. Additional discussion regarding this point is provided elsewhere (7,11).

Crack propagation tests in these alloys similarly indicated that crack growth rates increased with the amount of S available to segregate. Compare the results for the C.P. alloy (0.01P, 0.014S) in the 1573/573 treatment (condition 2, Fig. 3) with those for the P.D. alloy (0.031P, but only 0.006S) after similar heat treatment (Fig. 4). The C.P. alloy, containing high S, exhibited faster LDIGF crack growth rates at equivalent stress

intensity and test temperature than did the P-Doped alloy. Since it has been shown that the high temperature yield strength of these two alloys is roughly equivalent for condition 2 (7,11), it cannot be argued that this difference in crack growth rates is primarily due to any effect of yield strength on the peak stresses ahead of a growing crack. The effects of austenitising treatment on crack growth in the C.P. alloy support such a conclusion, as specimens of condition 3 (1573/1223) or 4 (1223/0Q) both required a higher stress intensity to achieve the same crack growth rate as that in condition 2 (1573/573) specimens (7,11). The slower crack growth rates in the P.D. alloy, as well as in the step-austenitised or 1223K treatment is consistent with the argument that S, not P, is the element primarily responsible for LDIGF crack growth.

It should be noted that the P.D. specimen, condition 1 (1573/0Q), which should retain the majority of its S (and P) in solution, cracked more slowly than did the C.P. alloy, condition 2 (1573/573), in which the slower cooling rate and hold at 573K might be expected to reduce the amount of free sulphur. However, the level of sulphur in the P.D. alloy is markedly less than that in the C.P. alloy. Thus, the accompanying slower LDIGF crack growth rates again reflects the importance of the absoute amount of S with respect to the cracking process. These observations are wholly consistent with those made above in indicating that :

a) S, not P, is primarily responsible for LDIGF cracking;
b) S must be "available", presumably in elemental form;
c) the absolute amount of free S is the controlling factor.

The Auger analyses on the crack tip region (11) showed that both S and P were present in the highly stressed crack tip region, while only P was present in lowly stressed regions. Furthermore, the level of P on LDIGF facets was <u>not</u> significantly affected by the stress field of the crack. It appears that the stress field of a sharp crack assists S segregation to the regions ahead of a growing crack, anologous to the effects of stress on segregation of S ahead of a blunt notch.

The "apparent activation energies" for LDIGF crack growth have been calculated elsewhere (11). C.P. specimens exhibiting LDIGF exhibited "apparent activation energies" of 63 kcal/mole, over the range of temperatures shown in Fig. 3. This value is similar to the calculated activation energies for diffusion of S in Fe by Ainslie and Seybolt (13), as well as that for Fe self diffusion as calculated by Hansell et al. (14). Additional work is foscusing on possible mechanisms for enhanced high temperature crack growth in air in these alloys.

CONCLUSIONS

1. The austenitising heat-treatment affects the susceptibility of a commercial purity 2 1/4Cr-1Mo steel to sustained load cracking at 773K in vacuum.

2. LDIGF crack initiation at 773K is due to segregation of S. The source of S appears to be due to that remaining in solid solution after quenching.

3. LDIGF crack growth over the temperature range 773-923K increased with increasing amounts of S.

4. The stress field of a notch (or sharp crack) assists segregation of S to prior austenite grain boundaries prior to crack initiation.

5. The presence of air increases high temperature crack growth rates by up to an order of magnitude.

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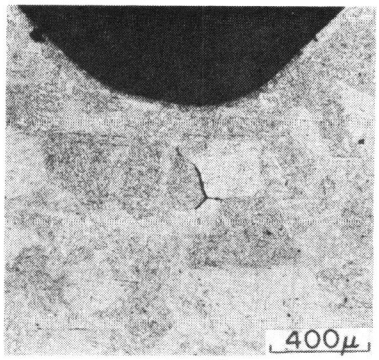

Fig. 1
Fracture Initiation Ahead of "Second" Notch in C.P. Specimen

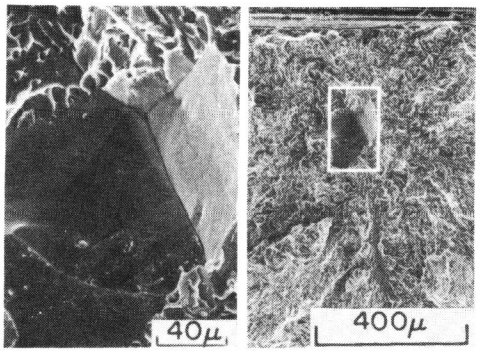

Fig. 2 Isolated LDIGF Facet Ahead of "Second" Notch

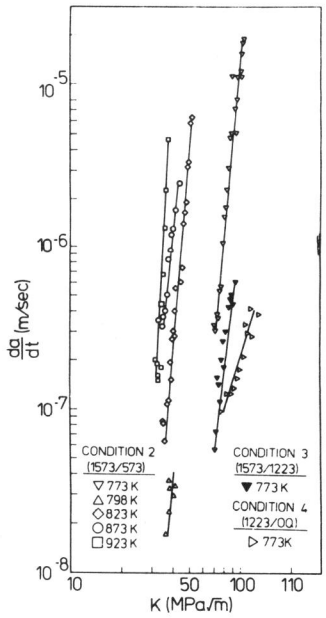

Fig. 3 Crack Growth-K Data for C.P. Specimens

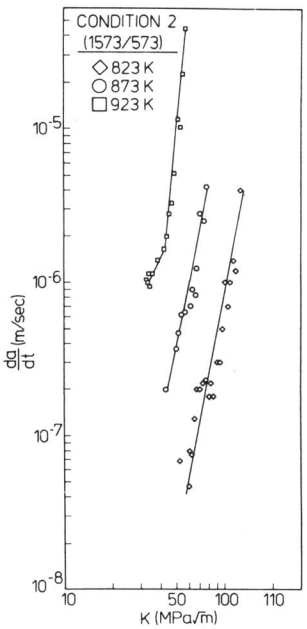

Fig. 4 Crack Growth-K Data for P.D. Specimens

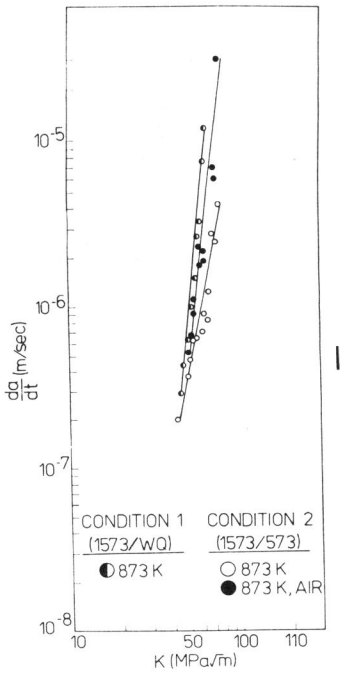

Fig. 5 Crack Growth-K Data for P.D. Specimens, 873K

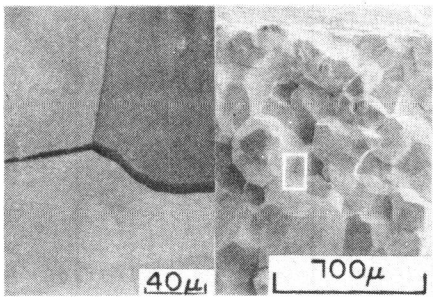

Fig. 6 LDIGF Fracture

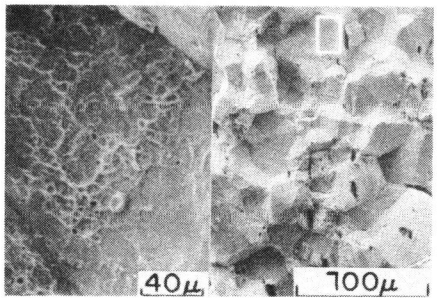

Fig. 7

Voiding on IG Facets at High K