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Annual Technical Progress Report II

THE STUDY OF DISLOCATION DYNAMICS ASSOCIATED WITH DUCTILE-BRITTLE
TRANSITION AND HYDROGEN EMBRITTLEMENT PHENOMENA OBSERVED IN BCC METALS

BY

William W. Gerberich and David G. Atteridge
Department of Chemical Engineering and Materials Science
University of Minnesota

March 1974

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Program Objectives and Summary

OBJECTIVES

The objectives of this study can be put as a series of questions concerning microscopic fracture process.

With regards to slow crack growth ductile fracture:

Does the crack grow by uniform steps about numerically equal to the crack-tip displacement?

Or is it a random microvoid by microvoid coalescence process?

With regards to the plastically-induced cleavage process:

Is the critical event the fact that a large number of grains can cleave at the crack tip?

Or is it the fact that after large numbers of grains have cleaved, the ligaments remaining start to tear rapidly and a plastic instability results?

How do dislocation dynamics affect the onset of plastically-induced cleavage?

With regards to the hydrogen-assisted cracking process:

Does the critical event involve atom-by-atom decohesion?

Or does a combination of critical hydrogen concentration and stress cause a whole grain boundary region to separate giving a discontinuous jump process?

What variables are most important and how can these be theoretically treated so as to provide guidelines for design via fracture mechanics?

SUMMARY

The completion of two laboratory set ups for acoustic emission and stress-wave emission capabilities, now allows recording of dislocation and cracking events. Mechanical facilities have been developed so that stress relaxation, dynamic loading, load drop, crack-opening displacement and other detailed flow and fracture tests may be run. Environmental set-ups, in various stages of completion, include low-temperature and gaseous environment capabilities.

Two very promising developments came from this last years work. The first is the theoretical and experimental analysis of both stress-intensity threshold, K_{TH} , and crack growth rate, da/dt , conditions for hydrogen-assisted cracking. From these, several critical test programs have evolved which should resolve the role of both the stress field and the long range diffusion of hydrogen in the embrittlement process. This has considerable ramifications on current theories which hold to either decohesion, surface energy or pressure concepts. The second development concerns the ability to associate a single stress-wave emission with a single discontinuous fracture event of finite area. Detailed calibrations have allowed us to quantify this relationship with some degree of accuracy. What does this allow us to do? Up to now, only after the fact investigations of the phenomena listed under the objectives was possible using fractographic or scanning microscopy techniques. Now, it is possible to study such growth processes in situ. The ramifications are many fold:

- i. We can follow the plastic instability mechanism for ductile fracture in detail.
- ii. Bonding energy, dislocation dynamic and microscopy fracture models for plastically-induced cleavage can be critically assessed.

- iii. We can evaluate the various theoretical models that have been proposed for hydrogen-assisted and stress-corrosion cracking phenomena.

With respect to the initial program objective for studying the ductile-brittle transition, all test specimens have been prepared and readied for testing except for pre-fatigue cracking of some fracture toughness specimens. Initial tests on acoustic emission, load-drop measurements and impact testing indicate that the rest of the testing should proceed smoothly.

This report will consist of three major parts:

- I. A description of the new test facilities and ramifications of the stress-wave technique for following microscopic fracture events.
- II. The development of stress-field approaches to the study of hydrogen-assisted cracking.
- III. The ductile-brittle fracture transition in Fe-Base alloys.

I. QUANTITATION OF THE RELATIONSHIP BETWEEN SLOW CRACK GROWTH MECHANISMS
AND ACOUSTIC STRESS WAVE EMISSION OCCURING DURING CRACK GROWTH

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I-1. Laboratory Instrumentation
George Martin

I-1-1. INTRODUCTION

Several changes have been made in the laboratory instrumentation within the past year. A closed-loop hydraulic testing machine has been acquired. A recording oscillograph has been added to the acoustic emission equipment. Both of these instruments have enhanced the versatility and capability of the laboratory in studying the mechanical properties of materials.

I-1-2. HYDRAULIC TESTING MACHINE

The hydraulic testing machine is a closed-loop feedback instrument manufactured by the MTS Systems Corporation, Minneapolis, Minnesota. The basic scheme of the machine is shown in Figure 1.

The machine can be used in either load or position feedback modes. Thus, a mean load or position and a load or position amplitude can be applied to a specimen. The position or stroke is measured using an LVDT. The load is measured using a bridge circuit. The hydraulic pump supplies the actuator which is operated by the servo controller. The hydraulic actuator applies the load or position program to the specimen.

The program commands to the system originate in the function generator. This generator has ramp, square, and sine waveforms and a frequency range of .01 to 1100 Hz. The load range of the system is $\pm 20,000$ pounds and the position range is 6 in.

Several devices are available for recording the system output. A x-y plotter or a panel meter is useful in the low frequency range. The limit

Figure 1. Basic scheme of the MTS Hydraulic Testing Machine.

detectors and an oscilloscope are utilized at high frequencies.

The MTS is an extremely versatile instrument. Some of the applications of this machine in the laboratory are:

- 1) pre-cracking and post-cracking specimens with fatigue cycling,
- 2) studying fatigue crack propagation as a function of stress amplitude,
- 3) stress relaxation and static loading tests,
- 4) experiments at high strain rates.

I-1-3. ACOUSTIC EMISSION INSTRUMENTATION

The purpose of this instrumentation is to measure the acoustic emissions generated by the rapid release of energy in a material. The basic scheme of acoustic emission instrumentation is shown in Figure 2. The acoustic emission or pressure wave is picked up by the piezoelectric transducer and converted to an electrical signal. This signal is amplified, filtered, processed, and then recorded by output devices.

Two types of instrumentation are available in the laboratory--a high frequency apparatus and a low frequency apparatus. The high frequency apparatus is the Dunegan/Endevco package system. This system is pass-banded from 100 KHz to 300 KHz. The system contains a processor which counts the number of times the acoustic emission signal exceeds a given threshold amplitude. The output from the system, either a count rate or a total count, is dependent upon the number of counts per acoustic emission event and the number of events. A diagram of this system is shown in Figure 3.

The low frequency apparatus measures discrete acoustic emission

Figure 2. Acoustic emission instrumentation.

Figure 3. Diagram of the high frequency acoustic emission apparatus

signals. Figure 4 is a diagram of this apparatus. The signal from the transducer is amplified by the charge amplifier, pass-banded between 3 KHz and 40 KHz, amplified, and recorded. The system can measure acoustic emission amplitudes from .001 g to 3000 g. The recording devices include an oscilloscope, an audio speaker, a tape recorder, and a U.V. direct writing oscillograph.

The tape recorder is an Ampex 7-channel tape deck. Using this device, a 32-to-1 reduction in the observed frequency of the acoustic emission signal can be achieved by reducing the tape speed.

The oscillograph is a SE Laboratories U.V. Type SE 2005 Recorder equipped with an A5000 Galvanometer. The principle of operation of this instrument depends on the light from a U.V. lamp being deflected by a small mirror attached to the galvanometer suspension. This movement is caused by current passing through a coil attached to the galvanometer suspension. The galvanometer is liquid-damped and has a flat frequency response to 3000 cps.

The combination of the tape recorder and the oscillograph permits the acoustic emission signals to be recorded on photographic paper. The frequency of an acoustic emission signal is reduced below 3000 cps using the speed reduction capability of the tape recorder. A record of the acoustic emission signals as a function of time is then produced by playing the tape through the recording oscillograph.

Figure 4. Diagram of the low frequency acoustic emission apparatus.

I-2. Analysis of Incremental Cracking by the Stress-Wave Emission Technique Jaydev D. Desai and William W. Gerberich

I-2-1. INTRODUCTION

Acoustic emission may be defined as a pressure or stress wave generated during dynamic processes in materials. These emissions can be considered at two separate detection levels. First, there is the continuous emission associated with plastic deformation processes⁽¹⁾. This type of emission may be detected with a differential transducer (e.g., lead-zirconate titanate) amplified to a very high gain, and filtered with a high pass of 100 kHz or higher. Secondly, there are the larger elastic waves associated with mechanical crack jumps which have been called stress-wave emission (SWE)^(2,3). This type may be detected with a commercial accelerometer, amplified to a somewhat lower gain, and filtered with a band ranging from 3-40 kHz. The present investigation utilized the latter technique. The noise problem can be virtually eliminated by the combination of accelerometer and filter. The transducer will convert an elastic wave into an electrical signal that may be viewed on an oscilloscope, tape recorded or used to drive an audio-amplifier.

The emission of an elastic stress wave from a discontinuous crack step can be correlated to a load drop. This load drop may be interpreted via a theoretical compliance analysis in terms of crack area swept out by an advancing crack. Thus it was proposed⁽¹⁻⁶⁾ that any discrete stress-wave emission associated with a fracture process could be interpreted in terms of an incremental fracture area.

Gerberich and Hartbower⁽⁴⁾ derived an approximate relationship between the incremental area swept out, ΔA , the sum of stress wave amplitudes,

Σg , the modulus of elasticity, E , and the applied stress intensity, K , giving

$$\Delta A \approx \frac{(\Sigma g)^2 E}{K^2}$$

The above formulation was semi-quantitative in nature and assumed an infinite plate analysis for a relatively narrow specimen. Gerberich et. al.⁽⁵⁾ also proposed

$$g \approx \frac{2\Delta AK^2}{C_1 EL}$$

where g was the amplitude of a single emission, L was the distance between grips, and C_1 was a constant equal to 0.02 lb-sec²/in. Again, an infinite plate analysis was assumed. Unfortunately, there was a transcription error in the derivation and g should have been proportional to both K and ΔA as was suggested in two previous publications^(4,6). Furthermore, the pertinent data had only been established at large load drops and, hence, large crack increments.

Using a slightly different technique for monitoring the acoustic emission, Dunegan and Tetelman⁽⁷⁾ and Harris, et al⁽⁸⁾ reported that slow crack growth under hydrogen embrittlement or fatigue conditions gave

$$\frac{dN}{dA} = DK^n$$

where dN/dA is the number of counts per unit area swept out by the crack and D , n are constants. The quantitative difference is that this count rate technique counts a discrete pulse many times while the stress wave emission technique of this investigation counts each SWE only once. Nevertheless, the qualitative similarity is striking with respect to stress wave emission amplitude (or counts) dependence on incremental crack area and

applied stress intensity.

Because of the many semi-empirical approaches suggested to date, the aim of the present investigation was two fold:

- (1) To derive and experimentally establish an exact relationship between stress-wave amplitude, g , load drop, ΔP , and incremental crack area, ΔA , for the specimen configuration used in the experimental investigation.
- (2) To perform an experimental correlation of relatively small discontinuous jumps to small amplitude acoustic emission. In this way a relationship appropriate to the small discontinuous steps associated with non-propagating cleavage microcracks could be evolved⁽⁵⁾.

I-2-2. THEORETICAL CONSIDERATIONS

I-2-2-1. SWE ANALYSIS

A relationship between load drop, SWE amplitude and incremental crack-ing is first derived for the compact tension specimen shown in Figure 1. The compliance, C_s , of a specimen under tension is given in terms of plate extension, δ , and load, P , by

$$C_s = \delta / P \quad (1)$$

The elastic strain energy of the plate is,

$$U = \frac{1}{2} P \delta = \frac{1}{2} P^2 C_s = \delta^2 / 2C_s \quad (2)$$

For the fixed grip condition, the change in strain energy for an incremental crack extension from a_0 to a_1 is given by

FIGURE 1. COMPACT TENSION SPECIMEN

$$-\Delta U = \delta^2 / 2C_{s(a_0)} - \delta^2 / 2C_{s(a_1)} \quad (3)$$

where $C_{s(a_0)}$ is the compliance at crack length, a_0 , and $C_{s(a_1)}$ at crack length a_1 . Combining Eqs. (1) and (3)

$$\begin{aligned} -\Delta U &= \frac{[C_{s(a_1)} - C_{s(a_0)}]}{2C_{s(a_0)} C_{s(a_1)}} P^2 C_{s(a_0)}^2 \\ &= \left(\frac{\delta}{P_1} - \frac{\delta}{P_0} \right) \frac{\delta/P_0}{\delta/P_1} \cdot \frac{P_0^2}{2} \\ &= \frac{\delta(P_0 - P_1)}{2} = \frac{\Delta P \delta}{2} \quad (4) \end{aligned}$$

Here, ΔP is simply the load drop associated with incremental crack extension in a specimen being pulled by a very stiff testing machine.

The specimen compliance can be determined from the Irwin-Kies relationship (9,10) which is

$$G = \frac{K^2}{E} = \frac{P^2}{2B} \frac{dC_s}{da} \quad (5)$$

The stress intensity for the compact - tension specimen is given by

$$K = \frac{P(a)^{\frac{1}{2}}}{BW} Y \quad (6)$$

where $Y = [29.6 - 185.5 (a/W) + 655.7 (a/W)^2 - 1017 (a/W)^3 + 639 (a/W)^4]$ Greenspan⁽¹²⁾ has shown that compliance can be written in terms of specimen length L , specimen width, W , thickness, B , crack length, a , and modulus of elasticity, E , by

$$C_s = \frac{L}{WBE} \{f(a/W)\} \quad (7)$$

The same form as Eq. (7) can be fit to the compliance results given in Figure 2 where dimensionless compliance, $\delta BE/P$, is plotted against dimensionless crack length. The compliance analysis, as given elsewhere⁽¹³⁾ was verified experimentally for the present test configuration. From Figure 2, it was found that

$$C_s \approx \frac{L}{WBE} \{0.8(a/W)^{\frac{1}{2}} Y^2\} \quad (8)$$

where Y is given by Eq. (6). Energy release as obtained from the Irwin-Kies relationship, Eq. (5), can be equated to Eq. (4) as indicated in Section I-2-2-2. For small crack increments, K can be assumed to be constant, giving

$$\frac{K^2}{E} \Delta a \approx \frac{P}{2B} \Delta PC_s \quad (9)$$

Writing P in terms of K from Eq. (6) and using Eq. (8) for C_s gives

$$\Delta P \approx \frac{2.5 KW^{\frac{1}{2}} B \Delta a}{YL} \quad (10)$$

Here, $B\Delta a$ is simply the area swept out by the advancing crack, ΔA . As will be shown in the experimental section, $\Delta P/B$ can be related to the stress wave amplitude, g , by

$$g = m\Delta P/B \quad (11)$$

where m is a proportionality constant. From Eqs. (10) and (11) it follows that

$$g \approx \frac{2.5 mKW^{\frac{1}{2}} \Delta A}{YBL} \quad (12)$$

FIGURE 2. DIMENSIONLESS COMPLIANCE AS A FUNCTION OF CRACK LENGTH

Eq. (12) shows that stress wave amplitude is proportional to both stress intensity and incremental area swept out by the advancing crack. This analysis should predict values of g reasonably well for small crack increments. For large crack increments, however, Eq. (10) would not be accurate and hence Eq. (12) would be in error. Since there might be some question about the usefulness of Eq. (10), it is appropriate to derive the exact relationship.

1-2-2-2. STRESS INTENSITY - COMPLIANCE RELATIONSHIP

It is desirable to prove the substance of Eq. (9). First, the strain energy release rate about a symmetrically loaded crack in an infinite plate may be given by

$$G = \frac{K^2}{E} = \sigma^2 \pi a / E \quad (13)$$

In the context of infinitesimal crack extensions, the increment of energy released via Eq. (13) can be equated to that of Eq. (4). Taken per unit thickness, B , this becomes

$$\frac{\Delta U}{B} = - \int_{a_0}^{a_1} \frac{\sigma^2 \pi a}{E} da = - \frac{\Delta P \delta}{2B} \quad (14)$$

Now, the integral in Eq. (14) can be approximated to be

$$\frac{\Delta U}{B} = \frac{\pi \sigma^2}{2E} [a_1^2 - a_0^2] \approx \frac{\pi \sigma^2}{2E} [2\Delta a a_0] ; \quad \Delta a \ll a \quad (15)$$

Furthermore, since $K^2 \approx \pi \sigma^2 a_0$, Eq. (15) may be given as

$$\frac{\Delta U}{B} \approx \frac{K^2}{E} (\Delta a) \quad (16)$$

Substituting this into Eq. (14) gives

$$\frac{K^2}{E} (\Delta a) \simeq - \frac{\Delta P \delta}{2B} \quad (17)$$

Since $\delta = PC_s$, Eq. (17) finally becomes

$$\frac{K^2}{E} (\Delta a) \simeq - \frac{P}{2B} \Delta PC_s \quad (18)$$

As the absolute value of ΔP is used in Eq. (9), we have dropped the minus sign.

I-2-2-3. EXACT LOAD DROP COMPLIANCE RELATIONSHIP

As the crack grows and a new compliance is reached, the load path may be that of fixed grip, constant load or some situation in between. An appropriate assessment by area would be to equate the energy change for a fixed grip situation to that of constant load minus the energy difference illustrated schematically in Figure 3. This gives

$$\frac{1}{2} \delta_o (P_o - P_1) = \frac{1}{2} P_o (\delta_1 - \delta_o) - \frac{1}{2} \Delta P (\delta_1 - \delta_o) \quad (19)$$

Substituting load-compliance for δ_o and δ_1 in equation (19) leads to

$$\Delta P = P_o \left[\frac{C_s(a_1) - C_s(a_o)}{C_s(a_1)} \right] = P_o \left[1 - \frac{C_s(a_o)}{C_s(a_1)} \right] \quad (20)$$

Energy considerations in fixed load and fixed grip conditions have been further discussed elsewhere^(9,14,15). For the purpose of the present investigation, it will be sufficient to compare the approximate Eq. (10) with the exact Eq. (20).

Figure 3

Effect of small crack extension on energy release following fixed grip or constant load paths

I-2-3. EXPERIMENTAL TECHNIQUE

Crack-line loaded (compact-tension) specimens of 7075-T6 aluminum were used for the experiment. The properties and heat treatment for this material are given in ref. (16). The specimens were fatigue pre-cracked at an applied stress intensity range of $20,000 \text{ psi-in}^{\frac{1}{2}}$. About 10,000 cycles of tension fatigue produced 0.10 inches of crack growth. The specimens were then tested in a 10,000 pound capacity Instron testing machine at increasing load. To keep the load range on maximum sensitivity, the Instron was continuously zero suppressed. In this way, accurate measurements of load drops could be made even at high applied loads.

The amplitude of a single elastic stress wave (SWE) associated with the load drop was measured in terms of acceleration, g , using the set-up shown in Figure 4. Two accelerometers with flat frequency response in the range of 2-6000 cps with resonance at 30,000 cps and charge sensitivities of 57 pc/g and 62 pc/g, were attached to the specimen grips. The electrical signal passed through the charge amplifier and then through the band-pass filter. The signal was recorded on tape as well as on the storage oscilloscope, allowing the amplitude of the stress waves to be measured.

Crack opening displacements between knife-edges of compact tension specimen were measured using a crack opening (COD) gage. The attachment of the gage to the specimen is schematically shown in Figure 5. The non-dimensionalized compliance calibration curve shown in Figure 2 was established with a number of load-displacement records from specimens with different crack lengths. The curve can be used for a given specimen configuration with any material thickness or width dimensions. Knowing displacement from

FIGURE 4. SET UP FOR RECORDING LARGE ELASTIC STRESS WAVES

Figure 5.

Schematic of crack opening displacement (COD) gage and its attachment

a displacement gage, the crack can be determined from Figure 2. This method is fairly accurate for measuring gross crack extensions but its accuracy is limited for small discontinuous steps.

I-2-4. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 6 shows typical stress wave emissions, (a) for a large crack extension and (b) a small crack extension, respectively. A typical time-displacement record is shown in Figure 7. Each discontinuous jump corresponds to a load drop, ΔP , and a stress wave amplitude, g .

Figure 8 graphically depicts the relationship between stress wave amplitude, g , and load drop/thickness, $\Delta P/B$, for four different thicknesses of specimens. It is clear that there is a linear relationship between g and $\Delta P/B$, with a constant of proportionality, m , having the value of $0.05 \text{ in}^2/\text{lb sec}^2$. The amplitude of stress wave, g , should be proportional to stress intensity change, ΔK , and since $\Delta K \propto \Delta P/B$ it follows that $g \propto \Delta P/B$.

Table I shows some experimental observations. Crack lengths before and after pop-in were calculated from respective load-displacement values using the calibration curve shown in Figure 2 or given by Eq. (8). Table 2 shows incremental crack extensions, Δa , incremental area, ΔA , and calculated and observed values of ΔP and g .

Also demonstrated here is how well the approximate and exact analyses predict load drop from compliance considerations. The approximate calculation for ΔP is largely dependent on the C_s^2 difference between the start and end of the crack increment. It is only dependent upon the C_s difference for the exact analysis. Thus, if C_s is in error, then one would expect a discrepancy between these two calculations. It was noted

TABLE 1: EXPERIMENTAL OBSERVATIONS

Thickness B (in)	P _i (lbs)	P _f (lbs)	V _i (mv)	V _f (mv)	$\frac{V_{iBE}}{P_i}$	$\frac{V_{fBE}}{P_f}$	a _i (in)	a _f (in)	Y _{av}	K _{av} (psi-in ^{1/2})
0.067	429	419	11.2	11.205	48.48	49.66	1.2042	1.217	12.96	36304
	483	470	12.97	13.00	49.87	51.20	1.2192	1.2331	13.05	41244
	506	486	14.06	14.10	51.60	53.86	1.2371	1.250	13.24	44121
	548	470	15.93	16.05	53.99	63.42	1.2560	1.3367	13.52	48129
	492	456	16.8	16.9	63.42	68.83	1.3367	1.3725	14.44	48349
0.13	1110	1101	9.8	9.84	31.82	32.21	0.9405	0.9495	11.17	36997
	1437	1424	14.9	14.92	37.37	37.76	1.0504	1.0572	11.77	53279
	1464	1451.6	15.55	15.59	38.28	38.70	1.0658	1.0728	11.87	55170
	1523	1489	16.70	16.77	39.52	40.59	1.0858	1.1022	12.01	58463
0.19	1228	1227	7.4	7.41	31.74	31.81	0.9388	0.9404	11.16	27960
	1408	1394	8.55	8.59	31.98	32.46	0.9444	0.955	11.19	32220
	1465	1455	9.03	9.08	32.47	32.87	0.9552	0.964	11.24	33900
	1593	1592	10.00	--	33.06	--	0.9682	--	11.30	--
0.25	1471.8	1469	6.1	6.105	28.49	28.57	0.8536	0.8560	10.84	23746
	1607	1586	6.8	6.83	29.09	29.60	0.8711	0.8852	10.88	26339
	1684	1682.8	7.26	--	29.64	--	0.8866	--	--	--
	1715	1691	7.45	7.51	29.86	30.53	0.8924	0.9094	10.96	28663

Figure 6. Typical Stress wave emissions

(b)

(a)

Figure 7.

Schematic of a typical time-displacement record

Figure 8.

Relationship between stress wave amplitude and load drop/thickness

that the thin specimens did lose some planarity in that there was a tendency towards lateral buckling at high stress intensities. This caused the displacement gage points to translate perpendicular to the loading plane in addition to the usual vertical displacement. The result was that some error existed, particularly for the smallest thicknesses. One may note in the calculation column of Table 2 that relatively good agreement was obtained for the larger thicknesses where lateral buckling was not evident.

Even though such discrepancies exist, the approach used is sufficiently accurate to possess a strong predictive quality. This is shown in Figures 9, 10, and 11 which graphically demonstrate the relationships of Eqs. (10), (12), and (20). It can be seen that there is a very good agreement between experimental and theoretical results.

From Eq. (20) and Figure 9, it is clear that the larger the incremental crack extension, Δa , the larger will be the load drop. This is as expected considering that for larger crack extensions, compliance must change by a larger amount. Eqs. (10) and (12) are shown schematically in Figure 12. Part (c) and (d) follow from (a) and (b) and the linear relationship between g and $\Delta P/B$.

It is next appropriate to ascertain how this analysis might be applied to microcracking phenomena. Gerberich et al.⁽⁵⁾ reported SWE observations of cleavage microcracking in 1020 steel tested to failure at 77°K. The fracture surface, as observed by scanning electron microscopy, was seen to consist of a series of cleavage microcracks, some of which had occurred prior to the onset of fracture instability. It was observed that the SWE

TABLE 2: FRACTURE AND ACOUSTIC EMISSION ANALYSIS

Thickness B (in)	Δa $\times 10^{-3}$ (in)	ΔA $\times 10^{-3}$ (in ²)	ΔP (lbs)		g (in/sec ²)	
			observed	calculated	observed	calculated
0.067	12.80	0.8576	10	10.3	7.08	6.0
	13.90	0.9313	13	12.6	8.67	10.0
	21.90	1.467	20	21.3	14.4	10.0
	80.77	5.400	78	81.5	56.8	40.0
	35.77	2.397	36	38.7	23.7	20.0
0.13	8.94	1.162	9	13.4	11.3	4.0
	6.78	0.882	13	14.8	11.7	4.8
	7.00	1.609	12.4	15.9	12.4	6.0
	16.45	2.139	34.0	40.2	30.6	12.8
0.19	1.59	0.3016	1.0	2.7	2.2	0.6
	10.63	2.0188	14.0	20.8	17.1	4.0
	8.83	1.6788	10.0	17.8	14.9	3.0
	--	--	1.0	--	--	0.3
0.25	2.36	0.5853	2.8	4.1	3.8	1
	14.11	3.497	21.0	27.7	24.9	5.6
	--	--	1.2	--	--	2.4
	17.00	4.216	24.0	37.6	32.4	8.0

+ From Eq. (14)

++ From Eq. (10)

Figure 9.

Graphical representation of the relationship in Equation (10)

Figure 10. Graphical representation of the relationship in Equation (12)

Figure 11. Graphical representation of the relationship in Equation (14)

Figure 12. Schematic of the relationships between ΔP , Δa and g at constant $\frac{K_{av}}{Y_{av}}$

up to the point of instability were associated with non-propagating cleavage microcracks. These SWE ranged from 0.002 to 0.05 g in amplitude and were proposed to represent a crack jump associated with one incremental area traversing one grain. The appropriate values for the specimen type used and test data observed are:

$$K = 40,000 \text{ psi} - \text{in}^{\frac{1}{2}} ; f(a/W) = 11.7$$

$$a = 0.7 \text{ in} ; W = 1.875 \text{ in} , L = 1.25 \text{ in}$$

grain size ranging from 0.00067 in. to
0.0025 in. in diameter

$$\Delta A \simeq 0.35 \text{ to } 48 \times 10^{-6} \text{ in}^2$$

Using these values in Eq. (12) leads to calculated values of 0.0026 to 0.036 g which are very close to the observed values of 0.002 to 0.05 g . Because of this good correlation with the exact analysis, the present approach can be used with some confidence in assessing the character of microcracking processes.

I-2-5. CONCLUSIONS

1. A theoretical relationship has been derived between load drops and crack growth steps for the crack-line loaded (compact tension) specimen.
2. Experimental observations of SWE associated with discontinuous crack growth have verified that stress wave amplitude, g , is directly proportional to load drop per unit thickness, $\Delta P/B$.
3. The above two relationships demonstrated that SWE amplitude was proportional to both applied stress intensity, K , and area swept out by the advancing crack, ΔA . The analysis for the compact tension specimen gave

$$g \simeq \frac{2.5mKW^{\frac{1}{2}}\Delta A}{BYL}$$

where W , B , Y and L describe the specimen geometry. The proportionality constant, m , has been found to be $0.05 \text{ in}^2/\text{lb-sec}^2$.

4. This relationship was found to hold for large crack jumps on the order of 0.4 inches in length as well as small incremental crack areas on the order of 10^{-6} in^2 .

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LIST OF SYMBOLS

K	stress intensity, $\text{psi-in}^{\frac{1}{2}}$, applied
P	load, lbs
B	specimen thickness, in
W	specimen width, in
a	crack length, in
L	distance between loading points, in
E	Young's Modulus, psi
g	stress wave amplitude, in/sec^2
ΔP	load drop, pounds
Δa	incremental crack extension, in
ΔA	incremental crack area, in^2
C_s	specimen compliance, in/lb
δ	extension of the specimen, in
U	strain energy of the specimen
G	strain energy release rate, in-lb/in^2
m	proportionality constant between g and $\Delta P/B$
SWE	stress wave emission
COD or V	crack opening displacement

I-3. An Acoustic Emission Investigation of Microscopic Ductile Fracture
William W. Gerberich, David G. Atteridge, and Joseph Lessar

I-3-1. INTRODUCTION

How can the details of the microscopic slow crack growth process be delineated? Of course, one accepted way is an ex post facto investigation of the fracture surfaces via electron transmission or scanning fractographic techniques. Some additional insight is possible by sectioning perpendicular to the fracture plane and using standard metallographic techniques. But none of these give unambiguous detail about the chronology or character of the cracking events. In situ measurements are required to know the external conditions at the time of the event as well as the character (i.e. size, frequency) of the internal event. Some in situ measurements such as crack-opening displacement, electrical resistance and ultrasonic scanning techniques give relatively gross indications of the summation of many microscopic events. However, it is the acoustic emission technique that has the promise of providing analysis of each individual microscopic growth event.

In Section I-2, it was shown that a single acoustic emission event (stress-wave amplitude) can be correlated to the area traversed by an advancing crack in the corresponding instant. The procedure was to first relate load drop (ΔP) to compliance change. Then, the experimental compliance curve was fit to the polynomial used to determine stress intensities (K) in compact tension samples, given by

$$K = \frac{P(a)^{\frac{1}{2}}}{BW} Y \quad (1)$$

with

$$Y = [29.6 - 185.5(a/W) + 655.7(a/W)^2 - 1017(a/W)^3 + 639(a/W)^4]$$

Here, P is applied load and B, W , refer to specimen thickness, width and crack length. With the compliance - load drop and compliance- Y relationship, it was found that

$$\Delta P = \frac{3.5 K \Delta A W^{\frac{1}{2}}}{Y L} \quad (2)$$

where ΔA is the incremental area swept out by the crack and L is the distance between load points. The constant differs somewhat from that in section I-2 due to a slightly different specimen configuration. From the same investigation, it was found that the load drop in a single fracture step could be correlated to the amplitude of the single acoustic event accompanying that load drop. For more than 50 observations representing different thickness, it was found that

$$g = m \frac{\Delta P}{B} \quad (3)$$

where g is the SWE amplitude, m is a constant of $0.05 \text{ in}^2/\text{lb-sec}^2$ and ΔP is the load drop. Equations (2) and (3) lead to

$$\Delta A = \frac{Y B L g}{3.5 m K W^{\frac{1}{2}}} \quad (4)$$

Having this relationship, it was desirable to run an incremental slow crack growth test to see

- (1) if all of the area swept out by the advancing crack could be accounted for by the summation of stress-wave amplitudes and Eq. (4);
- (2) what additional details of the step-by-step growth process could be obtained.

I-3-2. EXPERIMENTAL PROCEDURE

An AISI 4340 steel compact-tension sample was austenitized at for 1 hour, quenched and tempered for 2 hours at 480°C . As is indicated in section III-1, this would result in the following tensile properties: ultimate strength, 187 ksi or 1,290 MN/m²; yield strength, 173 ksi or 1,190 MN/m²; and 7% elongation. The compact tension sample was then pre-fatigue cracked at a ΔK of 20,000 psi-in^{1/2} (21.8 MN/m^{3/2}) for about 70,000 cycles. The pre-fatigue cracked specimen was pulled in an Instron machine. Instrumentation included two accelerometers, having sensitivities of 60 p c/g. The signals were pass-band filtered between 3000 and 40,000 Hz and then amplified so that a 10 volt signal represented either 1 g or 0.1 g full scale. The signals were then attenuated slightly so that a full scale recording on an instrumentation tape recorder with 40,000 Hz frequency response could be maintained.

The instrumentation also included a calibrated crack-opening-displacement gage. After the specimen had been loaded so that significant SWE and crack growth indications from the displacement gage has been recorded, it was unloaded. The recorder load-displacement curve is shown in Figure 1. After the specimen was unloaded, it was fatigue cracked once again at a ΔK of 20,000 psi-in^{1/2} (21.8 MN/m^{3/2}) to outline the slow crack growth region. This region was examined in the scanning electron microscope with respect to fracture mode and planimetered with respect to total area of growth. Subsequent tape playback of both channels allowed all SWE amplitudes to be analysed with respect to time of occurrence and corresponding stress intensity factors.

Figure 1. Load versus crack-opening displacement.

1-3-3. RESULTS AND DISCUSSION

The crack extension determined from the load-displacement curve in Figure 1 corresponds to 0.02 inches (0.05 cm) of growth. However, a macrograph of the fracture surface in Figure 2 indicates that the slow growth region was closer to 0.045 inches (0.114 cm) in length. This discrepancy is discussed later. The area corresponding to the growth region in Figure 2 was found to be 0.029 in^2 (0.187 cm^2). To the point of unloading, 323 SWE were observed ranging up to 0.23 g. The SWE amplitudes are plotted according to frequency of occurrence in Figure 3. Four stress waves with amplitudes greater than 0.12 g are not indicated here but are included in the analyses. Ignoring the details of the distribution for the moment, one can sum up the amplitude of all waves, obtaining Σg equal to 7.62 g. As the crack length was nearly constant, Y did not vary greatly during the test. This allowed a simple application of Eq. (4) to the data as a whole. Using an $(a/W)_{\text{AVG.}} \simeq 0.66$ gave $Y_{\text{AVG.}}$ from Eq. (1) to be 21.6. The biggest variation during the test was the load and hence the stress intensity at which the SWE occurred. As can be seen from Eq. (4), the same crack area produced at higher stress intensity levels would produce higher stress wave amplitudes. For proper utilization of Eq. (4), each area increment should be individually calculated from each stress wave amplitude. As a reasonable approximation, a single stress intensity was used by weighting the stress intensity to the number of events occurring during ten equal time intervals of growth. In this way a typical stress intensity factor was determined to be $68,000 \text{ psi-in}^{\frac{1}{2}}$ ($74 \text{ MN/m}^{\frac{3}{2}}$). This value in conjunction with the specimen dimensions in Figure 1 and an L of

Figure 2. Macrograph of fracture surface.

Figure 3. Distribution of the number of stress waves emitted versus stress wave amplitude.

one inch, gave a calculated value of ΔA to be 0.0088 in^2 (0.057 cm^2).

As is derived in Section II-2-2, a slightly more accurate method may be used to determine Eqs. (2) and (4). This does not require a curve fitting procedure to fit the compliance but uses compliance directly. This resulted in a calculated area that was within 10 percent of the above value.

Since either value determined from Σg was about one-third the area actually planimetered, one must question the accuracy or usefulness of the technique. One possibility is that the relationship between stress-wave amplitude and ΔP , which was determined from aluminum "pop-in" data is not directly applicable to steel. A second source of error is the experimental scatter in the data used to derive Eq. (3), which varied by about a factor of three*. A third possibility is that not all of the SWE associated with the crack area detected on the fracture surface were recorded. This later possibility is suggested because:

- (a) During a small hold at maximum load just before unloading and during the unloading process, a number of SWE were observed on the oscilloscope. Unfortunately, the tape has been turned off. It is not known whether these would be associated with crack growth or surfaces rubbing during closure.
- (b) The crack extension calculated from the load-displacement curve, to the point of unloading, was only 0.02 inches or about 40 percent of that observed on the fracture surface. Although the crack opening displacement technique could overestimate Δa due to plastic deformation at the crack tip, it should not underestimate Δa .
- (c) A fracture surface marking, about midway down the slow crack growth region, appeared to be a major crack arrest mark. This could be indicative of subsequent crack growth during the closure process.

If the later argument is weighted heavily, then one could say that the technique is probably recording all major and minor crack events associated with

*

This not considered a large scatter since the relationship held for about three orders of magnitude.

the slow crack growth process. Even if the other sources of error were present, the relative distribution of SWE amplitudes would give relative indications of the type of microscopic growth involved. With this in mind, the following hypotheses for slow crack growth in this steel are explored.

I-3-4. POSSIBLE GROWTH PROCESSES

If one examine the histogram of the SWE amplitudes, several interpretations could be made.

- (1) First, one could make the naive assumption that all SWE represent identical crack movements. The variation in amplitude could be partially explained by the variation in K according to Eq. (4). If the crack extended as a single front encompassing the total thickness, then a single jump would be the average Δa in Figure 2 divided by the number of stress waves ($N_{SWE} = 323$). The resulting value of 0.00014 in (3.5 μ) is small compared to the typical crack-tip displacement of 0.00044 in. (11 μ) as calculated from

$$2V_c \approx \frac{K^2}{2\sigma_{ys}E} \quad (5)$$

where the K value of 68,000 psi-in^{1/2} (74 MN/m^{3/2}) represents the typical value.

- (2) Secondly, one could make the same uniform jump process argument but now invoke circular regions of microvoid coalescence such as the process zone suggested by Krafft⁽¹⁾. This would give zones about 0.01 inches in diameter which are too large to be of significance.
- (3) Both of these "uniform" type of crack step processes must be rejected. First, they are not sufficiently close to the crack tip displacement in magnitude. Even more important, they do not explain why large variations in SWE amplitude occur over a narrow increment of K . That is, small and large jumps are intermixed throughout the growth process. Although still somewhat ideal, the proposed model is schematically shown in Figure 4. At the start of slow crack growth, a series of thumb nail cracks, represented by ΔA_i , could form. These would be associated with the SWE amplitudes corresponding to the frequency

Figure 4. Schematic of step-wise slow crack growth.

distribution I in Figure 3. As soon as all or nearly all the ΔA_I developed across the thickness, then the crack could move forward over the remaining shaded ligament represented by ΔA_{II} in Figure 4. This later movement, encompassing the entire thickness, could be associated with the larger SWE in distribution II, Figure 3.

To test this later hypothesis out, one assumption is made - that each major growth step is about numerically equal to the crack tip displacement. The area associated with ΔA_I can be calculated from Eq. (4) using K_{MEDIAN} or K_{MODE} and the typical stress intensity factor during which growth was taking place. The typical SWE amplitude for distribution I was about 0.01 g. This led to a calculated ΔA_I of $11.5 \times 10^{-6} \text{ in}^2$ ($7400 \mu^2$). If the thumb nail cracks were semi-elliptical, then the dimension, $2\Delta b$, can be determined from

$$2\Delta b = \frac{4\Delta A_I}{\pi \Delta a} \quad (6)$$

to be 0.033 inches (.084 cm). The average specimen thickness over which the crack was growing was not the entire thickness but only about 90 percent of it, i.e. 0.68 inches (1.7 cm). Using this thickness and $2\Delta b$, the number of thumb nail cracks could be determined from

$$N_{\Delta A_I} = \frac{B}{2\Delta b} = 20.5 \quad (7)$$

This allowed the area of the remaining ligament, ΔA_{II} , to be calculated from

$$\Delta A_{II} = 2V_c B - \Delta A_I (B/2\Delta b) \quad (8)$$

giving ΔA_{II} to be $64 \times 10^{-6} \text{ in}^2$ ($42,000 \mu^2$). How do these various calculations compare to the physical observation? First, a series of 20

small crack fronts across a thick specimen is not unreasonable. Similar scalloped crack fronts have been observed in low alloy steel samples⁽²⁾. Secondly, a ΔA_{II} of $64 \times 10^{-6} \text{ in}^{-2}$ would represent a typical SWE amplitude of 0.055 g as calculated from Eq. (4). Significantly, the g_{MEDIAN} or g_{MODE} for distribution II in Figure 3 is almost exactly that. At a lower K value where growth first started, the necessary SWE amplitude corresponding to ΔA_{II} would only be 0.032 g. Again, this is consistent with Figure 3. Thirdly, the number of large jumps represented by the 37 SWE in distribution II would indicate that $(2V_c)N_{\Delta A_{II}}$ or 0.0163 inches (0.0415 cm) of growth had occurred. Although this is less than half of that indicated in the micrograph, it is similar to that calculated from the load - displacement curve. One final comparison is the total area $(2V_c)N_{\Delta A_{II}}$ calculated from the 37 large SWE compared to the total area calculated from Eq. (4). These values are 0.011 in^{-2} (0.071 cm^2) and 0.0088 in^{-2} (0.057 cm^2), respectively. Thus, the hypothesis seems to be self-consistent.

I-3-5. CONCLUSIONS

1. Acoustic emission techniques should be useful in sorting out the various microscopic crack events associated with slow crack growth.
2. The area of a single crack event is proportional to the amplitude of the stress wave associated with it.
3. 323 stress waves of amplitudes ranging up to 0.23 g were observed as a crack slowly grew 0.029 in^2 (0.187 cm^2) in a high-strength steel.
4. Calculation of the total area swept out by the advancing crack was made from the summation of the stress wave amplitudes. As this value

was about one-third of the actual value planimetered, this indicates that either the approach is in error, the technique is not detecting all growth or that some growth occurred upon unloading.

5. Additional tests are required to ascertain if the acoustic emission technique is measuring all of the area associated with the slow crack growth process.
6. The histogram of SWE amplitudes is either asymmetric or bimodal. This indicates that a series of small crack areas intermixed with larger jumps accompanies the ductile rupture process in high strength 4340 steel.
7. A tentative hypothesis is that one unit of slow crack growth is made up of a series of small crack-tip displacement "thumb nail" cracks followed by a larger instability. Assuming these units are approximately repeated as the crack grows is consistent with a bimodal frequency distribution of stress-wave amplitudes (crack areas).

I-3-6 REFERENCES

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II. DETERMINATION OF THE PHENOMENA CONTROLLING CRACK PROPAGATION
IN METAL SUSCEPTIBLE TO HYDROGEN EMBRITTLEMENT

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II-1. Threshold Stress Intensity and Crack Growth Modelling for Hydrogen Embrittlement

William W. Gerberich and Yew-Tsung Chen

II-1-1. INTRODUCTION

As discussed in the program summary, one of the most promising areas of research is that of time-dependent embrittlement phenomena such as stress-corrosion and hydrogen-assisted cracking. Such powerful experimental techniques as acoustic emission, electron fractography, scanning and non-dispersive x-ray and Auger spectroscopy are readily available. In conjunction with the experimental and analytical methods of fracture mechanics, we are gaining considerable insight into such formidable problem areas.

II-1-2. CURRENT RESULTS

In the appendix, three papers which have evolved from the past years effort are given. The first by W. W. Gerberich will appear in the symposium volume by ASM as part of the Seven Springs Conference on Hydrogen in Metals. In this, a review of existing knowledge as well as some new results were presented on threshold stress intensity (equilibrium conditions) and slow crack growth (kinetic conditions) phenomena in martensitic steels. In the second paper, by W. W. Gerberich and Y. T. Chen, a detailed analysis of the threshold stress intensity model is described in terms of fracture mechanics and thermodynamics. This will appear shortly in Metallurgical Transactions. Finally, a somewhat shorter paper concerning the pressure dependence of the threshold stress intensity will appear in Engineering Fracture Mechanics. A fourth paper concerning kinetic growth conditions is in preparation. From these papers, the following hypotheses and conclusions

are emerging:

- (1) Equilibrium conditions for threshold stress intensity can be described and applied to elastic, plane-strain plastic, and plane stress plastic conditions. The basic consideration is the pressure tensor of the stress field and the hydrogen concentration.
- (2) Kinetic conditions for crack growth rate under plane-strain or plane stress conditions can be described for the various stages of crack growth experimentally observed: stage I, predominantly elastic with intergranular or quasi-cleavage microfracture; stage II, elastic-plastic intergranular or quasi-cleavage; stage III, predominantly plastic with ductile rupture or intergranular microfracture. The basic considerations are the pressure tensor gradient, the concentration and the diffusivity of hydrogen.
- (3) In both of the foregoing models, hydrogen concentration, pressure (stress), yield strength, stress field loading mode, thickness, and temperature dependencies of the embrittlement process may be predicted.

These models have been applied to a large body of data in the literature as well as a considerable evaluation in our own laboratory. Although much of our data are in the attached papers, some of the detailed tabulations are not. For the sake of completeness, a detailed listing of crack propagation observations are given in Tables I through IX. These represent the variables of yield strength (tempering temperature), thickness (plane stress or plane strain) and applied stress intensity on crack propagation rate. The compact tension specimen, testing techniques and charging and plating and baking conditions to achieve 2.6 ppm hydrogen are adequately described in the appended papers.

This initial research has been extraordinarily useful in pinpointing several critical areas of investigation:

- (1) What is the effect of hydrogen source on threshold stress

intensity, K_{TH} , and crack growth kinetics, da/dt ?

- (2) What is the effect of prior austenitic grain size on both K_{TH} and da/dt ?
- (3) Does hydrogen cracking occur atom-by-atom as a decohesion mechanism or grain by grain as a major discontinuous microscopic growth process?
- (4) How do alloying additions and tempering or aging treatments affect hydrogen trapping which in turn strongly affects diffusivity?
- (5) As a result of trapping, does the precipitation of different volume fractions of coherent, semi-coherent or non-coherent intermetallic compounds in maraging steel promote gross differences in hydrogen-assisted slow crack growth rates?

Many of these questions have been incorporated as new tasks as discussed in the following sections, II-2 and II-3. Additional discussion is presented in the attached renewal proposal.

Table I: COMPOSITION AND YIELD STRENGTH OF AISI 4340

Composition, wt.%							
C	P	S	Mn	Si	Cr	Mo	Ni
0.40	0.035	0.04	0.80	0.21	0.80	0.25	1.9

Yield Strength Estimate		
Temper	R_c (ave 5 readings)	R_c Yield Strength, 1000 psi
200°C	51.2	226
300°C	49.5	220
400°C	48.0	211
480°C	43.4	180
550°C	40.3	169

Table II: THE EFFECT OF TEMPERING TEMPERATURE ON
THRESHOLD STRESS INTENSITY AND CRACK GROWTH RATE*

Temp. T. °C	200	300	400	480	550
K_{TH} ksi-in $^{\frac{1}{2}}$	11	16.5	18	29	46
$(\frac{da}{dt})_{ave}^{II**}$ x10 $^{-4}$ in/sec	-	24	7	1.85	0.096
$(K_I)^{II***}$ ksi-in $^{\frac{1}{2}}$	-	20-31	22.5-40	33-46.5	47-59

* For 0.75 inch thick sample.

** Average crack growth rate in stage II.

*** Range of stress intensity in stage II.

Table III: THE EFFECT OF THICKNESS ON THRESHOLD STRESS
INTENSITY*

Thickness, inch	<u>0.75</u>	<u>0.45</u>	<u>0.15</u>
K_{TH} , ksi-in $^{\frac{1}{2}}$	46	55	78

* Samples tempered at 550°C

Table IV: THE EFFECT OF THICKNESS ON CRACK GROWTH RATE
FOR 300°C TEMPERED SAMPLE

Thickness, inch	<u>0.75</u>	<u>0.45</u>	<u>0.35</u>	<u>0.25</u>	<u>0.15</u>
$(\frac{da}{dt})_{ave}^{II}$ x10 $^{-4}$ in/sec	24	1.75	1	0.125	0.061
$(K_I)^{II}$ ksi-in $^{\frac{1}{2}}$	20-31	31-38	31-40	24-30	34-39

Table V: THE EFFECT OF THICKNESS ON CRACK GROWTH RATE
FOR 480°C TEMPERED SAMPLE

Thickness, inch	<u>0.75</u>	<u>0.45</u>	<u>0.35</u>	<u>0.25</u>	<u>0.15</u>
$(\frac{da}{dt})_{ave}^{II}$ x10 $^{-4}$ in/sec	1.85	0.07	0.014	0.0017	0.0107
$(K_I)^{II}$ ksi-in $^{\frac{1}{2}}$	33-46.5	58-70	84-87	98-110	140-159

Table VI: FRACTURE ANALYSIS DATA FOR DETERMINING STRESS INTENSITY AND CRACK GROWTH RATE
OF AISI 4340 TEMPERED AT FIVE STRENGTH LEVELS

Specimen tempered at 300°C, 0.75" thick (1st test)

Step	a (in)	P (lbs)	Y	K (ksi-in ^{3/2})	K _{ave} (ksi-in ^{3/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.76	1505	9.94	16.3				
2	0.77	1475	10.3	16.6	16.5	0.01		
3	0.78	1450	10.41	16.4	16.5	0.01	64.8	1.54
4	0.79	1425	10.7	16.6	16.5	0.01	99.6	1.005
5	0.8	1410	11	16.9	16.7	0.01	50.4	1.985
6	0.81	1380	11.2	16.9	16.9	0.01	30	3.33
7	0.82	1375	11.4	17.1	17	0.01	28.8	3.48
8	0.83	1360	11.65	17.3	17.2	0.01	26.4	3.79
9	0.84	1340	11.9	17.4	17.3	0.01	13.2	7.58
10	0.85	1325	12.18	17.6	17.5	0.01	20.4	4.9
11	0.86	1310	12.5	17.8	17.7	0.01	31.2	3.2
12	0.87	1305	12.7	18.1	18	0.01	16.8	5.95
13	0.89	1290	13.6	19.1	18.6	0.02	14.4	13.9
14	0.92	1280	14.4	20.1	19.6	0.03	18	16.5
15	0.96	1275	16.1	22.4	21.3	0.04	23	17.3

Table VI: (continued)

Specimen tempered at 300°C, 0.75" thick (2nd test)

Step	a (in)	P (lbs)	Y	K (ksi-in ^{3/2})	K _{ave} (ksi-in ^{3/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.8	2280	11	27.3				
2	0.81	2275	11.2	27.8	27.6	0.01	3.6	27.8
3	0.83	2260	11.6	28.6	28.2	0.02	9	22.2
4	0.85	2250	12.18	29.9	29.2	0.02	6	33.4
5	0.86	2240	12.5	30.5	30.2	0.01	4.8	20.9
6	0.87	2230	12.7	30.9	30.7	0.01	5.4	18.5
7	0.89	2220	13.6	32.9	31	0.02	7.8	25.6
8	0.92	2180	14.4	34.2	33.5	0.03	122.4	3.27**
9	0.93	2100	14.8	33.9	34	0.01	208.8	0.479
10	0.94	2020	15.3	33.7	33.8	0.01	105.6	0.95
11	0.95	1900	15.6	32.3	33	0.01	105.6	0.95
12	0.96	1800	16.1	31.6	32	0.01	99.6	1.01
13	0.97	1750	16.6	31.7	31.7	0.01	62.4	1.6
14	0.98	1680	16.9	30.9	31.3	0.01	86.4	1.155
15	0.99	1620	17.4	30.7	30.8	0.01	86.4	1.155

** After breaking the specimen, it was found that crack direction was perpendicular to crack tip after 8th grid.

Table VI (continued)

Specimen tempered at 400°C, 0.25" thick (1st test)

Step	a (in)	P (lbs)	Y	K (ksi-in ^{3/2})	K _{ave} (ksi-in ^{3/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.77	1590	10.3	17.9				
2	0.78	1575	10.42	17.9	17.9	0.01	123.6	0.749
3	0.79	1540	10.65	17.9	17.9	0.01	279.6	0.368
4	0.8	1500	10.95	17.9	17.9	0.01	194.4	0.516
5	0.81	1470	11.2	17.9	17.9	0.01	165.6	0.605
6	0.82	1450	11.4	17.9	17.9	0.01	50.4	2.0
7	0.83	1445	11.6	18.3	18.1	0.01	61.2	1.64
8	0.84	1420	11.9	18.4	18.3	0.01	115.2	0.87
9	0.85	1400	12.2	18.5	18.4	0.01	60	1.67
10	0.86	1390	12.5	18.8	18.6	0.01	57.6	1.74
11	0.87	1380	12.7	19.1	19	0.01	37.2	2.69
12	0.89	1350	13.6	20	19.5	0.02	110.4	1.81
13	0.9	1345	13.7	20.1	20.1	0.01	49.2	2.03
14	0.91	1340	14	20.4	20.2	0.01	22.8	4.39
15	0.92	1325	14.4	20.8	20.6	0.01	36	2.78
16	0.93	1300	14.8	21	20.9	0.01	76.8	1.305
17	0.94	1270	15.3	20.9	21	0.01	69.6	1.44
18	0.95	1260	15.6	21.4	21.2	0.01	19.2	5.21
19	0.96	1220	16.1	21.4	21.4	0.01	138	0.725

Table VI (continued)

Specimen tempered at 400°C, 0.75" thick (2nd test)

Step	a (in)	P (lbs)	Y	K (ksi-in ^{3/2})	K _{ave} (ksi-in ^{3/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.74	2800	9.75	29.8				
2	0.78	2750	10.41	31.2	30.5	0.04	24	16.6
3	0.79	2675	10.7	31.2	31.2	0.01	37.2	2.7
4	0.8	2550	11	30.6	31	0.01	79.2	1.26
5	0.82	2525	11.35	31.3	31	0.02	16.8	11.85
6	0.83	2500	11.6	31.6	31.4	0.01	27.6	3.62
7	0.86	2475	12.5	33.7	32.7	0.02	10.8	18.5
8	0.87	2450	12.7	33.9	33.8	0.01	13.2	7.6
9	0.88	2425	13.25	35	34.5	0.01	9.6	10.3
10	0.9	2400	13.7	35.8	35.4	0.01	20.4	4.91
11	0.92	2370	14.4	37.2	36.5	0.02	20.4	9.84
12	0.93	2320	14.8	37.4	37.3	0.01	15.6	6.43
13	0.95	2300	15.6	39.1	38.3	0.02	4.2	47.6

Table VI (continued)

Specimen tempered at 480°C, 0.75" thick (1st test)

Step	a (in)	P (lbs)	Y	K (ksi-in ^{3/2})	K _{ave} (ksi-in ^{3/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.76	2270	9.94	24.6				
2	0.77	2220	10.3	24.9	24.7	0.01	4554	0.022
3	0.79	2190	10.7	25.5	25.2	0.02	2830.8	0.0706
4	0.81	2175	11.2	26.6	26.1	0.02	756	0.264
5	0.82	2155	11.35	26.7	26.6	0.01	1909.2	0.0524
6	0.83	2140	11.6	27.1	26.9	0.01	1942.8	0.0515
7	0.84	2100	11.9	27.2	27.1	0.01	5646	0.0177
8	0.85	2080	12.2	27.7	27.5	0.01	2209.2	0.0452
9	0.86	2080	12.5	28.3	28	0.01	654	0.153
10	0.87	2080	12.7	28.8	28.5	0.01	417.6	0.24
11	0.88	2075	13.25	30	29.4	0.01	3374.4	0.296
12	0.89	2075	13.65	30.9	30.4	0.01	11568	0.00864
13	0.9	2060	13.7	30.8	30.8	0.01	2182.8	0.0458
14	0.91	2020	14	30.8	30.8	0.01	5137.2	0.0195
15	0.92	2015	14.4	31.6	31.2	0.01	5181.6	0.0193
16	0.93	2000	14.8	32.3	32	0.01	717.6	0.139
17	0.94	1990	15.3	33.2	32.7	0.01	1699.2	0.059
18	0.95	1975	15.6	33.6	33.4	0.01	3000	0.0333

Table VI (continued)

Specimen tempered at 480°C, 0.75" thick (2nd test)

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.76	3100	9.94	33.6				
2	0.77	3090	10.3	34.7	34.2	0.01	15.6	6.42
3	0.79	3070	10.7	35.8	35.2	0.02	56.4	3.55
4	0.8	3050	11	36.6	36.2	0.01	45.6	2.2
5	0.81	3020	11.2	36.8	36.7	0.01	103.2	0.97
6	0.82	3000	11.4	37.3	37	0.01	45.6	2.2
7	0.83	2980	11.6	37.8	37.5	0.01	48	2.08
8	0.84	2950	11.9	38.3	38	0.01	66	1.52
9	0.86	2910	12.5	39.6	39	0.02	180	1.11
10	0.87	2880	12.7	39.9	39.7	0.01	158.4	0.633
11	0.9	2780	13.7	41.5	40.7	0.03	402	0.75
12	0.91	2750	14	41.9	41.7	0.01	94.2	1.06
13	0.92	2740	14.4	43	42.5	0.01	56.2	1.78
14	0.94	2650	15.3	44.2	43.6	0.02	250.8	0.76
15	0.95	2600	15.6	44.2	44.2	0.01	111.6	0.895

Table VI (continued)

Specimen tempered at 550°C, 0.75" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{3/2})	K _{ave} (ksi-in ^{3/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.76	4220	9.94	45.7				
2	0.77	4210	10.3	47.6	46.7	0.01	307.2	0.345
3	0.78	4190	10.41	47.7	47.6	0.01	3944.4	0.0296
4	0.79	4080	10.7	47.6	47.7	0.01	1730.4	0.0613
5	0.8	4070	11	48.8	48.2	0.01	2054.4	0.056
6	0.81	4025	11.2	49.6	49.2	0.01	2617.6	0.0406
7	0.82	3970	11.4	49.8	49.7	0.01	2184	0.0485
8	0.83	3905	11.65	49.8	49.8	0.01	391.2	0.271
9	0.84	3900	11.9	52.6	50.2	0.01	3507.2	0.0302
10	0.85	3820	12.2	51.2	51.0	0.01	1183.2	0.0895
11	0.86	3790	12.5	51.6	51.4	0.01	2234.4	0.0475
12	0.87	3730	12.7	51.7	51.6	0.01	2541.6	0.0417
13	0.88	3675	13.25	53.1	52.4	0.01	484.8	0.219
14	0.89	3650	13.65	54.4	53.7	0.01	1461.6	0.0725
15	0.9	3610	13.7	54	54.2	0.01	849.6	0.125
16	0.91	3590	14	54.8	54.4	0.01	1064.4	0.01
17	0.92	3560	14.4	55.8	55.3	0.01	1255.2	0.0845
18	0.94	3525	15.3	58.4	57.1	0.02	220.4	0.241
19	0.95	3520	15.6	60.2	59.4	0.01	500.4	0.212

Table VII. Fracture Analysis Data For Determining Stress Intensity and Crack Growth Rate of AISI 4340 With Different Thickness Tempered At 300°C

Specimen tempered at 300°C, 0.45" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.77	2200	10.3	33.5				
2	0.78	2060	10.41	31.7	32.6	0.01	1140	0.0878
3	0.79	1930	10.7	30.6	31.2	0.01	787.2	0.127
4	0.81	1920	11.2	31.8	31.2	0.02	31.2	6.41
5	0.82	1880	11.35	31.6	31.7	0.01	163.2	0.614
6	0.83	1850	11.6	31.8	31.7	0.01	57.6	1.74
7	0.85	1820	12.2	32.9	32.4	0.02	108	1.85
8	0.86	1800	12.5	33.3	33.1	0.01	56.4	1.78
9	0.87	1780	12.7	33.5	33.4	0.01	60.0	1.67
10	0.89	1760	13.6	35.4	34.5	0.02	64.8	3.08
11	0.9	1745	13.7	35.4	35.4	0.01	27.6	3.62
12	0.92	1700	14.4	36.2	35.8	0.02	166.8	1.2
13	0.93	1670	14.8	36.6	36.4	0.01	12	8.34
14	0.94	1650	15.3	37.4	37	0.01	64.8	1.54
15	0.96	1580	16.1	37.7	37.5	0.02	201.6	0.995

Table VII. (continued)

Specimen tempered at 300°C, 0.35" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.71	1462	9.1	31				
2	0.72	1430	9.3	31	31	0.01	844.8	0.118
3	0.73	1410	9.6	31.5	31.3	0.01	380.4	0.262
4	0.74	1405	9.75	31.9	31.7	0.01	136.8	0.731
5	0.75	1403	9.8	32	32	0.01	25.2	3.97
6	0.76	1400	9.94	32.4	32.2	0.01	36	2.78
7	0.77	1400	10.3	33.6	33	0.01	49.2	2.03
8	0.78	1400	10.41	34	33.8	0.01	15.6	6.41
9	0.79	1390	10.7	34.7	34.3	0.01	78	1.28
10	0.8	1380	11	35.4	35.1	0.01	170.4	0.587
11	0.81	1375	11.2	35.9	36	0.01	108	0.925
12	0.82	1350	11.35	35.7	35.8	0.01	28.8	3.47
13	0.83	1340	11.6	36.2	36	0.01	358.4	0.279
14	0.84	1320	11.9	36.6	36.4	0.01	258.4	0.388
15	0.85	1310	12.2	37.2	36.9	0.01	37.2	2.68
16	0.86	1305	12.5	38	37.6	0.01	127.2	0.785
17	0.87	1300	12.7	38.5	38.3	0.01	24	4.16
18	0.88	1285	13.25	39.7	39.1	0.01	103.2	0.97
19	0.89	1260	13.65	40	39.8	0.01	194.4	0.514
20	0.9	1240	13.7	39.6	39.8	0.01	194.4	0.514

Table VII. (continued)

Specimen tempered at 300°C, 0.25" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.74	930	9.75	29.6				
2	0.75	925	9.8	29.6	29.6	0.01	289.2	0.346
3	0.76	912	9.94	29.6	29.6	0.01	1417.2	0.0705
4	0.77	870	10.3	29.3	29.4	0.01	4286.4	0.0233
5	0.78	852	10.41	29	29.2	0.01	1753.2	0.057
6	0.79	830	10.7	29	29	0.01	2172	0.0461
7	0.8	818	11	29.4	29.2	0.01	1170	0.0855
8	0.81	776	11.2	28.4	28.9	0.01	1974	0.0506
9	0.82	750	11.35	27.8	28.1	0.01	730.8	0.137
10	0.83	745	11.6	28.2	28	0.01	232.8	0.43
11	0.84	702	11.9	27.3	27.8	0.01	1748.4	0.0573
12	0.85	686	12.2	27.3	27.3	0.01	480	0.208
13	0.86	660	12.5	27	27.1	0.01	522	0.194
14	0.87	652	12.7	27	27	0.01	111.6	0.895
15	0.88	615	13.25	26.6	26.8	0.01	1068	0.0936
16	0.89	589	13.65	26.2	26.4	0.01	801.6	0.1245
17	0.9	552	13.7	24.7	25.5	0.01	793.2	0.126
18	0.91	550	14	25.1	25	0.01	720	0.139
19	0.92	542	14.4	25.5	25.3	0.01	111.6	0.9
20	0.93	500	14.8	24.2	24.9	0.01	1171.2	0.0855

Table VII. (continued)

Specimen tempered at 300°C, 0.15" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.72	670	9.3	33.9				
2	0.73	662	9.6	34.6	34.3	0.01	843.6	0.1185
3	0.74	657	9.75	34.9	34.8	0.01	376.8	0.265
4	0.79	604	10.7	35.2	35	0.05	9841.2	0.0508
5	0.8	596	11	35.7	35.4	0.01	1902	0.0526
6	0.81	589	11.2	35.9	35.8	0.01	2612.4	0.0383
7	0.82	580	11.35	35.8	35.9	0.01	1749.6	0.0572
8	0.83	580	11.6	36.6	36.2	0.01	651.6	0.1535
9	0.84	575	11.9	37.2	36.9	0.01	1494	0.067
10	0.85	561	12.2	37.2	37.2	0.01	3825.6	0.0261
11	0.86	555	12.5	37.7	37.5	0.01	2282.4	0.0438
12	0.87	550	12.7	38	37.9	0.01	1899.6	0.0528
13	0.88	548	13.25	39.5	38.7	0.01	4480.8	0.0223
14	0.89	530	13.65	39.4	39.4	0.01	2452.8	0.0408
15	0.9	520	13.7	38.8	39.1	0.01	2574	0.0389

Table VIII. Fracture Analysis Data For Determining Stress Intensity And Crack Growth Rate of AISI 4340 With Different Thickness Tempered At 480°C

Specimen tempered at 480°C, 0.45" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.78	3710	10.41	57.2				
2	0.79	3680	10.7	58.3	57.8	0.01	1442.4	0.0694
3	0.8	3670	11	59.7	59	0.01	639.6	0.156
4	0.81	3590	11.2	59.5	59.6	0.01	3714	0.027
5	0.82	3550	11.35	59.6	59.6	0.01	1825.2	0.0548
6	0.83	3500	11.6	60	59.8	0.01	2583.6	0.0386
7	0.84	3450	11.9	60.8	60.4	0.01	3543.6	0.0282
8	0.85	3400	12.2	61.4	61.1	0.01	2433.6	0.0412
9	0.86	3380	12.5	62.5	62	0.01	855.6	0.117
10	0.87	3300	12.7	62	62.3	0.01	3606	0.0277
11	0.88	3250	13.25	63.7	62.8	0.01	2187.6	0.0457
12	0.89	3200	13.65	64.6	64.2	0.01	693.6	0.144
13	0.9	3180	13.7	64.5	64.5	0.01	174	0.575
14	0.91	3150	14	67.1	65.8	0.01	150	0.666
15	0.92	3060	14.4	65.2	66.2	0.01	3837.6	0.026
16	0.93	3040	14.8	66.6	66	0.01	1065.6	0.094
17	0.94	2980	15.3	67.5	67.1	0.01	2296.8	0.0437
18	0.95	2920	15.6	67.4	67.4	0.01	1638	0.061
19	0.96	2900	16.1	68.7	68.1	0.01	1152	0.0666
20	0.97	2880	16.6	70.6	69.7	0.01	696	0.1435

Table VIII. (continued)

Specimen tempered at 480°C, 0.35" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{3/2})	K _{ave} (ksi-in ^{3/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.72	3840	9.3	83.2				
2	0.73	3800	9.6	85.6	84.4	0.01	21066	0.00474
3	0.74	3760	9.75	85.4	85.5	0.01	55842	0.00179
4	0.75	3750	9.8	85.6	85.5	0.01	828	0.121
5	0.76	3730	9.94	86.4	86	0.01	15210	0.00656
6	0.77	3725	10.3	88.3	87.4	0.01	2700	0.037

Table VIII. (continued)

Specimen tempered at 480°C, 0.25" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{3/2})	K _{ave} (ksi-in ^{3/2})	Δa (in)	At (sec)	$\frac{da}{dt}$ (x10 ⁻⁴ in/sec)
1	0.72	3170	9.3	96.3				
2	0.73	3150	9.6	98.7	97.5	0.01	10.8	9.26
3	0.74	3100	9.75	98.7	98.7	0.01	163.2	0.577
4	0.75	3090	9.8	98.9	98.8	0.01	415.8	0.241
5	0.76	3080	9.94	99.5	99.2	0.01	426	0.235
6	0.77	2980	10.3	100.2	99.9	0.01	31590	0.00317
7	0.78	2900	10.41	98.6	99.4	0.01	83952	0.00119
8	0.79	2820	10.7	98.5	98.6	0.01	2466	0.0404
9	0.8	2780	11	99.8	99.2	0.01	34092	0.00302
10	0.81	2660	11.2	97.2	98.5	0.01	26784	0.00374
11	0.82	2640	11.35	97.8	97.5	0.01	22752	0.0044
12	0.83	2620	11.6	99.2	98.5	0.01	3330	0.03
13	0.84	2615	11.9	101.6	100.4	0.01	14292	0.007
14	0.85	2570	12.2	102.3	102	0.01	16992	0.0059
15	0.86	2550	12.5	104.1	103.2	0.01	32202	0.00311
16	0.87	2520	12.7	104.5	104.3	0.01	20016	0.005
17	0.88	2500	13.25	108.2	106.4	0.01	3312	0.0302
18	0.89	2470	13.65	110	109	0.01	24084	0.00414
19	0.9	2440	13.7	109.1	109.6	0.01	26460	0.00378
20	0.91	2410	14	110.2	109.6	0.01	18828	0.0053

Table VIII. (continued)

Specimen tempered at 480°C, 0.15" thick

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.84	2440	11.9	158				
2	0.85	2420	12.2	160.6	159.3	0.01	594	0.1685
3	0.86	2000	12.5	136	148.3	0.01	194052	0.000515
4	0.88	1995	13.25	143.8	140	0.02	522	0.384
5	0.89	1990	13.65	147.8	146	0.01	16614	0.00604
6	0.9	1885	13.7	140.5	144.2	0.01	5850	0.0171

Table IX. Fracture Analysis Data For Determining Stress Intensity And Crack Growth Rate
of AISI 4340 Tempered At 550°C

Specimen tempered at 550°C, 0.45" thick (1st test)

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
1	0.73	5180	9.6	73.5				
2	0.74	5170	9.75	74.6	74	0.01	13.2	8.2
3	0.75	5130	9.8	74.6	74.6	0.01	616.8	0.162
4	0.76	5010	9.94	74	74.3	0.01	2628	0.0381
5	0.77	5010	10.3	76.4	75.2	0.01	61.2	1.63
6	0.78	4920	10.41	76	76.2	0.01	2628	0.038
7	0.79	4900	10.7	77.6	76.8	0.01	546	1.83
8	0.8	4810	11	78.4	78	0.01	3592.8	0.0278
9	0.81	4800	11.2	79.6	79	0.01	160.8	0.622
10	0.82	4750	11.35	79.8	79.7	0.01	1680	0.0595
11	0.83	4620	11.6	79.5	79.7	0.01	6680.4	0.015
12	0.84	4570	11.9	80.5	80	0.01	3532.8	0.0283
13	0.85	4430	12.2	80	80.3	0.01	3482.4	0.0287
14	0.86	4360	12.5	80.7	80.3	0.01	11035.2	0.009
15	0.87	4300	12.7	80.9	80.8	0.01	8216.4	0.012
16	0.88	4240	13.25	83.1	82	0.01	3276	0.0306
17	0.89	4220	13.6	85	84	0.01	2262	0.0441

Table IX. (continued)

Specimen tempered at 550°C, 0.45" thick (2nd test)

Step	a (in)	P (lbs)	Y	K (ksi-in ^{1/2})	K _{ave} (ksi-in ^{1/2})	Δa (in)	Δt (sec)	$\frac{\Delta a}{\Delta t}$ (x10 ⁻⁴ in/sec)
12	0.75	4875	9.8	70.7				
13	0.76	4560	9.94	67.08	68.9	0.01	42588	0.00235
14	0.77	4560	10.3	69.5	68.3	0.01	612	0.163
15	0.78	4430	10.41	68.3	68.9	0.01	25686	0.00389
16	0.79	4400	10.7	69.7	69	0.01	9252	0.0108
17	0.8	4265	11	69.4	69.5	0.01	29556	0.00339
18	0.81	4265	11.2	70.7	70	0.01	596	0.168
19	0.82	4190	11.35	70.4	70.5	0.01	12150	0.00823
20	0.83	4125	11.6	70.8	70.6	0.01	18288	0.00547

Table IX. (continued)

Specimen tempered at 550°C, 0.45" thick (3rd test)

The specimen was loaded at $K \approx 55 \text{ ksi-in}^{\frac{1}{2}}$ for 48 hours indicating no apparant slow crack growth.

II-2. Studies of Hydrogen Embrittlement Cracking in 4340 Steel Using DCB Specimens

Jeffrey Garry

II-2-1. INTRODUCTION

Double cantilever beam specimens present a number of advantages in the study of hydrogen embrittlement. When loaded with a bolt, they represent a complete self-contained testing system. With a fixed arm deflection, the plane-strain stress intensity decreases with increasing crack length. If placed in a H_2 atmosphere, the specimen will crack until the critical stress intensity for hydrogen embrittlement is reached, whereupon the crack growth is arrested. The specimen can then be broken open and the crack length a measured and K_{IC} calculated from the compliance calibration. DCB specimens are compact, minimizing material requirements. No fatigue cracking is necessary, as a pop-in crack can be produced simply by loading the specimen until it cracks. The specimen is then reloaded. The pop-in crack is usually about 0.1" to 1" depending on the fracture toughness of the material. One disadvantage of the DCB specimen is the tendency for the arms to break off, as a result of cracks growing out of plane due to bending stresses in the arms. This is avoided by grooving the sides of the specimen to assure that the crack grows straight.

The goals of this study are:

- (i) Determination of K_{IC} for hydrogen embrittlement cracking as a function of H_2 pressure in the range from 1 mm Hg to 1 atm.
- (ii) Obtaining information about the nature of the hydrogen embrittlement cracking mechanism; either (a) atom by atom at the crack tip as proposed by Oriani^{1,2} in his decohesion theory or, (b) cracking occurring in large, discontinuous jumps, when the hydrogen concentration at the elastic-plastic boundary exceeds a critical value, as proposed by Gerberich³. By the use of acoustic emission techniques, we feel that we can gain some valuable insight

into this question.

- (iii) Kinetic studies: determination of a correlation between K_I , P_{H_2} and $d\bar{a}/dt$. Of special interest is $d\bar{a}/dt$ as a function of P_{H_2} at constant K_I . A threshold $d\bar{a}/dt$ should be reached, as the rate of chemisorption on the surface becomes the limiting reaction⁴.

II-2-2. EXPERIMENTAL PROCEDURES

The testing apparatus has been built and tested and samples are currently being machined. Actual testing should begin early in February. The apparatus consists of:

- (i) A H_2 environmental chamber consisting of a bell jar and vacuum system. The bell jar base contains gas and electrical feed-throughs as well as mechanical manipulators. The system is filled with Airco Ultra-pure Hydrogen (dew point $-97^\circ F$) and the pressure is controlled by a Cartesian manostat. The system has been tested and found capable of satisfactory pressure control in the range of 1 mm Hg to 1 atm.
- (ii) A miniature load cell which replaces the bolt in the DCB specimen, allowing measurement of load at all times. Since the arm displacement, V , is constant, we can calculate the crack length $\bar{a}$ from the compliance. Therefore both K_I and $\bar{a}$ are known as a function of time for kinetic studies. The load cell consists of a hollow bolt with a load pin carrying the strain gage. Both the bolt and load pin are heat-treated 4340 steel and are plated with cadmium as a hydrogen diffusion barrier. The load cell was calibrated in the Instron tensile tester and found to be very close to linear in load vs. strain. The load cell and calibration are shown in Figures 1 and 2.

The double cantilever beam specimen used is shown in Figure 3. Using the compliance calibration of Mostovoy et al⁵;

$$c = \frac{2}{3EI} [(\bar{a} + a_0)^3 + h^2 \bar{a}] \quad (1)$$

where;

- c = compliance
- E = Young's modulus
- I = moment of inertia of one of the arms = $bh^3/12$
- a_0 = an empirical rotation correction equal to $0.6h$
- h = one half the specimen height
- b = specimen width

Load Cell Components - Full Size

Figure 1. DCB Specimen Load Cell

Figure 2. DCB Specimen Load Cell Calibration

DCB Specimen - Full Scale

Since $P = v/c$ (2)

where v = total deflection of the two arms at the load point
 P = load

The expression for K_I is

$$K_I = \frac{v E h [3h (\underline{a} + 0.6h)^2 + h^3]^{\frac{1}{2}}}{4 [(\underline{a} + 0.6h)^3 + h^2 \underline{a}]} \quad (3)$$

This expression is for DCB specimens without side grooves. For a specimen with side grooves of depth less than 0.1b, Freed and Krafft⁶ have shown that K_I can be corrected for side grooving by a multiplicative factor of $(b/b_n)^{\frac{1}{2}}$, where b_n is the reduced specimen width due to side grooving. This gives the relation:

$$K_I = \left(\frac{b}{b_n}\right)^{\frac{1}{2}} \frac{v E h [3h (\underline{a} + 0.6h)^2 + h^3]^{\frac{1}{2}}}{4 [(\underline{a} + 0.6h)^3 + h^2 \underline{a}]} \quad (4)$$

In the DCB specimen, v is constant. Knowing v and P , $\underline{a}$ can be calculated from equations (1) and (2). Then K_I can be found from equation (4). Figure 4 shows K_I vs. $\underline{a}$ for several values of v .

Stress wave emission techniques will be used to investigate the microscopic mechanism of hydrogen embrittlement cracking. Cracking may be occurring atom by atom at the crack tip. The stress waves generated by this type of cracking are not detectable. Since all hydrogen embrittlement cracking exhibits, SWE, the crack may grow atom by atom until it triggers a void, inclusion or other defect. It then jumps, giving off an emission. Desai and Gerberich⁷ have demonstrated a correlation between incremental fracture area, ΔA , and SWE amplitude, g . By comparing the sum of the SWE amplitudes with the total fracture area, the percentage of fracture area

Figure 4

created in events large enough to cause SWE can be calculated. If only a small percentage of the fracture area can be attributed to SWE events, it would tend to support the decohesion theory of Oriani^{1,2}. If, however, a large percentage of the fracture area can be correlated to SWE events, it would tend to confirm the theory of Gerberich³, that the cracking initiates at the elastic-plastic boundary when a critical hydrogen concentration is reached. To further test these hypotheses, specimens will be loaded and placed in a H_2 atmosphere until the first signs of SWE are detected. The specimen will then be rapidly unloaded by means of a mechanical manipulator. The specimen will then be sectioned to see whether the crack is growing at the crack tip or possibly at the elastic - plastic boundary.

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II-3. The Effect of Pre-Austenitic Grain Size on Time Dependent Embrittlement Joseph Lessar

II-3-1. INTRODUCTION

The phenomena of time-dependent embrittlement processes have been an area of study for some time. As of the present, there is much evidence to support the theory that embrittlement of steels is probably hydrogen induced.

Presently, several investigations are now in progress in an effort to learn more of the phenomenon termed "hydrogen embrittlement" as it is related to stress-corrosion cracking.

The most common measurements used in the study of hydrogen embrittlement are crack-growth kinetics (da/dt), threshold stress intensities (K_{th}), and mode of fracture.

The effect of parameters such as test temperature⁽¹⁾, test environment⁽¹⁾, state of stress⁽⁴⁾, and yield strength⁽²⁾ on da/dt and K_{th} have been studied quite thoroughly. However, there has been relatively little investigation as to the effect of grain size on da/dt , K_{th} , and fracture mode.

As part of a larger investigation into the phenomenon of hydrogen embrittlement, an attempt will be made to determine the influence of grain size. K_{th} , da/dt , and fracture mode are to be studied as a function of pre-austenitic grain size.

II-3-2. EXPERIMENTAL PLAN

The test specimen will be of the Double Cantilever Beam (DCB)⁽³⁾ design. This specimen design was chosen because of its simplicity and the

information that it yields. Because of its unique design, the DCB is self-loading and has a useful stress intensity (K) range of K_{IC} to approximately $0.1 K_{IC}$. (Most other self-loading specimen types have a range of K_{IC} to $\sim 0.5 K_{IC}$.) Because K_{th} , in some cases, can be near $0.1 K_{IC}$, the DCB specimen design is necessitated.

Thirty 4340 alloy steel DCB test specimen will be heat treated to produce a constant yield strength of $\sim 220,000$ psi, and three grain sizes: $\sim 20\mu$, $\sim 50\mu$, and $\sim 125\mu$. Half of the specimens are to be tested in a molecular hydrogen (H_2) atmosphere. The remaining specimens will be cathodically charged with atomic hydrogen, cadmium plated, and baked for a short period of time to homogenize the hydrogen⁽⁴⁾.

The monitoring of da/dt and K_{th} can be done in several ways. Because of the configuration of the DCB test specimen, if the load as a function of time is known, da/dt , dk/dt , and K_{th} can be found. At the present time a load cell is being designed to be used with the DCB specimen.

Plotted in Figure 1 is the result of the grain size determination that is completed. The results indicate that at a given temperature, once a critical grain size has been reached, growth apparently stops at least for times up to 16 hours and less. These critical sizes are $\sim 30\mu$ ($900^\circ C$), 50μ ($1,000^\circ C$), and $\sim 120-140\mu$ ($1,100^\circ C$). The time needed to reach a critical grain size appears to be less than one hour for austenizing temperatures of $900^\circ C$ and $1,000^\circ C$, but greater than four hours for the $1,100^\circ C$ austenitizing temperature. The difference in the times needed to reach the critical grain size is probably due to the much higher impurity solubility at higher temperatures; and, therefore, the reduction of grain boundary pinning.

Figure 1. 4340 steel grain size versus austenitizing treatment.

Yet to be completed is the determination of a tempering schedule that will give a consistent yield stress (σ_{ys}) of about 220,000 psi.

II-3-3. GRAIN SIZE CONTROL

The development of a heat treating schedule to produce the desired grain sizes has almost been completed. The technique used in determining the heat treating schedule is as follows:

A 3/4" diameter rod of rolled 4340 steel was cut into one-inch-long sections. These samples were then austenitized for 1½ hours at 900°C, then quick quenched to assure uniformity of microstructure in all of the specimens. Next the sections were austenitized at several temperatures--900°C, 1,000°C, and 1,100°C for times varying from 1 to 16 hours. After austenitizing, the specimens were step-quenched to 650°C for ½ to 1 hours. This step-quench allowed the ferrite to precipitate out at the grain boundaries and in so doing, making grain size determination easier. The specimens were finally polished, etched, and photographed. The grain sizes were determined from these photos for each of the three different grain sizes.

The heat treatment of the specimens for grain size determination was done in open air furnaces. The presence of air allowed heavy oxidation formation and heavy decarburization to occur. To prevent occurrence of this with the test specimens, a vacuum furnace with an inert gas (argon) purging system will be utilized.

NOTE: The test specimens are now in the process of fabrication, the vacuum furnace is assembled, and several specimen load cells are under production.

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III. DETERMINATION OF CHANGES IN DISLOCATION DYNAMICS WHICH RESULT
IN THE DUCTILE-BRITTLE TRANSITION FOUND IN BCC METALS

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III-1. Acoustic Emission in Steels

William W. Gerberich, David G. Atteridge, and Yew-Tsung Chen

III-1-1. INTRODUCTION

Some preliminary results on acoustic emission in low strength steels were slightly discouraging. Indications were that the general level of activity was quite low, making analysis with standard commercial equipment difficult. To ascertain if this was the general case for Fe-base alloys, a series of tests on 4340 heat treated to different strength levels, along with initial tests on Fe and Fe-4% Si, were made.

III-1-2. EXPERIMENTAL PROCEDURE

Standard tensile bars with 0.10" x 0.25" x 1" gage sections were prepared and carefully ground so as to remove any potential brittle layers that could have developed during heat treatment. These specimens were loaded in an Instron at 0.05 inch/min to failure. Attached to the gage section were a linear variable differential transformer (LVDT) and a lead-zirconate-titanate (PZT) acoustic emission (AE) transducer. The latter was pass banded between 150 to 250 kHz. Count rate versus strain was facilitated with one x-y recorder. On an identically matched recorder, load versus strain was recorded. This allowed the stress-strain curve to be accurately superimposed on the acoustic emission-strain curve. This was essential in order to accurately assess acoustic emission count rate, $\dot{N}$, as a function of plastic strain. A typical recording of $\dot{N}$ used a reset clock set at one second intervals, so that the count would restart every second. For most of the 4340 samples, the ordinate represented 10^5 counts/second full scale. Where the yield strength was low, as in the 700°C tempered 4340 or

the Fe and Fe-4% Si, it was necessary to increase the sensitivity so that 10^4 or 10^3 counts/sec full scale were recordable.

III-1-3. RESULTS AND DISCUSSION

Some typical results for the 4340 steel are shown in Figure 1. The stress-strain curves have been superimposed on the original recording of the AE - strain curves. It is significant that as the stress-strain curve first deviates from linearity, the AE count rate is detected. In these instances, there is no question that the onset of count rate is commensurate with plastic deformation. It is of interest that the overall count rate level increases then decreases with increasing tempering temperature. A second feature is that the width of the AE count rate curve decreases with increasing tempering temperature. That is, the acoustic emission was spread out over a smaller plastic strain range as the work-hardening decreased. This was even more pronounced with the Fe and Fe-4% Si data where observable acoustic emission occurred over a plastic strain range about an order of magnitude less than that indicated in Figure 1.

In order to make a quantitative assessment, a procedure previously used⁽¹⁾ to relate $\dot{N}$ to plastic strain was a form of the Gilman⁽²⁾ model as represented by

$$\dot{N} = m_p \epsilon_p e^{-\phi \epsilon_p} \quad (1)$$

where m_p is some dislocation multiplication factor, ϵ_p is the plastic strain and ϕ is a work-hardening parameter. The best constants, as chosen for m_p and ϕ to give a fit to the AE data in Figure 1, are given in Table III-1. Analysis of the data is dependent upon how one

Figure 1

Figure 1. Relationship between stress-strain behavior for 4340 steel and stress wave emission.

TABLE III-1: TENSILE AND ACOUSTIC EMISSION RESULTS

MATERIAL AND TEMPER	YIELD STRENGTH psi	ULTIMATE STRENGTH psi	ELONGATION %	$\dot{m}_p$ Sec ⁻¹	ϕ
Fe	15,700	29,000	46	1.01×10^7	13,150
Fe-4% Si	39,200	68,100	32	2.15×10^7	10,500
4340/700°C	122,000	139,000	11.5	2.67×10^7	2,800
4340/580°C	159,000	171,000	7.5	2.84×10^8	1,430
4340/480°C	173,000	187,000	7	3.50×10^8	1,430
4340/400°C	198,000	214,000	5	3.16×10^8	1,250
4340/400°C	198,000	219,000	5	3.40×10^8	1,320
4340/300°C	208,000	239,000	6	2.96×10^8	1,110
4340/300°C	208,000	242,000	4	2.00×10^8	830
4340/200°C	223,000	280	5	3.62×10^7	1,020
4340/200°C	223,000	270	(1)	7.90×10^7	1,430

(1) loading pins broke.

relates $\dot{N}$ to the actual dislocation events involved in the plastic deformation process. First, consider the multiplication factor. From Table III-1, m_p data are plotted as a function of yield strength in Figure 2. The large increase in m_p with increasing yield reflects the fact that count rates were more than an order of magnitude less in Fe and Fe-4% Si as compared to high strength 4340 steel. The peak of m_p with increasing yield shown in Figure 2 is both interesting and disturbing. Certainly, at the lower yield strengths, fewer dislocations could be moving larger distances at lower energy levels so that the multiplication coefficient might be lower. It is not possible at the present time to conjecture why m_p decreases at the highest yield strength.

Next, consider the parameter ϕ as given in Table III-1. As a first approximation, it is seen that ϕ decreases with increasing yield strength. The interpretation of this would depend on how Eq. (1) is treated. One suggestion has been that $\dot{N}$ pertains to mobile dislocation density, ρ_m .⁽¹⁾ However, this is not compatible with the general observation that the density of stored dislocations increases with plastic strain. That is, Bergstrom⁽³⁾ has shown that the rate of increase in mobile dislocation density is

$$d\rho_m/d\epsilon_p = dc/d\epsilon_p + dr/d\epsilon_p \quad (2)$$

where $dc/d\epsilon_p$ is the rate of creation of dislocations and $dr/d\epsilon_p$ is the rate of remobilization of immobile dislocations. If the rate of dislocation annihilation is $da/d\epsilon_p$, then the rate of increase of stored dislocations, $d\rho_s/d\epsilon_p$, must be given as the difference between created and stored dislocations. Thus, Bergstrom finds⁽³⁾ that

Figure 2. Multiplication factor as a function of yield strength.

$$d\rho_s/d\epsilon_p = d\epsilon/d\epsilon_p - da/dr_p = d\rho_m/d\epsilon_p - dr/d\epsilon_p - da/d\epsilon_p \quad (3)$$

It is obvious then that $d\rho_m/d\epsilon_p$ cannot be negative since $d\rho_s/d\epsilon_p$ is observed to be positive from transmission microscopy studies. Clearly, since $\dot{N}$ decreases on the downside of the peak AE in Figure 1, then $\dot{N}$ cannot be associated with ρ_m since $d\rho_m/d\epsilon_p$ would then be negative on the downside of peak AE.

If $\dot{N}$ represents the rate of increase of mobile dislocations, then the data in Figure 1 as represented by Eq. (1) would not violate Eq. (3). Actually, $\dot{N}$ would represent the rate of increase with respect to time. To obtain the rate of increase with strain, we find

$$\frac{d\rho_m}{d\epsilon_p} = \frac{d\rho_m}{dt} \cdot \frac{dt}{d\epsilon_p} = \frac{1}{\dot{\epsilon}} \frac{d\rho_m}{dt} \quad (4)$$

since $d\rho_m/dt$ would be some large multiple, σ , of the observed AE count rate, Eqs. (1) and (4) would give

$$\frac{d\rho_m}{d\epsilon_p} = \frac{\sigma}{\dot{\epsilon}} m_p \epsilon_p e^{-\phi \epsilon_p} \quad (5)$$

where σ is on the order of $10^7/\text{in}^2$ or $1.5 \times 10^6/\text{cm}^2$. By integrating Eq. (5) one finds that

$$\rho_m = \frac{\sigma m_p}{\dot{\epsilon}} \left[A - \frac{1}{\phi^2} e^{-\phi \epsilon_p} - \frac{1}{\phi} \epsilon_p e^{-\phi \epsilon_p} \right] \quad (6)$$

where A is the integration constant. Since at $\epsilon_p = 0$, $\rho_m = 0$, the constant A is found to be $1/\phi^2$. If one now assumes in the initial stages of yielding that the rates of remobilization and annihilation are small compared to $d\rho_m/d\epsilon_p$, then ρ_m would give a reasonable estimate of

ρ_s . At least Eq. (6) would give a lower bound estimate of ρ_s . With this in mind, an estimate of the yield strength was calculated from the data in Table III-1. The procedure was as follows:

- i. Assume that $\dot{\rho}_m$ is zero at zero plastic strain.
- ii. Solve the integration constant, A.
- iii. Assume a constant $\alpha_m \dot{\rho} / \dot{\epsilon} \simeq 10^{18}$ and solve for $(\rho)_{\epsilon_p = 0.002}$ from Eq. (6).
- iv. Determine the flow stress from $\sigma_{ys} \simeq \alpha' E b \sqrt{\rho_{.002}}$ (7)

The only gross assumptions here are that $\alpha_m \dot{\rho} / \dot{\epsilon}$ is constant and that the AE is representative of moving dislocations in the initial stages of yielding. The result of this calculation is compared to the experimental data in Figure 3. It is seen that the trend in yield strength with ϕ is predicted. It is also noted that the theoretical estimate is a lower bound as suggested.

It would appear then that one might be able to simply express the flow stress in terms of some mobile dislocation multiplication function. The flow stress here would largely be represented by the large differences in the initial work-hardening capability in a high strength martensite as opposed to mild steel or Fe. Of course, it is not legitimate to use the identical parameters for all conditions tested. Nevertheless, the overriding consideration may be the rate of work hardening which occurs at minute plastic strains.

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Figure 3. Work hardening parameter as a function of yield strength.

III-2. Dislocation Dynamics in Fe-Base Systems Yew-Tsung Chen and William W. Gerberich

III-2-1. INTRODUCTION

The initial results from the acoustic emission and the change of strain rate tests in the present section raise serious questions about current approaches to dislocation dynamics.

Reservation No. 1.

Is it legitimate to treat strain rate sensitivity and dislocation dynamics in general by assuming mobile dislocation density, ρ_m , to be constant? J.C.M. Li⁽¹⁾ has questioned this procedure in a recent theoretical paper concerning the dynamic behavior of dislocation loops.

Reservation No. 2.

Can a linear extrapolation of the observed strain rate sensitivity, m' , at finite strains to the true value, m , at zero strain give realistic values? Of course, you need a realistic measure of $\partial \ln \rho_m / \partial \ln \dot{\epsilon}$ to assess this.

The present investigation along with proposed work will examine these reservation in detail.

III-2-2. EXPERIMENTAL PROCEDURE

As pertains to the experimental set-up, the present measurements utilized the same LVDT and X-Y recorder for the plot of load-strain as was described in Section III-1. The major difference was that a zero suppress was utilized on both stress and strain to allow accurate recordings of the load increment associated with a change of strain rate. Typical recordings are shown in Figure 1 for an order of magnitude change in strain rate. It is obvious that the Fe-4% Si alloy is considerably less sensitive to changes in strain rate than the pure polycrystalline Fe. From a series of such load changes at various strain rates, the log true stress

versus log true strain rate was plotted. This allowed $m' = \partial \ln \dot{\epsilon} / \partial \ln \sigma$, the strain rate sensitivity exponent, to be determined. In each series of tests, $(\partial \ln \dot{\epsilon} / \partial \ln \sigma)_\epsilon$ was determined as a function of strain so that the true value of m could be determined by extrapolation.

III-2-3. EXPERIMENTAL RESULTS

Results for pure Fe are shown in Figure 2. This is what one might expect for Fe with an m of 9 comparing favorably with the m of 7 obtained by Hildebrandt and Dickenscheid⁽²⁾. The increase of m' by a factor of three with increasing strain is similar to that observed by Mihalak⁽³⁾. Results for the Fe-4% Si are given in Figure 3. Again, this is similar to what has been determined for polycrystalline Fe-3% Si^(4,5) with m near 40 and m' increasing by less than a factor of two with strains up to 10 percent. The increase in m' with strain has been discussed by others^(4,5) and is considered to be due to the second term of the quantity, $\partial \ln \dot{\epsilon} / \partial \ln \sigma$. That is, the true value of m may be inferred from experimental observations of the dislocation velocity as given by

$$v = v_0 (\sigma / \sigma_u)^m \quad (1)$$

where σ_u is a constant determined at a dislocation velocity of $v_0 = 1$ cm/sec, and σ is the applied stress. Taking the log of Eq. (1) and differentiating with respect to stress gives

$$m = \frac{\partial \ln v}{\partial \ln \sigma} \quad (2)$$

However, if one takes the typical strain rate dependence in a crystal as

$$\dot{\epsilon} = \rho_m b v \quad (3)$$

Figure 2. Strain rate sensitivity exponent as a function of strain

Figure 3. Strain rate sensitivity exponent as a function of strain

then this can be decomposed into

$$m' = \frac{\partial \ln \dot{\epsilon}}{\partial \ln \sigma} = \frac{\partial \ln v}{\partial \ln \sigma} + \frac{\partial \ln \rho_m}{\partial \ln \sigma} \quad (4)$$

If the second term on the right hand side of Eq. (4) is zero at zero plastic strain, then $(m' = m)_{\epsilon_p = 0}$. One must question the wisdom of this approach, however, since the smallest change in going from $(\rho_m)_0$ to $(\rho_m)_{\epsilon_p}$ would represent a large $\partial \ln \rho_m / \partial \ln \sigma$. However, the fact is that $(m' = m)_{\epsilon_p = 0}$ does correspond reasonably well to m values taken from actual etch pit velocity measurements⁽⁵⁾.

In the following two sections, we first utilize the strain rate sensitivity measurements to interpret the yield stress, then attempt an analysis of $\partial \ln \rho_m / \partial \ln \sigma$ using the preliminary acoustic emission results.

III-2-4. YIELD STRESS ANALYSIS

In evaluating plastic flow behavior in Fe-base alloys, Bergstrom⁽⁶⁾ assumed that ρ_m was independent of plastic strain and in essence stated that $(m' = m)_{\epsilon_p}$ for all plastic strains. We know this to be incorrect. If we use the analysis for $\rho_m = f(\epsilon_p)$ as taken from section III-1, Bergstrom's⁽⁶⁾ analysis can be modified to

$$\sigma = \sigma_u \left[\frac{\dot{\epsilon}}{0.5 b \frac{\alpha}{\dot{\epsilon}} m_p v_o \left\{ A - \frac{1}{\phi^2} e^{-\phi \epsilon_p} - \frac{1}{\phi} \epsilon_p e^{-\phi \epsilon_p} \right\}} \right]^{1/m} + \alpha' \mu b \sqrt{\rho_o + m \epsilon_p} \quad (5)$$

where the first term includes both the athermal stress and strain rate sensitive portions and the second term is the work hardening term. The appropriate constants from sections III-1 and III-2, from Bergstrom⁽⁶⁾ and

from Hildebrandt and Dickenscheid⁽²⁾ are:

$$\begin{array}{ll}
 \sigma_u = 20 \text{ kg/mm}^2 & \alpha' = 0.8 \\
 \dot{\epsilon} = 10^{-3} \text{ sec}^{-1} & n = 9 \\
 v_o = 1 \text{ cm/sec} & u = 8 \times 10^3 \text{ kg/mm}^2 \\
 \alpha = 1.5 \times 10^6 / \text{cm}^2 & b = 2.5 \times 10^{-8} \text{ cm} \\
 m_p = 1 \times 10^7 & \rho_o = 1.5 \times 10^8 / \text{cm}^2 \\
 A = 0.58 \times 10^{-8} & M = 1.5 \times 10^{11} / \text{cm}^2 \\
 \phi = 13,150
 \end{array}$$

Inserting these values into Eq. (5) and evaluating at $\epsilon_p = 0.002$ (i.e. at yield), gives

$$\sigma_{.002} = 8.6 + 3.4 = 12.0 \text{ kg/mm}^2 \quad (6)$$

This compares to the observed yield strength value of 11 kg/mm^2 (15,700 psi). The largeness of the strain rate sensitive term may be due to an overestimate in m . The next section deals with this strain-rate exponent.

III-2-5. EFFECT OF $\partial \ln \rho_m / \partial \ln \sigma$ ON m .

If the acoustic emission data are giving a true trend in mobile dislocation density, then the second term in Eq. (4) could be evaluated. In conjunction with the strain rate sensitivity measurements of m' , this could make a powerful analysis technique. First, how do we evaluate $\partial \ln \rho_m / \partial \ln \sigma$? By the chain rule,

$$\frac{\partial \ln \rho_m}{\partial \ln \sigma} = \frac{\partial \ln \rho_m}{\partial \ln \epsilon_p} \cdot \frac{\partial \ln \epsilon_p}{\partial \ln \sigma} \quad (7)$$

The last term in Eq. (7) may be recognized from the relationship between true stress and true strain:

$$\begin{aligned}\sigma &= K \epsilon_p^n \\ \ln \sigma &= \ln K + n \ln \epsilon_p \\ n &= \partial \ln \sigma / \partial \ln \epsilon_p\end{aligned}\quad (8)$$

where n is the strain hardening exponent.

Combining Eqs. (7) and (8) gives

$$\frac{\partial \ln \rho_m}{\partial \ln \sigma} = \frac{\partial \ln \rho_m}{\partial \ln \epsilon_p} \cdot \frac{1}{n} \quad (9)$$

Next, we plot the $\ln \rho_m$ as a function of $\ln \epsilon_p$ as determined from Eq. (6) in section III-1. A graphical differentiation at the peak acoustic emission, $\epsilon_p = 0.000076$, gave

$$\left(\frac{\partial \ln \rho_m}{\partial \ln \epsilon_p} \right)_{\epsilon_p = 1/\phi} \simeq 1.35 \quad (10)$$

In combination with a measured strain hardening exponent of $n = 0.182$, Eqs. (9) and (10) would indicate that $\partial \ln \rho_m / \partial \ln \sigma$ was 7.4. At such small strains, the value of m' was no greater than 10. One is tempted to say that a large portion of the measured strain rate sensitivity is due to a rapidly changing mobile dislocation density.

At this time, we can make no claim that the acoustic emission result is giving us an unambiguous measure of mobile dislocation density. However, if it is giving even an approximate measure, then some very interesting questions are raised. In-depth measurements of m , m' and acoustic emission at various strain rates and test temperatures should be most informative.

III-2-6. REFERENCES

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III-3. Determination of the Ductile-Brittle Transition Temperature for Iron Binary Alloys

David G. Atteridge and Yet-Tsung Chen

III-3-1. INTRODUCTION

It is well known that bcc Fe alloys exhibit a ductile-brittle transition temperature (TT). The binary alloys for this study were chosen in hopes of increasing the understanding of why this transition takes place and how alloying elements effect the TT of the Fe Matrix. The current study includes Fe-Ni, Fe-Si and Fe-Pt alloys; the work performed during this research period concentrated on developing the TT curves for the Fe-Ni and Fe-Si alloys.

Ni and Si were chosen for this study as both have a solute softening effect on Fe but different effects on the TT, with Ni decreasing and Si increasing the TT. Also Ni is a transition element and Si is a non-transition element. This combination of similarities and differences will allow detailed study into many contradictory alloying element effects.

The results of the TT determinations will be used in determining the test temperatures used for the subsequent tensile and fracture toughness specimen studies performed on these alloys. The mechanical properties found at test temperatures above the below the given alloy's TT will be used to characterize the change in mechanical properties accompanying the TT phenomenon.

III-3-2. EXPERIMENTAL PROCEDURES

The alloys were subjected to thermal mechanical processing prior to test specimen machining in order to obtain a constant grain size for all

alloys. The alloys were subjected to a combination of forging and hot rolling in order to break up the as-cast structure and assure a homogeneous alloy. They were then austenitized and cold worked prior to an intermediate-temperature grain-growth treatment; the exact procedures and temperatures used are given in the previous annual report. Half-size Charpy impact specimens were then machined from the alloys and tested at various temperatures to determine the given alloys TT.

III-3-3. RESULTS AND DISCUSSION

The Fe-Ni results, Figure 1, again substantiate that the addition of Ni decreases the TT of Fe. The TT, shown as a function of composition in Figure 2, deviates slightly from a linear relationship between the alloy composition and the change in TT per atomic percent Ni. It ranged from $25^{\circ}\text{C/at.}\% \text{ Ni}$ at 1 at.% Ni to $22^{\circ}\text{C/at.}\% \text{ Ni}$ at 4 at.% Ni with an average value of $23.4^{\circ}\text{C/at.}\% \text{ Ni}$. This problem, along with that of predicting the change in TT with the addition of transition alloying elements, is discussed further in Section III-4.

The Fe-Si alloy results are shown in Figure 3. The TT exhibits a decrease at low Si concentrations and then an increase as the Si concentration is increased (Figure 4); this latter effect results in a change in TT of $23.3^{\circ}\text{C/at.}\% \text{ Si}$ at higher concentrations. Although it is felt that the original decrease in TT is indeed real, further testing is currently being conducted to substantiate these results.

The same type of experimental results for Si is reported by Leslie, although the interpretation of his results is confused by the inclusion of results for both grain-size "corrected" and "uncorrected" TT determinations⁽¹⁾

Figure 1. Fe-Ni alloy transition temperature determination

Figure 2. Transition temperature change determined by half-size Charpy impact specimens

Figure 3. Fe-Si alloy transition temperature determination

Figure 4. Transition temperature change determined by half-size Charpy impact specimens

The uncorrected TT results show the same trend as seen in Figure 4, while the corrected results show a continuously increasing TT for Si; Leslie argues that the "binary" alloy results are independent of grain size and thus uses the uncorrected results in his analysis.

The change in the effect of Si on ATT with changing Si composition seems at first glance to be contradictory. In fact, this change in effect can be predicted through the use of the Engle-Brewer Correlation if the reasoning used in the prediction of TT for the transition elements in Section III-4 is applied to non-transition elements such as Si. At low Si concentrations the increase in matrix s,p electrons per atom would lead to a decrease in TT, as the concentration of Si is increased, solute-solvent electronic configuration interaction leads to an ordered alloy which in turn leads to an increase in TT, due to the increased shear stress needed to move dislocations through the ordered alloy.⁽²⁾ The interacting of these two opposing effects would lead to the experimental results reported above. This problem and the possibility of developing a TT prediction model incorporating non-transition elements as well as transition elements is discussed further in the proposal for further work submitted with this report.

The trend toward an increase in upper-shelf impact energy with increasing alloy content evident for all alloys is thought to be due to the increased yield strength from solid solution hardening. The decrease in upper-shelf impact energy with increasing temperature is thought to be due to the decrease in yield strength as temperature is increased. The former ideas are based on the assumption that the plastic flow during impact testing in the upper-shelf region is approximately constant at all temperatures and

that very little change in the rate of work hardening takes place. Therefore, the plastic energy dissipated by the specimen is directly related to the yield strength. The effect of temperature on the tensile properties of these alloys is currently being investigated.

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III-4. Theoretical Modelling of the Ductile-Brittle Transition Found in BCC Transition Metal Alloys

David G. Atteridge and William W. Gerberich

III-4-1. INTRODUCTION

The physical phenomenon of bcc metals exhibiting a ductile-brittle transition temperature (TT) has been well documented, along with the change in TT (ΔTT) as a function of alloying content. Theoretical reasons for the ΔTT as a function of alloying composition and a model for predicting the sign and magnitude of this change have been much more elusive.

This paper presents an empirical correlation model developed in an effort to understand and predict the ΔTT of bcc transition metals as a function of dilute solid solution alloying additions. The proposed model incorporates size difference, electronic structure, cohesive energy, and solubility effects in predicting TT changes, and predicts the magnitude of both positive and negative changes.

III-4-2. SIZE EFFECT

Several investigators have suggested that atom size bears some relationship to the change in $TT^{(1,2)}$, and this indeed seems to be born out by the plot of a volume misfit parameter, ϵ_Ω , versus the TT change, as seen in Figure 1 (ϵ_Ω is described below). One tends to get increased change in the TT with increasing ϵ_Ω for both positive and negative TT deviations. These results lead to conflicting interpretation if it assumed that the resultant effect of a difference in size is independent of the given alloying addition. The authors have assumed that this correlation between increasing ϵ_Ω and the absolute magnitude of the TT change is fortuitous; we believe that other factors that affect the TT vary in essentially the same way as ϵ_Ω , leading to an apparent correlation of ϵ_Ω and $|\Delta TT|$.

Figure 1. Transition temperature change as a function of atom size differences

with alloying addition.

The theoretical analysis presented below predicts that as ϵ_Q increases the TT increases. This prediction comes from the effect on TT of a change in yield strength due to solid solution alloy additions; the change in yield strength is related to solute-solvent volume misfit through ϵ_Q . The analysis is based on a modified version of the Cottrell-Petch theory for grain size effect on TT ^(3,4).

The model takes into account localized orientation effects and solid solution hardening and may be given by

$$[(\sigma_i + \sigma_{ss})d^{\frac{1}{2}} + k_y] k_s \geq \beta \mu \gamma \quad (1)$$

where σ_{ss} is the solid-solution strengthening effect; β is the state of stress parameter which is 1, 1/2 and 1/6 respectively for torsion, tension and a sharp notch; μ is the shear modulus; γ is the effective surface energy; d is the grain size; and k_y and k_s are related by $k_y = m k_s$ where m is the Taylor orientation factor as discussed by Armstrong, et al.⁽⁵⁾. A metal exhibits brittle fracture at temperatures where the stress required to shear the metal (related to the terms on the left side of the inequality) is equal to or greater than the stress required to cleave the metal (related to the terms on the right side of the inequality); the TT is that temperature where the equality holds. If a simple exponential dependence of σ_i on temperature is assumed, as originally suggested by Petch⁽⁶⁾, it then follows that

$$\sigma_i = B \exp(-CT) \quad (2)$$

where B and C are constants.

Combining Eqs. (1) and (2) gives the transition temperature

$$TT = C^{-1} \ln \{ Bk_s d^{\frac{1}{2}} / (B\mu Y - \sigma_{ss} d^{\frac{1}{2}} k_s - k_y k_s) \} \quad (3)$$

It is seen that if Y decreases or if either σ_{ss} or k_y increase with addition of solute the TT will increase. If it is assumed that solute additions only affect σ_{ss} , it is possible to predict the effect of atom size and solute concentration on the transition temperature.

First, it is necessary to describe the atom size effect on yield strength. Rudman has described solid-solution strengthening in terms of atomic volume misfit,⁽⁷⁾ and Garfinkle has treated the effects of alloying additions on lattice dilation in non-isostructural systems using an average atomic volume,

$$\Omega = V/n \quad (4)$$

where V is the atomic volume which may be calculated from the atomic weight, density and Avagadro's number and n is the number of atoms per unit cell⁽⁸⁾. The volume misfit can then be described by

$$\epsilon_{\Omega} = \left| \frac{\Omega - \Omega_0}{\Omega_0} \right| \quad (5)$$

where Ω is the average atomic volume of the solute addition and Ω_0 is the average atomic volume of the base metal.

Friedel's concept that solid solution strengthening is simply proportional to concentration was used to reduce the experimental data to $\Delta\sigma_{LYS}/\text{at.}\%$ (LYS = lower yield strength)⁽⁹⁾. The relationship between $\Delta\sigma_{LYS}/\text{at.}\%$ and ϵ_{Ω} for Fe, Cr, Ta, and Nb base alloys, as determined

from Figure 2, is given by

$$\Delta\sigma_{\text{LYS}} = \alpha f [\epsilon_{\Omega}]^{\frac{1}{2}} \quad (6)$$

where α is about 17,000 psi and f is the solute addition in atomic percent. This empirical relationship is reasonably good if it is restricted to volume misfits less than about 0.6 and the Cu and Mn results are ignored. The authors feel that the latter is legitimate as Mn is a very complex atom and it is uncertain whether the simple misfit parameter described here is adequate, and precipitation of metallic Cu occurs to give rise to a precipitation hardening effect rather than solid solution hardening.

Using Eq. (6) as a measure of solid solution strengthening, combining this with Eq. (3) and differentiating leads to

$$\frac{dTT}{df} = \frac{A/C}{(D-E) - Af} \quad (7)$$

$$A = \alpha [\epsilon_{\Omega}]^{\frac{1}{2}} k_s d^{\frac{1}{2}}$$

$$D = \beta \mu Y$$

$$E = k_y k_s$$

It is obvious that Eq. (7) does not predict a linear change of TT with increasing solute concentration, but it definitely predicts an increase in TT with increasing solute additions.

Eq. (7) was then solved for Fe-binary solutions at 0.1 and 1 atomic percent alloy additions, as the data used to arrive at the normalized ΔTT data presented in Figure 1 came from alloys with compositions that usually fell within this range. The results are compared with data for elements

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Figure 2. Solid Solution Strengthening as a function of atom size difference

that increase the TT in Figure 3. The values used for the constants in Eq. (7) are given below

$$C \simeq \frac{1}{25}, \quad k_y = 700 \text{ psi-in}^{\frac{1}{2}}, \quad k_s = 225 \text{ psi-in}^{\frac{1}{2}}, \quad d = 10u$$

$$\beta = 1/6, \quad \gamma = 0.114 \text{ lb/in}, \quad \mu = 12 \times 10^6 \text{ psi}, \quad \alpha = 17,000 \text{ psi}$$

Considering the assumptions made, the fit is reasonable and clearly indicates that a positive increase in transition temperature could be explained wholly by an increase in the yield strength due to solid solution strengthening.

III-4-3. ELECTRONIC STRUCTURE AND COHESIVE ENERGY

The results of this section indicate that the decrease in TT for a given bcc transition element matrix can be explained as a function of solute crystal structure and cohesive energy for transition alloying elements exhibiting substitutional solid solubility. A review of the transition series elements that are found to lower the TT by the above criterion indicates that all of them exhibit either hcp or fcc as their stable structure or as one of their allotropic structures. Those elements increasing the TT and meeting the above criterion are found to exhibit bcc as their stable structure or as one of their allotropic structures.

In general, the elements exhibiting the fcc structure decrease the TT to a greater degree than elements exhibiting a hcp structure, particularly when elements in the same Period of the Periodic Table are compared. It was also noted that the change in TT generally increased as one proceeds to higher Periods for a given Group, in the Periodic Table. These generalizations can be quantized through the use of the Engle-Brewer Correlation (EBC) between structure and electronic configuration.

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Figure 3. Transition temperature change predicted by solid solution strengthening.

The EBC states that the three basic crystal structures that are found in metals can be directly correlated with the number of valence electrons in the s , p shell of the given element. (The s and p valence electrons are considered together in the EBC; thus the sum of the number of s and p valence electrons per atom will be used throughout this paper)⁽¹⁰⁾. The assumption that the type of bonding an element exhibits depends on the number of s , p electrons per atom (e/a) interacting with its neighbors is not new, and is well accepted in describing bonding in organic and inorganic chemistry for elements which only have s , p valence electrons. The EBC breaks with convention because this assumption is applied to metal atoms that have other types of valence electrons than just s , p .

The EBC is based upon the Valence Bond Model which assumes that the valence orbitals found for a given element exhibit essentially the same orbital configuration found in the hydrogen-type atom⁽¹¹⁻¹²⁾. This implies that the s , p electrons form bonding orbital configurations exhibiting long range interactions between other atoms besides nearest neighbors while d and/or f electrons can be thought of as bonding to nearest neighbors only and being directional in character. This indicates that the unfilled inner shell d and f electrons interact with nearest neighbors, and therefore contribute to the total cohesive energy of a given structure, but that the type of long range structure found in a given alloy is solely dependent upon the reaction of the outer shell s , p valence electrons with other than nearest neighbor atoms.

The basic hypothesis of the EBC, then, is that the electronic configuration found in a solid metal is not necessarily the same as that found in the

gas, and that once one knows either the solid electronic configuration or the crystal structure one knows the other^(10,13). Brewer incorporated this reasoning with the experimental work of Hume-Rothery to define the expected composition ranges of the structures⁽¹¹⁾. Hume-Rothery experimentally studied alloys of non-transition metals, which have only s, p valence electrons, and developed experimental s, p e/a composition ranges for these same structures. The EBC sets relatively fixed s, p e/a concentration limits for each crystal structure, and has been shown to be surprisingly successful in predicting both the correct sequence of phase changes in a given alloying system and the approximate composition stability ranges of the phases^(10,13). The stability proceeds from bcc to hcp to fcc as the number of s, p e/a increases; the predicted phase stability ranges as a function of s, p e/a are given below:

<u>Phase</u>	<u>Composition Range (s, p e/a)</u>
bcc	1.0 - 1.5
hcp	1.7 - 2.2
fcc	2.5 - 3.0

The simplified integer approximations of 1 s, p e/a for bcc, 2 s, p e/a for hcp, and 3 s, p e/a for fcc will be used in the calculations presented in this paper.

Once one has decided to use the integer s, p e/a approximations one can immediately determine the solid state electronic configurations for the transition elements exhibiting only one solid state crystal structure; the given crystal structure determines the number of s, p e/a, and the rest of the valence electrons are therefore d shell electrons. The structure used for the elements exhibiting allotropic phase transformations was the structure predicted to be stable in dilute solutions with the given bcc

metal. This was determined through the use of the phase stability rules, for elements exhibiting allotropy, pointed out in the explanation of the application of the EBC⁽¹⁰⁾.

The cohesive energies for the various transition elements can be calculated, after the electronic structures are determined, through the use of the graphs of cohesive energy per bonding electron given by Brewer⁽¹⁴⁾. These graphs present the cohesive energy per valence electron as a function of electron type and shell number designation.

A plot of the cohesive energy per s, p electron as a function of shell number and element is given in Figure 4. The cohesive energy attributed to the d electrons is also plotted in Figure 4 as a function of shell number and both the total number of d shell e/a and the number of bonding d shell e/a. The determination of the number of bonding d e/a is made from the fact that the d shell can accommodate only 10 electrons, and that once it is half full the added electrons must form non-bonding pairs. The formulas for calculating the number of bonding d e/a are given below.

For the total number of d e/a ≤ 5 ,

No. of bonding d e/a = total No. of d e/a.

For the total number of d e/a > 5 ,

No. of bonding d e/a = 10 - total no. of d e/a.

The cohesive energy contributed per s, p electron is essentially constant, although it does tend to increase slightly as the atomic weight increases. The cohesive energy for the 5d shell electrons goes through a maximum at 5 bonding d e/a even though the cohesive energy per bonding electron increases as the number of bonding d electrons decreases. The

FIGURE 4. COHESIVE ENERGY AS A FUNCTION OF ELECTRONIC STRUCTURE

results for the 3 and 4d shell electrons becomes more complex near 5 d bonding e/a , but still tend to follow the same trend*. The cohesive energy graphs were used to calculate the cohesive energies for all the transition series elements. The results of these calculations are plotted in Figure 5.

These results show that the change in TT is not a direct function of the change in cohesive energy upon alloying. Both elements decreasing and increasing the TT are found to exhibit larger cohesive energies than the respective matrix metals. This is demonstrated for Cr alloys wherein Ru and W both have approximately the same cohesive energy but produce opposite effects on TT . It is also evident that the increase in cohesive energy is not a function of the increase in total valence electrons, as Fe and Cr are in the middle of the periodic Table and elements on either side of them exhibit cohesive energies of much larger magnitudes.

In general the elements proceed from bcc to hcp to fcc as the number of total valence electrons increase. The cohesive energy also tends to increase as one goes from bcc to hcp to fcc, if one restricts the comparison to elements in a given Period. The cohesive energy for elements in a given Group increase as the Period number increases. There is also a tendency within a given Period for the cohesive energy in a given crystal structure to increase as the number of bonding electrons increase. This increase in the number of bonding electrons corresponds to an increase in the total number of valence electrons only up to a total of six valence electrons; from this number on the increase in total number of valence electrons is opposite to the

* It should be noted that as the number of bonding d electrons increase so do the possible bonding configurations and therefore the spread in energy between the lowest possible energy state and the highest possible energy state for the given electronic configuration. Brewer used the lowest energy states values for his calculations, as these were the only ones available. If he had used the average energy values it would have tended to eliminate the dip found in the energy curves near 5 d electrons⁽¹⁴⁾.

Figure 5. Cohesive energy as a function of element and structure.

increase in the number of bonding electrons.

This lack of direct correlation between TT and cohesive energy is not too surprising if one assumes that the observed TT in bcc metals is due to the large covalent character of their bonds. It is well known that the relatively open bcc structure would transform spontaneously into one of the close packed structures if it were not stabilized by strong directional bonds between atoms^(15,16). As dislocation induced slip requires "bending" of atomic bonds as the dislocation travels down the slip plane, it is postulated that the strong directionality of the bcc bonds makes slip increasingly difficult as the temperature is decreased. This would be due to an increase in the applied energy required to "bend" bonds as the thermal vibration component decreased. This effect would be similar to that found in Si, where one is able to propagate dislocations in a covalent material at sufficiently high temperatures where the thermal vibrations of atoms becomes significant⁽¹⁷⁾.

Strong directional bonding is not found in either the hcp or fcc metals as evidenced by their lack of strong temperature dependence of the yield strength. Their close packed structure also indicates their lack of directional bonds, as this is the maximum packing density one can achieve with spherically symmetrical balls.

This reasoning leads to the assumption that the over-riding consideration in determining the effect of a given substitutional alloying element on dislocation mobility would be the amount of covalent bond character it exhibited. The cohesive energy would be a secondary consideration, if it is assumed that the ability of a given atom to retain its innate bonding characteristics in a foreign environment increased as its cohesive energy

increased.

The above reasoning leads to the hypothesis for the electronic structure and cohesive energy model presented below. The model is based on two assumptions. The first is that if one starts with a bcc matrix and adds an element that increases the number of s, p e/a the increase in s, p bonds will increase the non-directional bonding interactions and promote slip by increasing the ease with which nearest neighbor bonds "bend" and transfer from one atom to another*. The second is that if one starts with a bcc material and adds another bcc element that increases the cohesive energy or the number of d e/a, that element will increase the covalent -- or directional-type -- bonding over that found in the matrix and promote cleavage by the formation of bonds with increased resistance to "bending", thereby decreasing the ease of plastic flow. As it is assumed that all bcc elements have 1 s, p e/a, the cohesive energy due to the s, p e/a changes very little with the addition of bcc alloying elements (Figure 4), and therefore the difference is ignored in the construction of the prediction model. It is postulated that the elements that increase the number of s, p bonds over the number of d bonds in bcc metals promote slip and decrease the TT while elements which have the opposite effect promote cleavage and increase the TT .

If the atomic bond structure and characteristics are dependent upon the number of s, p e/a, and one assumes that alloying elements in dilute

* It is assumed that the increase in the number of s, p e/a decreases the temperature dependent component of the Pierel's Force, thus decreasing the temperature dependence of the yield stress(18,19). This may explain the "solute softening" effect found in many binary bcc matrix alloys(20,21,22,23).

solution essentially exhibit their pure metal bonding characteristics, one can hypothesize a model for decreasing the TT as one adds hcp or fcc alloying elements to bcc metals. This decrease in TT is postulated to be due to a localized region around the alloying atom having its directional bonding characteristics reduced due to the localized increase in the number of s, p e/a associated with the alloying element. If this is so, one can assume as a first approximation that the size of the localized region affected would be related to the number of s, p e/a associated with the alloying element and available for interaction with the bcc matrix atoms. This model predicts that fcc metals, with 3 s, p e/a, would be more effective in lowering the TT than hcp metals, with 2 s, p e/a, which, as mentioned above, agrees with the experimental data.

The assumption is also made that two secondary effects are important. The first is the change in the relative number of valence s, p e/a to bonding d e/a between the alloying element and the bcc matrix element; this relative number of electrons, R_e , is expressed as a ratio of the s, p e/a to bonding d e/a for a given crystal structure. It is postulated that the higher the ratio of s, p e/a to bonding d e/a an element has, the more effective it will be in increasing dislocation mobility; conversely, it is assumed that the smaller this ratio is for a bcc alloying addition the greater will be the tendency for the element to decrease dislocation mobility.

The other factor deemed to be important is the cohesive energy of the given alloying element. Increasing the cohesive energy of a given element with a given structure and R_e is assumed to increase the retention of its bond characteristics, and therefore increase its effect upon the dislocation

mobility of the matrix. This quantity is entered into the calculation as a normalized cohesive energy ratio; the cohesive energy ratio, R_{CE} , is normalized for each structure and each Group in the Periodic Table. This is done by dividing the cohesive energy for a given element in a given structure by the cohesive energy of the element in Period IV in the same group and with the same electronic configuration; this procedure was possible as the cohesive energy was found to increase as the Period number increased.

All the various factors mentioned above were then combined into an electronic structure factor ϵ_e which is given below.

$$\epsilon_e = \epsilon_d - \epsilon_{s,p}$$

$$\epsilon_d = \frac{F}{A} \left(\frac{R_e^A}{R_e^M} \right) R_{CE}^A$$

$$\epsilon_{s,p} = G \left(\frac{R_e^A}{R_e^M} \right) R_{CE}^A$$

$$F = [2 - (\#_{s,p} e/a)_A] [2 - (\#_{s,p} e/a)_A]$$

$$G = (\#_{s,p} e/a)_A - 1$$

$$R_e = \frac{\#_{s,p} e/a}{\# \text{ bonding } d e/a}$$

$$R_{CE}^A = CE^A / CE^{A*}$$

$$CE^A = \text{Cohesive energy of alloy element A}$$

$$CE^{A*} = \text{Cohesive energy of element in Periodic IV and same Group as element A}$$

The matrix element parameters are designated by M ; the alloy parameters by A. The constants are simply put in so that, for this first approximation, only one term of ϵ_e is used for elements predicted to increase or decrease

the TT. The electronic structure factor was then plotted in Figure 6 utilizing the data for Fe, Cr, Ta, Nb, W and Mo base binary alloys used previously in this report.

The results of the plot of ϵ_e against ΔTT indicate that the efficiency of the elements lowering the TT is greatly affected by electronic configuration and cohesive energy levels, but that elements that raise the TT are essentially unaffected by a change in cohesive energy. These results were then combined with those of the previous sections where ϵ_Ω was derived. The composite size and electronic structure factors were combined to yield $(\epsilon_R = 10 \epsilon_\Omega + \epsilon_e)$; the results are plotted in Figure 7. It can be seen that the scatter in the data for the elements raising the TT has been considerably reduced, and that the data for the elements that decrease the TT cluster around a line which yields decreasing values of ϵ_R as the TT decreases.

III-4-4. SOLUBILITY

The authors feel that one of the major factors that contribute to the effectiveness of a given element in its effect on the TT is its inherent solid solubility. This paper deals only with the prediction of dilute solid solution effects so that clustering is not felt to be a significant contributing factor, but it is felt that an element that exhibits a low solid solubility will be more effective in its change in the TT than elements exhibiting high solubility.

This effect is hypothesized to come about by an increase in the number of solute atoms found at dislocations as the given element solubility decreases. It is felt that the low solubility elements will find a more

Figure 7. Transition temperature change predicted by solid solution strengthening and electronic structure.

compatible environment in the disordered region around a dislocation as a first step toward clustering or precipitation. The previous results presented in this paper have essentially assumed a random solid solution distribution; the introduction of a solid solubility parameter tries to take non-random distributions into account.

The model assumes that a decrease in solubility increases the effectiveness of a given atomic percent of solute due to an increase in the amount of solute at matrix dislocations. This assumes, as discussed above that the ease of moving existing dislocations is what controls the change in TT . There are several ways that solubility has been estimated in the literature. One is by assuming that the difference in atom size is inversely proportional to solubility⁽²⁴⁾; size difference has, however, already been used to characterize solid solution strengthening in the first section of the paper. Another way to describe solubility is to compare heats of sublimation, or cohesive energies, and assume that solubility is inversely proportional to some function of the difference⁽²⁵⁾. This latter approach is widely used in liquid chemistry and was used by Brewer in predicting the maximum solubilities of various combinations of transition elements; it will be used here also^(10,13).

The model that the calculations are based upon is essentially the normal solution model used to estimate miscibility as a function of temperature⁽²⁵⁾. The model assumes that the binding energy of solute to solvent atoms varies as the geometric mean of the energies and results in a energy function of the following type

$$T_c = \left(\frac{\bar{v}}{2R} \right) (\delta_1 - \delta_2)^2$$

$$\delta = \left(\frac{\Delta E}{v} \right)^{\frac{1}{2}}$$

where T_c is the critical temperature of mixing, δ is the solubility parameter, ΔE is the heat of sublimation (or cohesive energy), and v is the molar volume. The simplifying assumption that the solubility was inversely proportional to $(\Delta\delta)^{\frac{1}{2}}$ was made for the calculations used in this paper. The composite TT factor that was arrived at is given below

$$\epsilon_T = \epsilon_R(\epsilon_s + 1)$$

$$\epsilon_s = 10^{-3}(\Delta\delta)^{\frac{1}{2}}$$

The result of plotting this factor against TT is shown in Figure 8. It can be seen that the change in TT is a direct function of ϵ_T , with elements exhibiting a decrease in TT exhibiting a negative ϵ_T and elements exhibiting an increase in TT exhibiting a positive ϵ_T . The absolute value of ϵ_T increases as the absolute value of ΔTT increases.

III-4-5. DISCUSSION

The empirical model presented above predicts the ΔTT per at % solute atom for dilute solid-solution binary transition-metal alloys; both the sign and the relative magnitude of the TT changes are predicted. It incorporates solute-solvent size differences, electronic structure differences, and cohesive energy differences -- the latter two as determined by the EBC -- as a measure of the ease of plastic flow, which is postulated to control the TT.

In the development of the model it was found that the TT could not be directly correlated with the difference in cohesive energy between the solute and solvent atoms. It was shown that the cohesive energy tended to increase as the Period Number increased, particularly if one considered a given crystal structure and/or a given Group Number, and that the change in the

Figure 8. Transition temperature change predicted by solid solution strengthening, electronic structure and solid solution solubility.

cohesive energy within a given Period corresponds to the change in the number of bonding electrons, as opposed to the total number of valence electrons.

An increase in ΔT was found to be predicted by a solid solution strengthening model based on the size difference between solute-solvent atoms; the decrease in ΔT was found to require the inclusion of an electronic structure and cohesive energy term. The volume mismatch term ϵ_{Ω} and the electronic structure-cohesive energy change term ϵ_e are combined as given below to give the predicted ΔT , ϵ_R .

$$\epsilon_R = 10 \epsilon_{\Omega} + \epsilon_e$$

The basic ΔT estimate was then multiplied by a solubility parameter term ϵ_s to try and include postulated changes in ΔT for a given alloy content due to a non-random solute atom distribution; the composite equation, ϵ_T , is given below.

$$\epsilon_T = \epsilon_R (10^{-3} \epsilon_s + 1)$$

The authors feel that the exceptional agreement found between the prediction of the sign of ΔT for a given alloying element and that reported in the experimental results, along with the order of magnitude estimate of ΔT , indicates that this first-approximation model contains the basic atomic properties needed to explain the ΔT due to substitutional solid solution alloying. It was not expected that this model would be able to predict the absolute magnitude of ΔT for a variety of reasons. One of the problem areas is that both the model and the data reduction technique

($\Delta T_T/\text{at}\%$) essentially assume a constant change in ΔT_T as a function of alloying additions; this was found to be theoretically questionable, as shown in the Size Effect section where it was predicted that the change in T_T due to this effect was not directly proportional the $\text{at}\%$ alloy addition. Experimentally, several factors such as limited solubility, non-homogeneity, and change in grain growth rate or phase transformation characteristics may vary as a function of alloy content and tend to argue against a constant change in T_T as a function of $\text{at}\%$ solute. Also trace concentrations of contaminant elements may exert a large effect on ΔT_T through interaction with matrix, intentional alloying elements, or other trace contaminants which bring into question whether all experimentally reported results are solely due to the intentionally added alloying element. One case in point is the currently contested question of the effect of Co on the T_T of Fe^(26,27).

This model for predicting ΔT_T as a function of substitutional solid-solution alloying elements for binary transition-metal alloys was presented in hopes that it might help increase the understanding of the relationship between atomic interactions and alloy behavior and lead to practical multi-component prediction models for ΔT_T .

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APPENDIX A. EFFECT OF HYDROGEN ON HIGH-STRENGTH
AND MARTENSITIC STEELS

APPENDIX A. EFFECT OF HYDROGEN ON HIGH-STRENGTH AND MARTENSITIC STEELS

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SAMPLE ABSTRACT

ANGER ELECTRON SPECTROSCOPY STUDIES OF HIGH TEMPERATURE ALLOY SURFACES:
G. J. Dooley, III and T. W. Haas, Aerospace Research Lab., Wright-Patterson
AFB, Ohio

Metals are often found to be deficient in one or more respects when they are employed in their pure or unalloyed state. Consequently, minor amounts of alloying elements are often added. But the basic role played by these additions is not well understood. The technique of Auger electron spectroscopy makes it possible to establish a surface enrichment or surface depletion of the impurities or of the alloying elements present in a multi-component material. After determining the surface behavior of these materials as a function of temperature, correlations can be made between observed surface phenomena and other previously observed properties, for example, corrosion. The addition of tin, iron, chromium and nickel to zirconium, to form the Zircalloys, has been studied from a surface segregation viewpoint and the findings from this study have helped to explain the known stress rate sensitivity of the Zircalloys at certain temperatures as well as the fundamental differences between the corrosion behavior of Zircaloy-3 and that of Zircaloy-4. Similarly, the addition of aluminum and vanadium to titanium in the Ti-6Al-4V alloy has also been examined. This study is now being extended to include some of the nickel-based superalloys where again it is felt that a degradation or an improvement in certain physical and chemical properties can be correlated with the behavior of the bulk solid surfaces.

EFFECT OF HYDROGEN ON HIGH-STRENGTH AND MARTENSITIC STEELS:

W. W. Gerberich, Department of Chemical Engineering and Materials Science,
University of Minnesota, Minneapolis

Analysis of hydrogen-stress field interactions under equilibrium and kinetic conditions have led to viable threshold and crack growth rate criteria. Experimentally, these models are consistent with available data on low and medium alloy high strength, martensitic steels. The effects of geometrical, stress intensity, environmental and material variables are included. Observed decreases in threshold stress intensity with increasing yield strength, hydrogen concentration, or specimen thickness are predictable from pressure tensor considerations. Similarly, increasing crack propagation rates as produced by increasing the same variables, are predictable from pressure tensor gradient considerations. The complex behavior of stress intensity (K) dependent and independent crack growth rate, commonly referred to as Stage I, II, III growth, can be explained in terms of the pressure gradient. The transition from K-dependent to K-independent growth kinetics occurs at a K magnitude equal to about 10 percent of the yield strength. This is predictable from elastic-plastic considerations. Three orders of magnitude increases in crack growth rate with either increasing thickness, tempering temperature or alloying additions, are observed. These are hypothesized to be due to a state of stress effect, a combined state of stress and hydrogen trapping effect, and a hydrogen trapping effect, respectively.

EFFECT OF HYDROGEN ON HIGH-STRENGTH AND MARTENSITIC STEELS

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INTRODUCTION

The traditional historical review will be forfeited. This is partially for the sake of brevity and partially for the desire to slice through the jumble of conflicting facts and theories. Before going on, however, the author would be remiss if Troiano (1-4) and his coworkers were not mentioned since developments in the hydrogen embrittlement of high strength steels have followed much of their lead. This is not to diminish the work of others and it is hoped that the reader will gain a historical perspective as the past is gradually woven throughout the paper.

It is first desired to present a coherent picture of what variables affect threshold stress intensity, crack growth rate and time to failure. To accomplish this purpose, what seems to be the interconnecting threads will first be extracted from some experimental evidence. Recent theoretical developments will then be incorporated into models for equilibrium and kinetic cracking conditions. Finally, a discussion of threshold stress intensity and crack growth rate data will cover geometrical, stress intensity, environmental and material variables. The validity of interconnecting threads will be confirmed where possible.

Let's examine Figure 1 (5). In each case there is a threshold stress intensity below which there is no failure. Secondly, larger applied stress intensities produce shorter times to failure. Thirdly, alloy composition can have a drastic effect on the total time to failure. On the other hand, alloy composition has little effect on the threshold stress intensity. In connection to this latter point, it may be noted that yield strength levels were

nearly constant. This independence of threshold stress intensity is not always observed. There is adequate evidence (6,7) that the threshold stress intensity, K_{TH} , is drastically affected by yield strength. That is, for the same steel tempered to a lower yield strength, K_{TH} increases as indicated in Figure 2. In addition, there is also a large increase in time to failure. Thus, for the same composition steel, tempering effects on microstructure and yield strength may change both kinetic and equilibrium conditions.

Considering the kinetics of crack growth, it is mind-boggling to attempt an assessment of the different behaviors observed. Intergranular, quasi-cleavage and ductile rupture type failures are all observed, sometimes in the same specimen (8). The crack growth kinetics are affected by a myriad of variables such that six orders of magnitude variation in da/dt is possible. At one time, it was thought that da/dt was proportional to K or K^2 (9-11). More recent studies (12,13) have further muddled the situation by suggesting that a plateau region exists where da/dt is independent of K . This has been associated with crack branching (12,13) although not necessarily dependent on it. In fact, steels exhibiting no branching have still been observed to exhibit the plateau region (14). This type of behavior is exhibited in Figure 3 for a range of materials and environments. The crack growth rate regions are labeled according to a convention instituted by Carter (12), where stage II represents the plateau region. Several fascinating points are included in Figure 3. First, although the yield strengths are about the same, more than five orders of magnitude in crack growth rate are observed at an applied K of 40,000 psi-in^{1/2} (36.4 MN-m^{-3/2}). Secondly, AISI 4340, mildly charged with hydrogen (15), exhibits almost identical kinetics to that tested in an aqueous solution of 3 1/2% NaCl (14). However, a similar alloy tested in dry H₂S gas (16) demonstrates order of magnitude faster kinetics. Thirdly, it would appear that stage II kinetics are observed for at least three drastically different types of environments.

These observations on thresholds and growth kinetics give rise to some provocative questions:

1. Why do some alloys exhibit stage I growth kinetics while others exhibit stages I, II and III?
2. What affects the threshold stress intensity?
3. How do thickness, yield strength and applied stress intensity affect the triaxial state of stress.
4. How does the triaxial state of stress affect threshold (equilibrium) and crack growth rate (kinetic) conditions?
5. Does the degree of precipitation or the inclusion count affect apparent diffusivity of hydrogen in high strength steels?
6. Can any changes in apparent diffusivity be directly related to crack growth kinetics and hence time to failure?

7. How do tempering and thermal-mechanical treatments affect susceptibility to hydrogen embrittlement?

Table 1. Variables in Hydrogen-Related Cracking

Geometrical:	Thickness	- Plane Stress or Plane Strain
	Crack-tip Radius	- $f_A(K, C_{ys})$
Stress Intensity:	Load	- Usually proportional
	Dimensions	- $f_B(a, B, W)$
	Loading Type	- Opening Mode I
		- In Plane Shear Mode II Anti Plane Shear Mode III
Environmental:	Test Temperature Environment	- Effect on Diffusivity
		- External (Solutions Mol. H ₂ , Atomic H) Internal (Degree of Charging)
	Strain Rate	- Normally $d\epsilon/dt \rightarrow 0$
Material Variables:	Structure	- Martensitic, Bainitic Pearlitic or Ferritic
	Sub-Structure	- Defect Density, Precipitate Morphology, Grain Size
		- Electrochemistry (Anodic or Cathodic Crack Tip) Stacking Fault Energy (Effect on Slip or Diffusivity) Precipitation or Inclusion Content
	Alloy Content	

In order to approach those questions from an overall viewpoint, all major variables have been listed in Table 1. A general review of these variables can be obtained from the literature (7,17-23). Next, consider how these variables affect both K_{TH} and da/dt . This is shown by the interaction diagram in Figure 4; from the nomenclature listed at the end of the paper, one can follow how these parameters control K_{TH} and da/dt . Further discussion of these interactions follows.

EQUILIBRIUM CONDITIONS - THEORETICAL

Elastic Considerations for K_{TH}

Consider a cracked region under load. An initially uniform

concentration, C_0 , of interstitial atoms in the vicinity of the crack will collect in the dilatational region. In terms of the hydrostatic or triaxial stress tensor, σ_{11} , this is given by (24)

$$C_r = C_0 \exp (\sigma_{11} \bar{V}_H / 3RT) \quad (1)$$

The crack opening mode stress field is the most important one for time dependent embrittlement phenomena. An analysis of the hydrostatic pressure field coupled with Fick's first law of diffusion gave steady-state solute concentrations of (25)

$$C_r = C_0 \exp \left\{ \frac{2(1+\nu)\bar{V}_H K}{3\sqrt{2\pi r} RT} \right\} \quad (2)$$

It is seen that the higher the stress intensity, K , or the closer to the crack tip, the more the initial concentration, C_0 , is elevated. Further consideration of the stress-field interactions (18) determined that solute atoms would be driven along orthogonal trajectories to the tip of a crack in Mode I, away from the crack tip in Mode II and would be stationary in Mode III. Additional discussion of stress field effects are given elsewhere (26-28). How does this apply to threshold stress intensity? Assuming that a critical amount of hydrogen is necessary for the critical cracking event, Eq. (2) may be used directly. All one has to stipulate is that some point r in front of the crack represents the equilibrium concentration, $C_{eq}(r)$, required for cracking. Thus, the condition for a threshold stress intensity, K_{TH} , is:

$$K_{\text{applied}} = K_{TH} \Big|_{C_{eq} = C_{cr}} \quad \text{Equilibrium just achieves the critical event}$$

$$K_{\text{applied}} > K_{TH} \Big|_{C_{eq} > C_{cr}} \quad \text{Equilibrium is not achieved (3) and cracking proceeds under non-equilibrium conditions}$$

$$K_{\text{applied}} < K_{TH} \Big|_{C_{eq} < C_{cr}} \quad \text{Equilibrium does not achieve critical event and no cracking occurs at long times}$$

At the threshold, it follows from Eqs. (2) and (3) that

$$K_{TH} = \ln\left(\frac{C_{CR}}{C_0}\right) \frac{3RT\sqrt{2\pi r}}{2(1+\nu)\bar{V}_H} \quad (4)$$

One instance where this equation might suffice is if the extent of the plastic region at the crack tip is limited to less than a grain diameter, d . Here, one could invoke the possibility that it is mostly the elastic gradient that is feeding hydrogen into the grain boundary or the grain contiguous to the crack tip. In this event, Eq. (4) would become

$$K_{TH} \approx \ln\left(\frac{C_{CR}}{C_0}\right) \frac{3RT\sqrt{2\pi d}}{2(1+\nu)\bar{V}_H} ; d \geq R_I \quad (5)$$

where R_I is the plane strain plastic zone size under Mode I loading. For a typical grain size of 10μ and a C_{CR}/C_0 of 3, this would represent a K_{TH} of 11,400 psi-in^{1/2} ($10.4 \text{ MN-m}^{-3/2}$). Even though this is quite appropriate to high strength steels, it does not explain the yield strength effect on K_{TH} depicted in Figure 2. In order to account for this, the plastic stress field equations should be considered.

Plastic Considerations for K_{TH}

Both plane strain and plane stress will be discussed in that order. A schematic of the model for plane strain is depicted in Figure 5. The tip of a real crack has a finite notch root radius, ρ . Therefore, in the plastic region under constraint (i.e. a thick plate which develops σ_{22} stresses), the maximum principal stress may become as large as three times the yield strength. In Figure 5, the triaxial stress tensor, σ_{ij} , is represented in the plastic region. At the same time, σ_{ij} increases in the elastic region with a $1/\sqrt{x}$ character as the crack tip is approached. Where these two stress distributions meet at a distance, X_{CR} , the dilatational stress will be highest. One may also note that the driving force, $d\sigma_{ij}/dx$, for hydrogen diffusion drives the hydrogen into the region of highest dilatation.

Hill's slip-line field equations for plane strain, as given by Wang (29), are

$$\sigma_{x,y,z} = \sigma_{ys} \left[\left(0, 1, \frac{1}{2}\right) + \ln \left(1 + \frac{x}{\rho}\right) \right] \quad (6)$$

Here, the digits in the first set of parentheses refer sequential-

ly to the σ_{11} stresses. Thus, the triaxial tension is

$$\frac{\sigma_{11}}{3} = \frac{1}{3} [\sigma_{xx} + \sigma_{yy} + \sigma_{zz}] = \sigma_{ys} [\ln(1 + \frac{\epsilon}{\phi}) + \frac{1}{2}] \quad (7)$$

Since the plastic constraint factor, pcf, has formally been defined as the ratio of maximum principal stress to the yield strength, it is apparent that Eqs. (6) and (7) give the triaxial tension as

$$\frac{\sigma_{11}}{3} = \sigma_{ys} [\text{pcf} - \frac{1}{2}] \quad (8)$$

Additional discussion about the usefulness of this solution to real materials is given elsewhere (23). Combination of Eqs. (1) and (8) give

$$C_{eq}|_{\text{plane strain}} = C_o \exp \{ \sigma_{ys} [\text{pcf} - \frac{1}{2}] \bar{V}_H / RT \} \quad (9)$$

This directly demonstrates the concentration build-up dependence on yield strength. It is also possible to demonstrate a stress intensity dependence since pcf is known to be a function of stress intensity. This is given by (30)

$$\text{pcf} \approx 1 + \alpha (K / \sigma_{ys}) \quad (10)$$

where $\alpha = 2 \ln^{-\frac{1}{2}}$. If one now uses this with the threshold criterion, Eqs. (1), (3), (8), and (10) give

$$K_{TH}|_{\text{plane strain}} = \frac{RT}{\alpha \bar{V}_H} \ln \left(\frac{C_{cr}}{C_o} \right) + \frac{\sigma_{ys}}{2\alpha} \quad (11)$$

which includes concentration, yield strength and stress intensity dependence.

Next consider the situation for plane stress where $\sigma_{zz} = 0$. Here, there is no sharp gradient of stress in the plastic region and for practical purposes the pressure tensor may be considered nearly constant. In this case, one can utilize the principal stresses in a mildly work-hardening material due to Hutchinson (31) and obtain for $\sigma_{11}/3$ a value of $0.57 \sigma_{ys}$. Thus Eq. (1) would become

$$C_{eq} \text{ plane stress} = C_o \exp[0.57 \sigma_{ys} \bar{V}_H / RT] \quad (12)$$

It is obvious, then, why steels under plane stress conditions have great difficulty in cracking if yield strengths are low near 100,000 psi (6.9×10^8 N/m²). Here constraint is difficult to achieve and Eq. (12) would predict $C_{eq}/C_o \rightarrow 1$.

Transitional Behavior for K_{TH}

First, a transition from predominantly elastic behavior to plastic behavior is possible (23). More important, however, is the transition from plane strain to plane stress. Consider an intermediate thickness plate loaded such that the center was under plane strain and the surfaces were under plane stress. The plane strain region would be given in terms of thickness, B , and plane stress plastic zone radius, r_y , by $B - 2r_y$. The hydrogen would collect in the plane strain region of the center of the thick plate according to Eq. (9) and at the surfaces according to Eq. (12). Now, if the pressure tensor appropriate to the collection of hydrogen for the total crack front is simply a weighted average, then

$$\left(\frac{\sigma_{11}}{3}\right)_{AVE.} = \left\{ \left(\frac{\sigma_{11}}{3}\right)_{\text{Plane Strain}} \left(\frac{B - 2r_y}{B}\right) + \left(\frac{\sigma_{11}}{3}\right)_{\text{Plane Stress}} \left(\frac{2r_y}{B}\right) \right\} \quad (13)$$

Combining Eqs. (8), (10), (12), and (13) leads to

$$\left(\frac{\sigma_{11}}{3}\right)_{AVE.} = \left\{ \frac{\sigma_{ys}}{2} + K - \frac{2r_y K}{B} + \frac{0.14 \sigma_{ys} r_y}{B} \right\} \quad (14)$$

This, in conjunction with Eq. (1), then leads to a threshold stress intensity for plate thicknesses intermediate to plane strain and plane stress. This is given by

$$K_{TH} \Big|_{\text{Transition}} = \frac{\frac{RT}{\alpha \bar{V}_H} \ln \left(\frac{C_{CR}}{C_o} \right) - \frac{\sigma_{ys}}{2\alpha} \left[1 + \frac{0.28 r_y}{B} \right]}{1 - 2 r_y / B} \quad (15)$$

This appropriately reduces to Eq. (11) if $2r_y/B \ll 1$, i.e. plane strain behavior. For typical initial concentration levels, this would indicate that K_{TH} would increase fairly rapidly as $2r_y \rightarrow B$.

EQUILIBRIUM CONDITIONS - EXPERIMENTAL

Yield Strength Dependence of K_{TH}

Cathodically charged specimens of 4340 tempered to five different strength levels are shown in Figure 6. The 0.75 inch thick specimens insured plane strain conditions. Thus, Eq. (11) is appropriate and if used directly with C_{CR}/C_0 as constant, the dotted line results. This represents the data at high strength levels but not at the lowest. Part of this discrepancy is proposed to be due to a dependency of C_{CR}/C_0 on yield strength level. For example, there are the data of Farrell and Quarrell (32) that indicate larger concentrations of hydrogen are necessary to produce embrittlement in steels of successively lower yield strength. This could be interpreted as $C_{CR} \propto 1/\sigma_{ys}$. On the other hand, Kim and Loginow (33) recently demonstrated that hydrogen from an external source dissolves in high strength steels more readily than in lower strength ones. Thus, the initial solubility might be proportional to yield strength, i.e. $C_0 \propto \sigma_{ys}$. Considering either one of these, the yield strength dependence might be assumed as

$$C_{CR}/C_0 \approx \beta/\sigma_{ys} \quad (16)$$

where β is a constant for a single environment and a single class of steel. For the present hydrogen charging method, it was known that the 200,000 psi yield strength level contained $C_0 \approx 2.6$ ppm (34). If C_{CR} is taken as 6 ppm, then Eq. (16) would indicate that β is 460,000 psi (3.2×10^9 N/m²). When combined with Eq. (11), this fits the data very well in Figure 6.

Yield Strength Dependence of K_{ISCC}

One could argue that equilibrium conditions for concentration of hydrogen about the tip of a crack should be relatively independent of the source of hydrogen. This would be the case if concentration gradient effects were negligible compared to the stress potential. Using this as a basis, the same constant of proportionality that predicted the hydrogen data was used to predict K_{ISCC} . All of the K_{ISCC} data representative of 0.4C steels were collected (6-23, 35-38) and plotted as a function of yield strength in Figure 7. It is seen that the equilibrium model as represented by Eqs. (11) and (16) fit the data extremely well.

Next, consider different classes of steel where the critical concentration for cracking or hydrogen uptake from an environment

might be different. This could change the functional dependence of C_{CR}/C_0 but it will be assumed that only the constant in Eq. (16) is affected. Two such classes of steels might be the 9Ni - 4Co - XC and 18 Ni-maraging steels (12-14, 17, 22, 35-38). K_{ISCC} data for these were collected and plotted as a function of yield strength in Figure 8. As before, an increasing susceptibility results as the yield strength increases. Most of the 9Ni - 4Co data are displaced slightly to the right of the curve that was also given in Figure 7, i.e. for $\beta = 460,000$ psi (3.18×10^9 N/m²). This would indicate a slightly greater tolerance for hydrogen as compared to low-alloy steels. A large increase in β is indicated for the 18Ni - maraging steels indicative of their superior resistance to embrittlement. In both the 9Ni - 4Co and 18Ni - maraging steels, there is a large degree of scatter at the lower yield strength levels. The predominance of data gave K_{ISCC} values larger than that predicted. This may be attributed to the inability to achieve fully plane strain conditions at high K_{ISCC} values. For this reason, it is appropriate to consider how much the degree of plane strain could affect K_{ISCC} .

Transitional Behavior

The plane strain to plane stress transition occurs gradually according to Eq. (15). Evaluation of cathodically-charged 4340 heat treated to the 170,000 psi (1.17×10^9 N/m²) yield strength level has been carried out on 0.15, 0.45 and 0.75 inch thick samples. Their corresponding threshold values are given in Figure 9, plotted as a function of r_y/B . Both the trend in the data and the absolute magnitude of K_{TH} are reasonably well predicted. For comparison, some data of Johnson, et al (39) on threshold stress intensities for H-11 steel tested in distilled water and hydrogen gas are also given. At intermediate values of r_y/B near 0.1, a somewhat greater deviation of K_{TH} from that predicted by Eq. (15) is observed. This could be partially due to estimates of K_{ISCC} or the plastic zone size or due to the inadequacy of the model. Still, the magnitudes and trends are generally predicted.

Alloy Effects on K_{TH} or K_{ISCC}

Sandoz (7) has made an exhaustive study of alloying effects on 4340 steel involving Cr, Mo, S, P, Co, C and Mn additions. He also ran a series of tests in gaseous, K_{IH2} ; anodic aqueous, $K_{ISCC}(Cu)$; cathodic aqueous, $K_{ISCC}(Hg)$; open circuit aqueous, K_{ISCC} ; and charged, K_{IH} charge environments. A summary of this data along with some effects of Si additions on 4340 (22) are shown in Table 2. Although it is difficult to rationalize some of the heat-to-heat variability, the trends with alloy additions are quite revealing. For example, it is seen in the first five rows

of data that Cr, Mo, S, P, and Co additions have little or no effect on the threshold stress intensity. Similarly, Si additions have no effect on K_{ISCC} .

Table 2. Effect of Alloy Additions on Threshold Stress Intensity of 4340 Type Steel (Ref. 7 and 22)

Temper Range °C	Yield 1000 psi	Element Added Wt. %	Stress Intensity Threshold 1000 psi-in ^{1/2}			
			K_{IH2}	$K_{ISCC}(Cu)$	K_{ISCC}	$K_{ISCC}(H_2)$
360-480	182	0.01-2.08 Cr	64+4	-	35+4	-
400-540	183	0.01-1.18 Mo	88+4	-	44+3	-
440	185	0.003-0.023 S	80+6	-	38+2	-
440	185	0.002-0.026 P	48+4	-	35+4	-
400-480	185	0.39-2.83 Co	60+90	-	41+2	-
240-295	195	0.20-0.53 C	75+5	68(0.33C)	58+32	34+5
315-570	172	0.15-0.53 C	85+3	78+0	80+55	46+3
415	169	0.10-2.7 Mn	93+68	85+52	85+30	45+30*
205-260	202-240	0.10-2.15 Si	-	-	15+3	-
315-495	194-216	0.10-2.15 Si	-	-	20+3	4340

* Same range obtained for charged hydrogen conditions

The effects of C and Mn are quite different. If the specimens were cathodically polarized, i.e. attached to a magnesium electrode, there was little effect of C on K_{ISCC} . There also appeared to be no effect of C on $K_{ISCC}(Cu)$ or K_{IH2} tests representing anodic conditions. However, if tested in the open circuit condition, there was a drop in K_{ISCC} with increasing carbon content. This suggested that increasing the carbon content resulted in the crack tip gradually going from an anodic to a cathodic state (7). This would explain the variation in K_{ISCC} since the crack tip would be exposed to increasing proportions of atomic H versus molecular H_2 as the carbon content increased. The result was essentially the same with Mn additions in that the crack-tip became increasingly cathodic.

KINETIC CONDITIONS - THEORETICAL

Elastic Considerations for da/dt

At relatively low stress intensities, either intergranular or quasicleavage fractures have been observed (8). Stage I growth could be associated with primarily elastic loading where the

plastic zone is very small. Here, the long range diffusivity of hydrogen would be controlled by the elastic stress distribution. This is schematically depicted in Figure 10(a). For the model, the following assumptions are made:

- i. The plastic zone is within a region less than a grain size.
- ii. The crack nucleates over one grain, d .
- iii. The hydrogen collects in this grain from the immediate surrounding grains.
- iv. The crack grows intergranularly, one grain at a time.
- v. The growth step occurs when $C_0 = C_{CR}$.
- vi. Short-time diffusion kinetics are applicable.

Next, consider a single hydrogen atom moving at velocity, v , taking a time, d/v , to move from one grain to the next. If v is the average velocity of the hydrogen atoms and d is the average distance moved, then the concentration increases in the grain at the crack tip by $3C_0vt/d$. That is, the shaded region in Figure 10(a) adds to the original concentration of the grain contiguous to the crack tip depending on drift velocity and time. If the time between crack jumps is Δt_s , it follows that

$$C_{CR} \approx C_0 + \frac{3C_0 v \Delta t_s}{d} \quad (17)$$

Since the drift velocity for short time diffusion is

$$v = \frac{D}{RT} \bar{V}_H \frac{dp}{dx} \quad (18)$$

it follows from Eqs. (17) and (18) that the time between jumps is

$$\Delta t_s = \frac{(C_{CR} - C_0)dRT}{3C_0 D_A \bar{V}_H dp/dx} \quad (19)$$

On a local scale, da/dt is simply the average incremental crack jump divided by the average time between jumps. It follows that

$$\frac{da}{dt} = \frac{l_{CR}}{\Delta t_s} = \frac{3C_0 D_A \bar{V}_H dp/dx}{(C_{CR} - C_0)RT} \quad (20)$$

From the mean value theorem one can calculate the average value of dp/dx over the contributing region indicated in Figure 10(a) by using the opening mode solution (18). This finally leads to

$$\left. \frac{dp}{dx} \right|_{\text{AVE.}} = \frac{2K(1+\nu)}{9d^{3/2}} \quad (21)$$

From Eqs. (20) and (21), a first approximation for Stage I growth is

$$\left(\frac{da}{dt} \right)_I = \frac{2(1+\nu)C_o D_A \bar{V}_H K}{3d^{3/2} RT(C_{CR} - C_o)} \quad (22)$$

Plastic Considerations for da/dt

First, consider when the plastic zone exceeds several grains as indicated in Figure 10B. The crack tip blunts and a plastically constrained region forms with a stress distribution similar to that in Figure 5. Now, hydrogen flows away from the crack tip to approximately a grain length in front. Other assumptions i through vi are the same as above. Over the range of stress intensities normally encountered, p might range from a fraction of a grain to about a grain size in radius (40). This, in conjunction with Eq. (7), the mean value theorem, and the limits depicted in Figure 10 (b), leads to

$$\left. \frac{dp}{dx} \right|_{\text{AVE.}} \approx \frac{3\sigma_{ys}}{2d} \quad (23)$$

From Eqs. (20) and (23), a first approximation for stage II is

$$\left(\frac{da}{dt} \right)_{II} = \frac{9 C_o D_A \bar{V}_H \sigma_{ys}}{2d RT(C_{CR} - C_o)} \quad (24)$$

The main difference between this and stage I is that the triaxial stress gradient increases with stress intensity for I but is independent of stress intensity for II.

The second plastic consideration results when the stress intensity becomes large enough to produce a ductile rupture contribution to the jump process. In this case the growth process would be partially intergranular and partially ductile rupture as depicted in Figure 10(c). The crack jump distance might be given by (11)

$$l_{CR} \approx \frac{K^2}{\sigma_{ys} E} \quad (25)$$

With the other assumptions remaining nearly the same, this leads

to stage III growth kinetics. From Eqs. (20), (23) and (25),

$$\left(\frac{da}{dt}\right)_{III} \approx \frac{9C_o D_A \bar{V}_H K^2}{2\sigma_{ys} E d^2 RT(C_{CR} - C_o)} \quad (26)$$

The third plastic consideration is that of plane stress. Here, dp/dx becomes quite small but nevertheless finite. From experimental evidence (41,42) this appears to be given by

$$\left.\frac{dp}{dx}\right|_{\text{Plane Stress}} \approx M \sigma_{ys} \quad (27)$$

where M is on the order of 5 to 20 in^{-1} . In the plane stress region the crack growth is essentially by a ductile rupture process so that the resulting crack growth would be stage II modified by the reduced stress gradient. This gives

$$\left(\frac{da}{dt}\right)_{\text{Plane Stress}} \approx \frac{3C_o D_A \bar{V}_H MK^2}{EdRT (C_{CR} - C_o)} \quad (28)$$

Transitional Behavior for da/dt

The two most important are from stage I to stage II and plane strain to plane stress. The first is simply obtained by equating Eqs. (22) to (24) giving

$$K_{I \rightarrow II} = 5.2 d^{1/2} \sigma_{ys} \quad (29)$$

Note that this says the transition occurs when $d = (1/27)(K/\sigma_{ys})^2$. Since the plane strain plastic zone size is about $(1/6\pi)(K/\sigma_{ys})^2$, the picture shown in Figure 10(b) is not inconsistent.

The second transition would probably take place most often from plane strain stage II, Eq. (24), to plane stress, Eq. (28), as the specimen thickness increases. A parameter ψ appears in both of these as given by

$$\psi = \frac{3 D_A \bar{V}_H}{dRT \left(\frac{C_{CR} - C_o}{C_o} \right)} \quad (30)$$

This would be constant for any one environmental test condition and heat treatment. Thus, for a set of a data where only the specimen thickness was increased, the growth rate should increase between the limits given by

$$\left. \frac{MK^2\psi}{E} \right|_{\text{Plane Stress}} \leq \frac{da}{dt} \leq \left. \frac{3\sigma_{ys}\psi}{2} \right|_{\text{Plane Strain}} \quad (31)$$

How does the experimental data confirm or deny these models?

KINETIC CONDITIONS - EXPERIMENTAL

Elastic Conditions - Stage I

Early investigations on relatively susceptible materials tended to confirm a single stage of kinetics. This was indicated for B₁₁ (43) and 4340 (44) heat treated to high strength levels. These observations may have been partially due to the lack of plane strain conditions. That is, it is possible for Stage I and Stage III conditions to overlap or to go directly from threshold to Stage III kinetics, in thin specimens. In later investigations where plane strain conditions were insured, a Stage I region was observed for 300 M heat treated to 233,000 psi yield (13); for the materials in Figure 3 (12-16); for Grade 350 maraging steel (14); and for a number of other high-strength steels (12,22,40). The most complete set of data are the Grade 350 data as shown in Figure 11. Superimposed on this is the theoretical curve obtained in the following way. The threshold was calculated using $RT/\bar{V}_H$ equal to 1.77×10^5 psi (1.22×10^9 N/m²), a grain size of about 10 μ and C_{CR}/C_0 from Figure 8. This gave a calculated K_{TH} of 9400 psi-in^{1/2} whereas the observed one was 7000 psi-in^{1/2}. The $(da/dt)_I$ curve used the same values for d , C_{CR}/C_0 and $RT/\bar{V}_H$ with Eq.(22). As the apparent diffusivity was not known, the last data point was matched to Eq. (22) which necessitated that D_A be 4.8×10^{-7} cm²/sec. The rest of the curve followed. This back-calculated value of D_A is not unreasonable for low-alloy martensitic steel (45) but may be unusual for the typical maraging steel. For the peak-aged Grade 300 maraging steel in Figure 11, there is more than a two order magnitude difference in growth kinetics. This will be more fully discussed in the section on tempering and aging.

Plastic Conditions - Stages II and III

Besides the Stage II conditions depicted in Figure 3, extensive observations have been made by Carter (12) and Mostovoy,

et al (13) for SCC in aqueous solutions. In one 9Ni-4Co-0.45C steel, Mostovoy, et al (13) observed an extended range of constant da/dt ($0.12 \pm 0.08 \times 10^{-4}$ in./sec.) from about 20,000 to 60,000 psi-in^{1/2}. Stage II growth has also been observed between 20,000 and 50,000 psi-in^{1/2} on cathodically-charged specimens of 4340 tempered between 300°C and 550°C (40).

For the same specimens, Stage III conditions were observed at high stress intensity levels (40). The typical microscopic fracture mode feature is that increasing amounts of microvoid coalescence are observed. A comparison is shown in Figure (12). Here, the lower stress intensity sample was Stage II and nearly all intergranular while the Stage III sample exhibited combined intergranular and ductile rupture modes. This is consistent with the hypotheses in Figure 10 and the observations previously reported by Beachem (8). Stage III growth kinetics in aqueous solutions have been observed by Carter (12,14), Mostovoy, et al (13), Kortovich and Steigerwald (45), Krafft and Smith (46), and Li and Johnson (44).

It is of interest to examine the totality of one set of data exhibiting Stage I, II and III conditions. Since most is known about the 4340 system, the data in Figure 3 were replotted in Figure 13. The solid curves were calculated using Eqs. (22), (24) and (26) with the following data:

$$d \approx 10 \mu \approx 4 \times 10^{-4} \text{ in}$$

$$RT/\bar{V}_H = 1.77 \times 10^5 \text{ psi} = 1.22 \times 10^9 \text{ N/m}^2$$

$$C_{ys} = 2.18 \times 10^5 \text{ psi} = 1.5 \times 10^9 \text{ N/m}^2$$

$$E = 3 \times 10^7 \text{ psi} = 2.08 \times 10^{11} \text{ N/m}^2$$

$$D_A = 5 \times 10^{-8} \text{ cm}^2/\text{sec} = 0.8 \times 10^{-8} \text{ in}^2/\text{sec}$$

$$C_{CR}/C_0 = 2.11 \text{ (Figure 7)}$$

It is seen that the general features are reasonably well predicted. The only variable that could be much in variance is the apparent diffusivity. However, Kortovich and Steigerwald (45) have measured D_A to be 7.5×10^{-8} cm²/sec. from permeation experiments on high-strength 4340. Thus, the theory gives approximate da/dt behavior except perhaps at the highest K values where K_{IC} is approached. Here, more gross mechanical instabilities might prevail.

Table 3. Transition From K Dependent (I)
to K Independent (II) Growth Kinetics

Material	Yield Strength 1000 psi	$K_I \rightarrow II$ 1000 psi-in ^{1/2}	$K_I \rightarrow II/\sigma_{ys}$ in ^{-1/2}	Ref.
4340	194	24	0.124	12
4340	200	~22	0.110	1
4340	216	25	0.116	13
4340	219	27	0.123	16
300M	233	~22	0.095	13
9Ni-4Co-.45C	236	25	0.106	12
250 Maraging	246	46	0.188	14
300 Maraging (460°C/3)	263	13	0.050	12
300 Maraging	284	22	0.078	12
300 Maraging (482°C/6)	286	~35	0.122	14
300 Maraging (482°C/8)	316	20	0.063	12
350 Maraging (475°C/8)	299	>30	>0.101	12
350 Maraging	330	15	0.046	12

Average = 0.102

Transitional Behavior

If these various stages of growth are general phenomena, one might expect consistent transition behavior. Some data are available from an extensive listing by Carter (12) and isolated data by others. These data are given in Table 3. Although it is seen that $K_I \rightarrow II/\sigma_{ys}$ ranges from 0.046 to 0.188 in^{1/2}, the majority of the data cluster around 0.100 in^{1/2}. The typical grain diameter used throughout this study has been 4×10^{-4} in. If this is used with Eq. (29), a calculated value of $K_I \rightarrow II/\sigma_{ys}$ is 0.104 in^{1/2}. Lest this be regarded with awe, it should be pointed out that Carter (14) indicates some steels have linearly varying da/dt behavior from K_{ISCC} to K_{IC} . It could be that Stage II was bypassed or that threshold went directly to Stage III. More detailed determinations must be made to clarify this situation.

Considering the thickness transition, data obtained on cathodically-charged 4340 steel (40) are shown in Figure 14. For two tempering conditions an order of magnitude increases in thickness produces several orders of magnitude increase in growth rate. These data run the extremes from plane stress to plane strain.

Thus, for thicknesses much smaller or larger than those shown here, one would not expect a similar drastic effect on da/dt . For the data shown, the crack growth rate can be given empirically by

$$da/dt = mB^n \quad (32)$$

with

$$\left. \begin{array}{l} 300^\circ\text{C} \\ \text{temper} \end{array} \right\} \begin{array}{l} m = 5.6 \times 10^{-3} \\ n = 3.75 \end{array} \quad \left. \begin{array}{l} 480^\circ\text{C} \\ \text{temper} \end{array} \right\} \begin{array}{l} m = 2 \times 10^{-4} \\ n = 3.75 \end{array}$$

Here, B is in inches and da/dt is in inches/sec. One can compare these data to the theoretical extremes given by Eq. (31). For the 300°C temper, $K \approx 3 \times 10^4 \text{ psi-in}^{1/2}$, $\sigma_{ys} \approx 2.2 \times 10^5 \text{ psi}$ and with $M \approx 10 \text{ in}^{-1}$, this gives $da/dt = 3 \times 10^2 \psi$ for plane stress and $3.3 \times 10^5 \psi$ for plane strain. Choosing ψ to be $10^{-8} \text{ in / psi-sec}$, and equating these to Eq. (32) gives calculated values of $B_{\text{plane stress}} = 0.135 \text{ in.}$ and $B_{\text{plane strain}} = 0.87 \text{ in.}$ These probably represent reasonable lower and upper limits for crack velocity transition. Similarly, for the 480° temper, $K \approx 7.4 \times 10^4 \text{ psi-in}^{1/2}$, $\sigma_{ys} \approx 1.8 \times 10^5 \text{ psi}$ and with $M \approx 10 \text{ in}^{-1}$, gives $da/dt = 18 \times 10^2 \psi$ for plane stress and $2.7 \times 10^5 \psi$ for plane strain. Choosing ψ to be $10^{-9} \text{ in/psi-sec}$ gives calculated values of $B_{\text{plane stress}} = 0.28 \text{ in.}$ and $B_{\text{plane strain}} = 1.09 \text{ in.}$ from Eq. (32). These limits are reasonably consistent with the experimental observation of 100% shear crack propagation and predominantly flat fracture at the thickness extremes. The physical interpretations of the chosen values for ψ will be covered under the section on tempering effects.

Additional thickness effects have been observed under SCC conditions (45,46,37,13) for thin and thick specimens. The tabulation follows with the thickness (inches) being given in parentheses.

Material	Yield 1000 psi	K 1000 psi -in ^{1/2}	Thin da/dt in./sec.	Thick da/dt in./sec.	da/dt Ratio
4340	180	40	0.012×10^{-4} (0.067)	0.10×10^{-4} (0.33)	8.3
4340	206	50	0.06×10^{-4} (0.05)	13×10^{-4} (0.33)	22
9Ni-4Co- 0.45C	200	50	0.004×10^{-4} (0.05)	0.12×10^{-4} (0.50)	30

First, the thick specimens crack at much greater rates.

Furthermore, the greater the change in thickness, the greater the difference in da/dt . Although the observations are qualitatively the same as those in Figure 14, the evidence is insufficient to say that thickness effects will be quantitatively the same in all environments.

Environmental Effects

The temperature effect as it controls the apparent diffusivity is discussed elsewhere (19). What we will discuss here is room temperature data obtained under aqueous, gaseous and charged conditions. Most data have been collected on the 4000 series low alloy steels. A comparison of these steels tested under six drastically different environments is given in table 4. Stress intensity and yield strength levels were kept as constant as possible to eliminate any ambiguity. The atomic hydrogen results were obtained by Nelson, Williams and Tetelman who partially disassociated H_2 with a hot tungsten filament near the crack tip. Some of the data were extrapolated according to known pressure relationships (16,20) as given below.

$$\begin{aligned} H_2: \quad K = 20,800 \text{ psi-in}^{1/2}; \log(da/dt) &= -7.82 + 1.69 \log P \\ K = 36,000 \text{ psi-in}^{1/2}; \log(da/dt) &= -5.8 = 1.00 \log P \\ K = 54,100 \text{ psi-in}^{1/2}; \log(da/dt) &= -5.17 + 0.95 \log P \end{aligned}$$

$$\begin{aligned} H_2S: \quad K = 20,800 \text{ psi-in}^{1/2}; \log(da/dt) &= -2.39 + 1.35 \log P \\ K = 54,100 \text{ psi-in}^{1/2}; \log(da/dt) &= -2.00 + 1.07 \log P \end{aligned}$$

The first half of Table 4 considers thin specimens and it is seen that increasing da/dt results from charged hydrogen to aqueous to atomic hydrogen environments. Furthermore, for the same partial pressure, atomic hydrogen produces crack growth that is orders of magnitude faster than molecular hydrogen. In the second half of the Table, relatively thick samples are shown. Here, increasing susceptibility results from charged hydrogen to aqueous to H_2S environments. In a way similar to atomic hydrogen, the same partial pressures of H_2S produces orders of magnitude faster kinetics than molecular hydrogen. Although a direct comparison is not possible, H_2S and atomic H environments can be compared by taking into account the thickness effect. Comparing the thin to thick samples in duplicate environments, one finds a factor of six increase. If this factor is applied to the atomic H data, then a growth rate of about 4.8×10^{-4} in/sec would be expected for a 0.3 inch thick sample at 8×10^{-3} torr. This is an order magnitude faster than in the H_2S environment. Using Table 4, it appears as though one could consistently rank susceptibility of low alloy, high strength steels. With crack growth kinetics at atmospheric conditions as the criterion:

Charged H (moderately charged)
 3% NaCl or Distilled water
 1 atm. H₂
 Charged H (severely charged)
 1 atm. H₂S
 1 atm. atomic H

Increasing da/dt

Table 4. Environmental Effects on Crack Growth Rate

Mat'l	Thick in.	Yield 1000 psi	Environment	K 1000 ^{1/2} psi-in	da/dt 10 ⁻⁴ in/sec	Ref.
4340	0.15	211	Charged H	37	0.07	40
4340	0.067	213	H ₂ O	37	0.14	45
4340	0.05	207	3% NaCl	43	0.75	37
4340	0.05	207	H ₂ O	43	0.77	37
4130	0.063	200	8x10 ⁻³ torr H	41	0.8	21
4130	0.063	200	250 torr H	36	2.8	20
4130	0.063	200	8x10 ⁻³ torr H ₂	36	0.00012*	20
4340	0.35	211	Charged H	35	1.6	40
4340	0.33	205	H ₂ O	35	4.3	46
4335V	0.293	219	300 torr H ₂	40	11.0	16
4335V	0.293	219	0.40 torr H ₂	40	30.0	16
4335V	0.293	219	8x10 ⁻³ torr H ₂	40	0.00045*	16
4335V	0.293	219	8x10 ⁻³ torr H ₂ S	40	0.5*	16

* Extrapolated from pressure dependence.

Tempering and Aging Effects

It was observed in Figure (14) that there was more than an order of magnitude shift in crack growth rate comparing 300°C to 480°C tempers. This behavior was found to repeatedly exist regardless of whether aqueous, gaseous or charged H conditions were involved. All of the data (16,22,37,40,45-48) for 4340 type steels where K was approximately 30,000-60,000 psi-in^{1/2} was plotted in Figure 15. For both relatively thin sheets (plane stress) and relatively thick plate (plane strain), there appears to be about an order of magnitude decrease in da/dt for an increase of 100°C in tempering temperature. For tempering temperatures much below 250°C, however, this would not be the case since microstructural changes are sluggish.

Considering the effect of yield strength on the stress tensor, one might be tempted to attribute increased resistance solely to

decreasing yield strength. However, this can be shown not to be the case. As discussed above, it was shown that $\dot{\epsilon}$ values of 10^{-8} in/psi-sec (300°C) and 10^{-9} in/psi-sec (480°C) satisfied the conditions for plane stress and plane strain in Figure 14. At this point, the yield strength difference on da/dt was already taken into consideration from the mechanics viewpoint. However, in Figure 7, an additional effect of yield strength on C_{CR}/C_0 was indicated. Using this in conjunction with Eq. (30) and the above values of $\dot{\epsilon}$, it is found that in order to satisfy the observed growth rates, D_A 300°C $\approx 1.7 \times 10^{-6}$ cm²/sec and D_A 480°C $\approx 2.3 \times 10^{-7}$ cm²/sec. It would appear then that a large degree of the change in growth kinetics may be due to an increased apparent diffusivity at increasing tempering temperatures.

An analogous situation concerns the aging of maraging steels. Increasing the aging temperature reduced the crack velocity by two orders of magnitude, as seen in Figure 12. Of course this represents two different Grades of maraging steel. Less ambiguous data have been obtained by Stavros and Paxton (49) on Grade 250. For a slightly underaged condition of 427°C for 10 hours, the failure time was 200 hours. For a peak aged condition of 482°C for 3 1/2 hours, the failure time was 10,000 hours. This factor of 50 difference was essentially independent of applied stress intensity. Furthermore, the K_{IC} value for the underaged condition was greater than the peak aged meaning that the controlling parameter was a large difference in da/dt . Interestingly, slightly overaging at 482°C for 100 hours, dropped the failure time to 2000 hours. These seemingly anomalous results can be rationalized in terms of microstructural effects on apparent diffusivity, D_A .

Alloying Effects

There have been few kinetic studies where alloying content has been systematically varied. One major exception is the study by Carter (22) where Si was systematically varied in 4340 steel. These data, in addition to others on 4340 (46,47) and 300M (13), are shown in Figure 16. The striking result is for the low tempering temperature group where the Si addition of 0.043 atom fraction (2.15 wt.%) decreased the growth rate by two orders of magnitude. Here, the tempering temperature was nearly constant so this is not a factor. In addition, it could not be a yield strength effect since the highest Si steel had the highest yield strength. The only two possible recourses are that it is an electrochemical effect at the crack tip or a microstructural effect relating to D_A . The latter viewpoint is favored. An effect of microstructure on D_A was alluded to in the previous section. Some of the most extensive studies have been by Coe and Martin (50) and Evans and Rollason (51). The former gives a review of much of the literature as well as extensive data while the latter makes a precise

determination of how void content affects D_A through a trapping mechanism. Their results indicated that D_A could be lowered by more than order of magnitude by increasing the void content to 0.007.

How does this apply to complex microstructures such as high strength steels? Every precipitate, oxide, sulfide, etc. becomes a potential trapping site for hydrogen. Without proposing anything more than a void volume effect, if the particle fractures or the particle-matrix interface breaks down at the crack tip, D_A will be lowered. One might expect that steels with a greater potential for particle formers might have the lowest values for D_A . To test this hypothesis, measured values of D_A at room temperature were plotted as a function of the atom fraction of potential particle formers. The resulting plot in Figure 17 is certainly too consistent to be anything but a real effect.

Since da/dt is proportional to D_A , it is tempting to plot available crack growth rate data as a function of the potential particle formers available. Separating thick plate from thin sheet data, both groups demonstrate more than a two order of magnitude decrease in da/dt with increasing particle fraction in Figure 18. This result is even more dramatic than that shown in Figure 17. That is, f only varies from 0.05 to 0.10 which is a small variation. In fact, if one takes the steepest slope in Figure 17 indicated by the dotted line and superimposes it on Figure 18, the apparent effect of D_A is not sufficient to account for the variation in da/dt . However, the measurements for Figure 17 were made on annealed and/or quenched and tempered steels. If they had been severely deformed the results might have been different since the deformation effect is well documented (51,52). Certainly, in the case of a crack tip where tri-axial tension or severe plastic strains could create microvoids, the potential number of trap sites would explain why the plane strain values dip faster than the plane stress ones with increasing f in Figure 19. Here, voids would more likely open up under a state of plane strain compared to plane stress.

Accepting this hypothesis, it is now possible to explain both tempering and aging effects. The tempering could increase the volume fraction and/or types of precipitates that would easily break down under crack-tip conditions. This would decrease D_A by increasing the trap density. Similarly, maraging steels in the underaged condition might have few potential traps (i.e. the precipitates could be coherent with the lattice) whereas in the peak-aged conditions, there might be the maximum number of traps. It would then follow that in the slightly overaged condition, precipitate coalescence would produce fewer numbers of traps.

CONCLUSIONS

Equilibrium and kinetic models for threshold and crack growth conditions are consistent with available data on high strength steels.

It is reasonably certain that:

- a) Thresholds can be predicted based upon yield strength, concentration level and stress field variables. Increasing these variables decreases the threshold.
- b) Thresholds can be predicted under relatively plane stress and plane strain conditions. Increasing plate thickness decreases the threshold.
- c) Stage I, II and III crack growth rate observations can be explained on the basis of the hydrogen-stress field interaction and the type of microscopic growth process.
- d) Extremes of plane stress and plane strain growth kinetics are due to large differences in the pressure tensor gradient.

It is hypothesized but less certain that:

- a) The effect of alloying elements on threshold are generally small. Secondary effects are due to their influence on yield strength or initial hydrogen concentration levels.
- b) The effect of tempering temperature on threshold is only a yield strength effect. Increased tempers produce higher thresholds.
- c) The main effect of environment is to control the availability of atomic hydrogen at the crack tip.
- d) Tempering, aging and alloying parameters affect crack growth rate by controlling hydrogen trapping and yield strength. Alloy additions, which provide trap sites, may decrease kinetics by three orders of magnitude.

Careful kinetics analyses of different alloying systems under varying experimental conditions must precede development of more accurate theoretical models.

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NOMENCLATURE

a	- crack dimension	t_f	- time to failure
B	- specimen thickness	Δt_s	- time between jumps
C_0	- initial concentration	v	- solute drift velocity
C_{eq}	- equilibrium concentration	$\bar{V}_H$	- partial molar volume of hydrogen in Fe
C_{CR}	- critical concentration	W	- specimen width
d	- average grain diameter	X	- distance in front of tip
D_A	- apparent diffusivity	ρ	- crack-tip radius
K	- applied stress intensity	pcf	- plastic constraint
K_{TH}	- threshold stress intensity	$\sigma_{x,y,z}$	- normal stress
K_{ISCC}	- stress corrosion threshold	σ_{ii}	- normal stress tensor
K_{IC}	- plane strain toughness	σ_{ys}	- uniaxial yield strength
l_{CR}	- crack jump size	ϕ	- rate dependent parameter
r_y	- plastic zone radius	α, β, M, m, n	- constants
dp/dx	- hydrostatic gradient		
da/dt	- crack growth rate		

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A. STAGE I.
Intergranular or Quasi-Cleavage

B. STAGE III.
Intergranular or
Quasi-Cleavage

C. STAGE III.
Combined Fracture Modes, One
Being Ductile Rupture

(A) $K \approx 30,000 \text{ psi-in}^{1/2}$

(B) $K \approx 55,000 \text{ psi-in}^{1/2}$

10 μ

APPENDIX B. HYDROGEN-CONTROLLED CRACKING --
A MODEL FOR THRESHOLD STRESS INTENSITIES

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Hydrogen-Controlled Cracking — A Model for Threshold Stress Intensities

by W. W. Gerberich and Y. T. Chen

ABSTRACT

Threshold stress intensities, K_{TH} , below which no cracking will occur under stress-corrosion cracking or hydrogen-assisted cracking conditions, are discussed. A quantitative model, which suggests why K_{TH} exists, is derived. The controlling mechanism is proposed to be a critical concentration of hydrogen, its propensity to form being governed by yield strength, initial concentration, state of stress and temperature variables. Specifically it is proposed that

$$K_{\text{applied}} = K_{TH} \Big|_{C_{eq} = C_{cr}}$$

which means that the applied stress intensity equals the threshold when the equilibrium concentration of hydrogen at the crack tip just achieves the critical concentration. The mathematical model is derived for elastic, plane-strain plastic and plane-stress plastic conditions. Experimental verification of the general trends of all variables is obtained with high strength AISI 4340 steel.

INTRODUCTION

Ever since Carl Zapffe⁽¹⁾ made history with respect to how hydrogen flaking affected the quality of ship steel, industrial and academic interest in hydrogen-related failures has been enormous. Probably the most relevant quantitative steps were first taken by Troiano and co-workers^(2,3,4) who analysed hydrogen concentration, microstructural, yield strength, stress field and temperature effects in great detail. They were the first to propose the effect of a triaxial stress enhancement on the long-range diffusivity of hydrogen at the tip of a notch. This work culminated in the now-famous Campbell Memorial Lecture of 1960.⁽⁵⁾ Since then, there have been numerous attempts to bolster⁽⁶⁾ or detract⁽⁷⁾ from this concept with surface energy⁽⁷⁾ or stress-sorption theories⁽⁸⁾ and pressure theories⁽⁹⁾ coming in and out of vogue.

Although Troiano⁽⁵⁾ never demonstrated how the concentrated hydrogen at the crack tip lowered the cohesive strength and produced embrittlement, his basic principle of stress-induced hydrogen migration has held fast. Since his original work, fracture mechanics concepts have become generally accepted. Thus, much of what he originally said in terms of notches can be reframed more explicitly in terms of fracture mechanics analyses for cracks. One such work was by Liu⁽¹¹⁾ who demonstrated that the pressure field about a crack could account for long-range diffusivity of an interstitial such as hydrogen. He further indicated that the resulting equilibrium concentration at the crack tip could be large compared to the

initial concentration. More recent investigations⁽¹¹⁻¹⁵⁾ have added several new dimensions to this basic concept. The point is that the stress intensity approach should be directly applicable in implementing theories of time-dependent embrittlement phenomena.

Although a raft of experimental evidence, correlating stress intensity and crack growth rates, has evolved for steel and titanium alloys, there is no unanimity of thought as to what controls the kinetics. Several kinetic models have been proposed,^(10,16,17) but all are either semi-empirical in nature or do not adequately represent the stress-field conditions at the tip of a crack. Considering the interest which the kinetic phenomenon has received, it is somewhat disconcerting that relatively little theoretical attention has been addressed to the equilibrium condition. Of course, there has been a great deal of experimental evidence gathered.⁽¹⁷⁻³⁰⁾ However, the fact remains that there has been no quantitative assessment as to why a threshold stress intensity should exist. The present study is an attempt to do that.

Using fracture mechanics approaches, it should be possible to quantitatively assess both the equilibrium conditions for the onset of cracking and the kinetic conditions for slow crack growth. The crack growth rate, da/dt , and the threshold stress intensity, K_{TH} , may be described by

$$da/dt = f\{K_{applied}\} g\{n\}; K_{app} - K_{TH}, da/dt = 0$$

where f is a function of applied stress intensity and g is a function of

n other variables such as concentration and temperature. The experimental situation is schematically shown in Figure 1. This has been drawn in accordance with the type of observations obtained for stress-corrosion cracking or hydrogen-assisted cracking. Several points are obvious. First, the time to failure decreases with increasing K which implies that da/dt is an increasing⁺ function of K_{applied} . Secondly, there is no failure for stress intensities below K_{TH} , i.e. $da/dt \sim 0$. Finally, both the threshold and the time to failure are increased as the yield strength is decreased. This means that both the kinetic conditions, which control da/dt , and the critical equilibrium conditions, which control K_{TH} , become more difficult to achieve at low yield strengths.

In an attempt to synthesize some of the known effects associated with time-dependent embrittlement, a quantitative assessment of the stress field effect was made. Those stress field solutions that have been reasonably well corroborated by experimental evidence were utilized. Although both equilibrium and kinetic solutions could have been attempted, this initial work is concerned mainly with an equilibrium model since there is less uncertainty here about boundary conditions and mathematical descriptions. Some experimental work on cathodically-charged AISI 4340 steel is also reported in terms of threshold stress intensities. The majority of the experimental evidence comes from the literature in terms of both stress-corrosion-cracking and hydrogen-assisted-cracking thresholds for low, medium and high alloy steels.

⁺In many cases, there is a range of stress intensity where da/dt is nearly constant. (22)

THEORETICAL MODEL

The solution for solute migration in a stress field has been available for some time now.⁽³¹⁾ The interaction is given by

$$U = p\Delta v \quad (1)$$

where p is the pressure tensor of the stress field and Δv is the change in the atomic volume due to the insertion of a solute atom. This leads to solute concentration build up at any point, r , within the stress field, given by⁽³²⁾

$$C_r = C_0 \exp(p\Delta v/kT) \quad (2)$$

where C_0 is the initially uniform concentration and kT is as usual. Alternatively, this can be given as⁽³³⁾

$$C_r = C_0 \exp(\sigma_{ii} \bar{V}_H / 3RT) \quad (3)$$

where $\bar{V}_H$ is the partial molal volume, $R=kN$ with N being Avogadro's number and σ_{ii} is the summation of the principal normal stresses. For the elastic field about an edge dislocation, Li⁽³⁴⁾ has shown that concentration build-ups of hydrogen about dislocations in iron can be 5 to 50 times as great as the initial concentration within 25 to 10 Å of the core. He also demonstrated that solute atoms flowed along orthogonal trajectories

or gradients to the iso-pressure curves which caused hydrogen to be fed into the core of the dislocation.

In a similar way, solute atoms may be driven by a long range dilatational stress field to the crack tip. It has been shown that the critical parameter is the stress intensity factor, K , which controls the magnitude of the pressure tensor.⁽¹¹⁻¹⁴⁾ However, just like the stress field of a dislocation is no longer described by the elastic field equations as one approaches the core, the stress field of a crack is not described by the elastic field equations as one approaches the crack tip. First, the elastic stress fields will be considered; secondly, how the stress field may be approximated under conditions of plastic flow; and finally, how the field equations vary as constrained flow (plane strain) gives way to unconstrained flow (plane stress).

Elastic Considerations for Mode I

The Mode I or crack opening mode stress field is the most important one for time-dependent embrittlement phenomena. An analysis of the hydrostatic pressure field coupled with Fick's first law of diffusion yielded steady-state solute concentration gradients given by⁽¹¹⁾

$$C_r = C_o \exp \left\{ \frac{2(1+\nu) \bar{V}_H K}{3\sqrt{2\pi r} RT} \right\} \quad (4)$$

where K is the applied stress intensity and ν is poisson's ratio.

Considering this dilatational interaction, St. John and Gerberich⁽¹³⁾

determined that solute atoms would be driven along orthogonal trajectories to the tip of a crack in Mode I, away from the tip of a crack in Mode II, and would be stationary under Mode III. However, Harrison, et al.⁽¹²⁾ have demonstrated that the second-order elastic interactions could produce a strong driving force that could predominate near the singularity. Very close to the crack tip this would produce a Mode III stress field interaction with a resulting concentration build-up of solutes. Nevertheless, the experimental results⁽¹³⁾ demonstrated that Mode I produced embrittlement in minutes while at stress intensities three times as high, Mode III produced no embrittlement during long hold times. In lieu of additional experimental evidence, calculations will consider only the first-order elastic interaction effect.

How does this apply to a threshold stress intensity under Mode I?

Assuming that a critical amount of hydrogen is necessary for the critical cracking event, then the conditions under which this hydrogen will collect are given by Eq. (4). All one has to stipulate is that the point r in front of the crack represents the equilibrium concentration, $C_{eq}(r)$, that is equal to the critical concentration, C_{cr} , required for embrittlement. Thus the condition for a threshold stress intensity, K_{TH} , is:

$$K_{applied} = K_{TH} \Big|_{C_{eq} = C_{cr}} \quad \left\{ \begin{array}{l} \text{Equilibrium just achieves} \\ \text{the critical event} \end{array} \right\} \quad (5a)$$

$$K_{applied} > K_{TH} \Big|_{C_{eq} > C_{cr}} \quad \left\{ \begin{array}{l} \text{Equilibrium is not achieved} \\ \text{and cracking proceeds under} \\ \text{non-equilibrium conditions} \end{array} \right\} \quad (5b)$$

$$K_{\text{applied}} < K_{\text{TH}} \Big|_{C_{\text{eq}} < C_{\text{cr}}} \quad \left\{ \begin{array}{l} \text{Equilibrium does not achieve} \\ \text{critical event and no cracking} \\ \text{occurs at long times.} \end{array} \right\} \quad (5c)$$

At the threshold then, it follows from Eqs. (4) and (5) that

$$K_{\text{TH}} = \ln\left(\frac{C_{\text{cr}}}{C_0}\right) \frac{3RT\sqrt{2\pi r}}{2(1+\nu)V_H} \quad (6)$$

One instance where this equation might suffice is if the extent of the plastic region at the crack tip is very confined and limited to less than a grain diameter, d . Here, one could invoke the possibility that it is mostly the elastic gradient that is feeding hydrogen into the grain boundary or the grain contiguous to the crack tip. The failure criterion would then be that sufficient hydrogen would collect in the whole grain or the grain boundary at the crack tip to nucleate fracture. In this event, Eq. (6) would become

$$K_{\text{TH}} \approx \ln\left(\frac{C_{\text{cr}}}{C_0}\right) \frac{3RT\sqrt{2\pi d}}{2(1+\nu)V_H} ; \quad d \geq R_I \quad (7)$$

where R_I is the plane strain plastic zone size under Mode I loading.

For a typical grain size of 10μ and a C_{cr}/C_0 of 3, this would represent a K_{TH} of $11,400 \text{ psi-in}^{1/2}$ ($10.4 \text{ MN-m}^{3/2}$) which is appropriate to very high strength steels.

One can attempt to extend this approach to situations where more extensive yielding occurs by associating r with the elastic-plastic boundary.

If one considers the extent of the plastic zone diameter under plane strain,⁽³⁵⁾ then

$$R_I = \frac{K^2}{3\pi\sigma_{ys}^2} \quad (8)$$

where σ_{ys} is the yield strength. Eqs. (4) and (8) then give

$$C_{eq} = C_o \exp \left\{ \frac{2(1+\nu) \bar{V}_H \sigma_{ys}}{\sqrt{6} RT} \right\} \quad (9)$$

It is perhaps significant that at room temperature with $\nu = 0.3$, this gives a C_{eq}/C_o of 1.35 for a 50,000 psi (3.45×10^8 N/m²) yield strength steel and a C_{eq}/C_o of 4.5 for a 250,000 psi (1.72×10^9 N/m²) yield strength one. Thus, it is not surprising that some low yield strength materials are not susceptible to hydrogen embrittlement unless initial concentrations are very high. Although this may qualitatively indicate one reason for the yield strength level effect, it does not give any means for assessing the threshold stress intensity. That is, as soon as one defines r in terms of an elastic-plastic boundary which is K^2 dependent, stress intensity is eliminated from the equation. This would suggest that the threshold conditions for hydrogen embrittlement are independent of stress intensity level. Experimentally, this is known not to be the case. But even more than this, it may be inferred from Figure 1 that any analysis for the threshold conditions should involve both a stress intensity and yield strength dependence. In order to account for this, the plastic stress field equations should be considered.

Plastic Considerations for Mode I

Obviously, in many instances the plastic deformation extends beyond a single grain and crack nucleation may proceed by one of several modes — intergranular, transgranular cleavage, or microvoid coalescence.⁽³⁶⁾ Since it does not matter to the stress field whether the hydrogen concentrates within the grain or the grain boundary, for matters of calculation these separate failure mechanisms will be collectively considered. Both plane strain and plane stress will be discussed in that order.

A schematic of the model for plane strain is depicted in Figure 2. The tip of a real crack has a finite notch root radius, ρ . Therefore, in a plastic region under constraint (i.e. a thick plate which develops σ_{zz} stresses), the stress builds up from the crack tip to some distance in the bulk where the maximum principal stress may be three times the yield strength. In Figure 2, the normal stress tensor, σ_{11} , is represented in the plastic region. At the same time σ_{11} increases with a $1/\sqrt{x}$ character as it approaches the crack tip in the elastic region. In both the elastic and plastic regions, the driving force, $d\sigma_{11}/dx$, for hydrogen diffusion drives the hydrogen into the region of highest dilatation.

Hill's slip-line field equations for plane strain, as given by Wang,⁽³⁷⁾ are

$$\sigma_{x,y,z} = \sigma_{ys} \left[(0.1, \frac{1}{2}) + \ln(1 + \frac{x}{\rho}) \right] \quad (10)$$

Here, the digits in the first set of parentheses refer sequentially to the σ_{11} stresses. Thus, the triaxial tension is

$$\frac{\sigma_{11}}{3} = \frac{1}{3} [\sigma_{xx} + \sigma_{yy} + \sigma_{zz}] = \sigma_{ys} \left[\ln \left(1 + \frac{x}{\rho} \right) + \frac{1}{2} \right] \quad (11)$$

Since the plastic constraint factor, pcf, has formally been defined as the ratio of maximum principal stress to the yield strength, from Eqs. (10) and (11), it is apparent that the triaxial tension may also be written as

$$\frac{\sigma_{11}}{3} = \sigma_{ys} \left[\text{pcf} - \frac{1}{2} \right] \quad (12)$$

One may gain some confidence in this result, by comparing it to numerical solutions for constrained plastic flow.^(38,39) For example, take the maximum plastic constraint factor of 2.82 due to a Von Mises yield criterion and you find that $\sigma_{11}/3$ in a non-strain hardening material is $2.32\sigma_{ys}$ from Eq. (12). A similar triaxial stress state may be calculated from stresses given by Hutchinson⁽³⁹⁾ for a slightly work-hardening material, recognizing that

$$\frac{\sigma_{11}}{3} = (\sigma_{rr} + \sigma_{\theta\theta} + \sigma_{zz}) \quad ; \quad \sigma_{zz} = \nu(\sigma_{rr} + \sigma_{\theta\theta}) \quad (13)$$

His maximum non-dimensionalized values of σ_{rr} and $\sigma_{\theta\theta}$ were 2.95 and 1.85. With $\nu = \frac{1}{2}$ in the plastic region, this gives $\sigma_{11}/3 = 2.40\sigma_{ys}$ which is very close to Hill's analysis. Considering the mesh size used in the numerical analysis and the difference in work hardening, the agreement is reasonable.

Assuming then that Eq. (12) is reasonable, this in conjunction with Eq. (3) leads to

$$C_{eq} \Big|_{\text{plane strain}} = C_0 \exp \{ \sigma_{ys} [\text{pcf} - \frac{1}{2}] \bar{V}_H / RT \} \quad (14)$$

This directly demonstrates the concentration build-up dependence on yield strength similar to that given by Eq. (9). In this later case, however, it is also possible to show the stress intensity dependence since pcf is known to be a function of stress intensity.⁽⁴⁰⁾ This is given by⁺

$$pcf \approx 1 + \alpha(K/\sigma_{ys}) \quad (15)$$

where $\alpha = 2 \ln^{-\frac{1}{2}}$. If one now uses this with the threshold criterion, Eqs. (3), (5) and (15) give

$$K_{TH} = \frac{RT}{\alpha \bar{V}_H} \ln \left(\frac{C_{cr}}{C_0} \right) - \frac{\sigma_{ys}}{2\alpha} \quad (16)$$

which includes the concentration, yield strength and stress intensity dependence of time-dependent cracking.

Next, consider the situation for plane stress where $\sigma_{zz} = 0$. Here, there is no sharp gradient of stress in the plastic region and for practical purposes the pressure tensor may be considered nearly constant. In this case, one can utilize the principal stresses in a mildly work-hardening material due to Hutchinson⁽³⁹⁾ and obtain for $\sigma_{11}/3$ a value of $0.57 \sigma_{ys}$. Thus, Eq. (3) would become

$$C_{eq} \Big|_{\text{plane stress}} = C_0 \exp \{ 0.57 \sigma_{ys} \bar{V}_H / RT \} \quad (17)$$

⁺ Although it would be best to have an analytical solution in terms of the crack-tip radius dependence of stress intensity so that Eq. (11) could be used directly, this is not possible at this time. Thus, the empirical equation proposed by Hahn and Rosenfield⁽⁴⁰⁾ and based on considerable data by Krafft⁽⁴¹⁾ has been utilized.

It is obvious then why materials under plane stress conditions have great difficulty in cracking if yield strengths are low near 100,000 psi ($6.9 \times 10^8 \text{ N/m}^2$). Here, constraint is difficult to achieve and Eq. (17) would predict $C_{eq}/C_o \rightarrow 1$. Thus, it would be nearly impossible to obtain embrittlement except at the highest concentration levels. Even for relatively high yield strength materials C_{eq}/C_o for plane stress may be half or less than half of the plane strain value. Thus, at least part of the reason plane strain failures are more frequently observed is because of the ease with which hydrogen can collect.

Transitional Behavior

Several types of transitions may be possible from the mechanical effects alone. The first may be a transition from largely elastic to plane strain plastic behavior. Relatively few cases are purely elastic wherein Eq. (7) is fully descriptive. In the first place, most K_{TH} values are higher than the estimate given in the example. This is partially due to the very high yield strengths required to satisfy $d \geq R_I$. In the example, a yield strength of 230,000 psi would be required to contain plasticity. This is a greater yield strength than possessed by the vast majority of high strength steels except for special thermal-mechanical treatments or maraging steels. Thus, it may be assumed that the vast majority of hydrogen embrittlement problems are associated with plane strain, elastic-plastic behavior.

The second transition may occur when transcending from plane strain to plane stress. First, consider an intermediate thickness plate

loaded such that the center was under plane strain and the surfaces were under plane stress. The result would be that schematically shown in Figure 3. Here, the plane strain region would be given in terms of thickness, B , and plane stress plastic zone radius, r_y , by $B - 2r_y$. It is next assumed that hydrogen collects in the plane strain region at the center of the thick plate according to Eq. (14). At the plane stress surfaces, it would collect according to Eq. (17). Now, if the pressure tensor appropriate to the collection of hydrogen for the total crack front is simply a weighted average proportional to the fraction of thickness under plane strain, then p_{ave} becomes

$$p_{ave} = \left[p_{\text{plane strain}} \left(\frac{B - 2r_y}{B} \right) + p_{\text{plane stress}} \left(\frac{2r_y}{B} \right) \right] \quad (18)$$

Combining Eqs (12), (15), (17) and (18) leads to

$$p_{ave} = \left\{ \frac{\sigma_{ys}}{2} + K - \frac{2r_y K}{B} + \frac{0.14 \sigma_{ys} r_y}{B} \right\} \quad (19)$$

A threshold stress intensity for transitional behavior is obtained from Eqs. (3) and (19) to be

$$K_{TH} = \frac{\frac{RT}{\alpha V_H} \ln \left(\frac{C}{C_0} \right) - \frac{\sigma_{ys}}{2\alpha} \left[1 + \frac{0.28 r_y}{B} \right]}{1 - \frac{2r_y}{B}} \quad (20)$$

This reduces to Eq. (16) if $2r_y/B \ll 1$, i.e. plane strain behavior. At the other extreme, Eq. (20) indicates that K_{TH} is infinite under any 100% plane stress condition except where the numerator tends to zero as $2r_y/B \rightarrow 1$.

In fact, this could occur at relatively high initial concentrations, $C_{cr}/C_o = 2$, in a material with a yield strength of 220,000 psi (1.52×10^9 N/m²). However, the quantitative nature of this limit can only be very approximate due to the assumptions involved and the empirical nature of Eq. (15).

Now that the theoretical model for threshold stress intensity has been developed, it is appropriate to apply this to experimental data. Specifically, hydrogen embrittlement and stress-corrosion-cracking data over a range of yield strength levels and plane strain to plane stress conditions will be analysed.

MATERIALS AND PROCEDURES

Since a large body of data already existed on hydrogen embrittlement and stress corrosion cracking susceptibility of 4340 steel, this was a logical material choice. The alloy composition is indicated in Table 1. All specimens were cut longitudinally with respect to rolling, austenitized at 850°C for one hour, oil-quenched and tempered at 550, 480, 400, 300 or 200°C for 2 hours. For characterization, hardnesses were measured and as indicated in Table I, approximate yield strengths ranged from 169,000 psi (1.17×10^9 N/m²) to 226,000 psi (1.56×10^9 N/m²). Fracture mechanics samples were prepared using the same heat-treatment procedures.

From previous data,⁽¹⁸⁾ it was anticipated that plane strain conditions could be maintained with 3/4 inch thick samples for all threshold intensities encountered except perhaps for the highest tempering temperature.

To obtain a range of plane stress to plane strain conditions, samples with thicknesses ranging from 0.15 to 0.75 inches were prepared. These were crack-line loaded samples of the compact tension type.⁽⁴²⁾ Prior to hydrogen charging, a pre-fatigue crack was introduced into each specimen by tension-tension fatigue. The ΔK range of about $10,000 \text{ psi-in}^{\frac{1}{2}}$, with $K_{\text{max}}/K_{\text{min}}$ equal to two, required about 70,000 cycles to grow the crack 0.08 inches long.

Hydrogen was introduced by means of cathodic charging at 25°C in an electrolyte consisting of 4 percent H_2SO_4 plus a poison. The later contained 2 g of yellow phosphorous in 40 ml of CS_2 and was added in the ratio of 10 ml to every 900 ml of electrolyte. The charging current density, I , was varied between 0.0001 and 0.20 amp/in^2 , since in this range, the initial concentration, C_0 , should be linearly related to I by⁽⁴³⁾

$$C_0 = 13.3 + 2.7 \log I \quad (21)$$

Here, C_0 is in ppm and I is in amp/in^2 . After charging for different times, several 3/4 inch thick samples were tested in the as-charged condition to evaluate the effective depth of the hydrogen penetration. Based upon these preliminary tests and known diffusion data, appropriate techniques for charging, cadmium plating and baking at 150°C were established. Although some inherent errors are involved in such a procedure, charging and baking times were adjusted for each specimen thickness so that the hydrogen concentration was as uniform as possible. The initial uniformly distributed concentration after baking was maintained at $C_0 \approx 2.6 \text{ ppm}$, based upon hydrogen entry into 200,000 psi yield strength 4340 steel.

After baking, the compact tension specimens were fitted with crack propagation gages having 20 grid lines at 0.01 inch intervals. These were then pulled in an Instron to a specified stress intensity and held. As the crack grew, the load dropped; nevertheless, under fixed grip conditions, this produced a nearly constant K value. Although crack propagation rates were determined, only K_{TH} will be reported at this time. Normally, where $da/dt \rightarrow 0$ over a 24-hour hold, this was taken as the threshold stress intensity. For the higher tempering temperatures, where some very slow growth rates were encountered, hold times approached 100 hours. Applied stress intensities were calculated from

$$K = \frac{P(a)^{\frac{1}{2}}}{B W} Y \quad (22)$$

where $Y = 29.6 - 185.5 (a/W) + 655.7 (a/W)^2 - 1017 (a/W)^3 + 639 (a/W)^4$

Here, P is the applied load, a is the crack length, B is the specimen thickness and W is the specimen width. At any time during the hold, K could be calculated from the recorded load and crack length from the crack propagation gages, using Eq. (22). It should be noted that the crack length was corrected for tunneling by a post-fracture analysis of the crack profile.

RESULTS AND DISCUSSION

Yield Strength Dependence of K_{TH}

Results of data obtained on 0.75 inch thick specimens of 4340 steel are shown for all yield strength levels in Figure 4. This thickness is sufficient to assure plane strain conditions for all five strength levels. Thus, Eq. (16) is appropriate and if used directly with C_{cr}/C_o as constant, the dotted line results. This represents the data at high strength levels reasonably well but at the lowest strength level, there is a considerable deviation. Part of this discrepancy is proposed to be due to a dependency of C_{cr}/C_o on yield strength level. For example, there are the data of Farrell and Quarrell⁽⁴⁴⁾ that indicate larger concentrations of hydrogen are necessary to produce embrittlement in steels of successively lower yield strength. This could be interpreted as $C_{cr} \propto 1/\sigma_{ys}$. On the other hand, Kim and Loginow⁽⁴⁵⁾ have recently demonstrated that hydrogen drawn from an external source dissolves in high strength steels more readily than in lower strength ones. Thus, the initial solubility might be proportional to yield strength, i.e. $C_o \propto \sigma_{ys}$. Considering either one of these, one might conclude that the ratio of C_{cr}/C_o would be dependent upon yield strength. As a first approximation, the yield strength dependence was assumed to be given by

$$C_{cr}/C_o \approx \beta/\sigma_{ys} \quad (23)$$

where β is a constant for a single environment and a single class of steel.

For the present hydrogen charging method, it was known that for the 200,000 psi yield strength level, $C_0 \approx 2.6$ ppm.⁽⁴⁴⁾ If C_{cr} is taken as 6 ppm, then Eq. (21) would indicate that β is 460,000 psi (3.2×10^9 N/m²). When combined with Eq. (16), this fits the data very well in Figure 4.

Concentration Dependence

There is relatively little if any concentration dependence on K_{TH} available in the literature. However, some data by Johnson, Morlet and Troiano⁽²⁾ had been obtained on notch round samples. These were 200,000 psi (1.38×10^9 N/m²) yield strength 4340 samples, charged and baked at different times to produce various initial concentrations of hydrogen. Although not available in the original article, Gerberich and Hartbower⁽¹⁶⁾ had converted the notched strength data to stress intensity factors. Using the lower bound applied stress intensity for no cracking during a 100 hour hold, these data are shown as K_{TH} in Figure 5. The C_{cr}/C_0 abscissa was obtained by using C_{cr} as representative of Figure 4 for a 200,000 psi yield strength 4340 and picking C_0 to range from 1.5 ppm to 4 ppm as the baking time decreased. The choices in C_0 are somewhat arbitrary and so a slightly different intercept and slope could have been depicted in Figure 4. Nevertheless, the fact would remain that absolute magnitudes are approximated and the general effect of increasing hydrogen amounts on decreasing K_{TH} is predictable.

Yield Strength Dependence of K_{ISCC}

One could argue that equilibrium conditions for concentration of hydrogen about the tip of a crack should be relatively independent of the source of hydrogen. This would be the case if concentration gradient effects were negligible compared to the stress potential. Using this as a basis, the same constant of proportionality that predicted the hydrogen data was used to predict threshold stress intensity for stress corrosion cracking (K_{ISCC}). All of the K_{ISCC} data for high strength steels such as 4340, H-11 and 300-M, representative of low alloy 0.4 carbon steels, were collected.⁽¹⁷⁻³⁰⁾ These K_{ISCC} data were plotted as a function of yield strength in Figure 6. It is seen that the equilibrium model as represented by Eqs. (16) and (23) fit the data extremely well. One may note that this curve is identical to the solid curve in Figure 4. In this case, the theory would say that the environment represented by distilled water or 3% NaCl solutions provided enough hydrogen so that equilibrium conditions reached a critical concentration similar to that which was obtainable from a cathodically-charged sample. It should be emphasized that the amount of time it could take to get to equilibrium might be different. Furthermore, any kinetic aspects of crack growth rate could be drastically different. Nevertheless, the thresholds could be the same.

Next, consider different classes of steel where the critical concentration for cracking or the hydrogen uptake from an environment might be different. This could change the functional dependence of C_{cr}/C_o but it will be assumed that only the constant in Eq. (23) is affected. Two

such classes of steels might be the 9Ni-4Co-xC and 18Ni-martensitic steels.⁽²¹⁻³⁰⁾ K_{ISCC} data for these were collected and plotted as a function of yield strength in Figure 7. As before, an increasing susceptibility results as the yield strength increases. Most of the 9Ni-4Co data are displaced slightly to the right of the curve that was also given in Figure 6, i.e. for $\beta = 460,000$ psi (3.18×10^9 N/m²). This would indicate a slightly greater tolerance for hydrogen or lower hydrogen uptake during stress corrosion cracking, either of which could increase β . A large increase in β is indicated for the 18Ni-martensitic steels, indicative of their superior resistance to embrittlement. In both the 9Ni-4Co and 18Ni-martensitic steels, there is a large degree of scatter at the lower yield strength levels, with the predominance of data being greater than that predicted. This may be attributed to the fact that fully plane strain conditions were not achieved at high K_{ISCC} values where the yield strengths were low. For this reason, it is appropriate to consider how much the degree of plane strain could affect K_{ISCC} .

Transitional Behavior

Before considering the thickness transition, a brief discussion of the elastic to plane-strain plastic transition is in order. Eqs. (7) and (16) indicate that this transition should occur when

$$\frac{\sigma_{ys}}{2\alpha} \approx \frac{RT}{2V_H} \ln \left[\frac{C_{cr}}{C_o} \right] \left[1 - \frac{3\sqrt{2\pi d}}{(1+\nu)} \right] \quad (24)$$

Using Eq. (23) as a measure of C_{cr}/C_o dependence and $d \approx 10\mu$ or 4×10^{-4} in, this transition would occur at a yield strength of 225,000 psi (1.55×10^9 N/m²). At this point, the plastic zone would be well within a single grain diameter. The calculated threshold stress intensity would be 7000 psi-in^{1/2} and it is perhaps significant that in all of the data observed in Figure 6, the lowest one was 8000 psi-in^{1/2}.

The plane strain to plane stress transition occurs gradually according to Eq. (20). Two extremes of behavior are shown in Figure 8 where cracking was carried out at two different thicknesses of 4340. The degree of plane strain involved in the slow crack growth portion is obviously different. As an indication of how drastically this affect can be, crack growth rates were measured on 0.75 and 0.15 inch thick samples. At an applied K of 29,000 psi-in^{1/2} (26.4 MN-m^{-3/2}) for the thick sample the crack growth rate was 25×10^{-4} in/sec. At an applied K of 37,000 psi-in^{1/2} (33.6 MN-m^{-3/2}) for the thin one, the growth rate was 0.06×10^{-4} in/sec. Thus, even at a higher stress intensity level, the growth rate was 400 times slower in the thin sample. Evaluation of the 170,000 psi (1.17×10^9 N/m²) yield strength material had been performed on 0.15, 0.45 and 0.75 inch thick samples. Their corresponding threshold values are given in Figure 9, plotted as a function of r_y/B . Both the trend in the data and the absolute magnitude of K_{TH} are reasonably well predicted.

For comparison, some data of Johnson, Et al.⁽²⁰⁾ on threshold stress intensities for H-11 steel tested in distilled water and hydrogen gas are also given in Figure 9. At intermediate values of r_y/B near 0.1,

a somewhat greater deviation of K_{TH} from the plane strain case is observed compared to what is predicted by Eq. (20). This could be partially attributed to the type of estimate used for r_y or partly due to the inadequacy of the model. Still, the magnitudes and trends are generally predicted. It is interesting that the differences between atmospheric hydrogen and water are slight, indicating that the source of hydrogen for equilibrium cracking is a second order effect. In Fact, Figure 9 represents three different sources of hydrogen, the K_{TH} of which are all reasonably predicted by Eqs. (20) and (23). One should not draw the erroneous conclusion that the environment has no consequence, however, since finite differences do exist and these would be significantly more pronounced where kinetic considerations prevail.

CONCLUSIONS

1. An equilibrium model for the threshold stress intensity required to cause hydrogen embrittlement has been derived.
2. The model may be applied to purely elastic, plane-strain plastic, or plane-stress plastic conditions.
3. The source of hydrogen is not the primary consideration in determining K_{TH} as the model is reasonably predictive for cathodic charging, distilled water and atmospheric hydrogen conditions.
4. Included in the model are stress intensity, yield strength, stress tensor, temperature, volume misfit, hydrogen concentration, and

specimen thickness effects, all of which must be a part of any viable threshold model.

5. Electrochemical effects for aqueous solutions, concentration gradient effects, hydrogen trapping theory and other microstructural considerations have not been sufficiently considered to make this a general model.
6. Nevertheless, experimental data verify the principal aspects of the model — the yield strength, hydrogen concentration and thickness variables.

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Table 1: COMPOSITION AND YIELD STRENGTH OF AISI 4340

Composition, wt. %							
<u>C</u>	<u>P</u>	<u>S</u>	<u>Mn</u>	<u>Si</u>	<u>Cr</u>	<u>Mo</u>	<u>Ni</u>
0.40	0.035	0.04	0.80	0.21	0.80	0.25	1.9

Yield Strength Estimate		
<u>Temper</u>	<u>R_C (ave. 5 readings)</u>	<u>R_C Yield Strength, 1000 psi</u>
200°C	51.2	226
300°C	49.5	220
400°C	48.0	211
480°C	43.4	180
550°C	40.3	169

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9. Threshold Stress Intensity in the Transition Region from Plane Strain to Plane Stress.

SIMPLE SUPERPOSITION OF STRESS STATES

r_y = PLANE STRESS PLASTIC ZONE RADIUS

$$K_{TH} = \frac{\frac{kT}{2V} \ln\left(\frac{c_{eq}}{c_0}\right) - \frac{\sigma_{ys}}{-4} \left[1 + \frac{0.28r_y}{B}\right]}{1 - 2r_y/B}$$

(A) 0.75 in. thick

(B) 0.15 in. thick

APPENDIX C. ON THE PRESSURE DEPENDENCY OF
THRESHOLD STRESS INTENSITY

Reprints removed