

TESTING OF THE DECOHESION THEORY OF HYDROGEN-INDUCED  
CRACK PROPAGATIONR.A. Oriani and P.H. Josephic  
U.S. Steel Research Laboratory  
Monroeville, Pennsylvania 15146

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Introduction

A recently developed theory<sup>1)</sup> of hydrogen-induced crack propagation in steels is based on Troiano's<sup>2)</sup> suggestion that dissolved hydrogen lowers the resistive cohesive force of the iron lattice. More specifically, the crack advances when the maximum elastic tensile stress,  $\sigma_z'$ , in the Elliott (non-Hookean) region of the crack tip equals  $F_m(c')$ , the maximum resistive cohesive force between the atoms as reduced by the stress-induced, large hydrogen concentration. The rate of crack advance is controlled by the major kinetic impedance in the processes by which hydrogen enters the highly elastically stressed region to achieve the concentration necessary to cause  $F_m(c')$  to equal  $\sigma_z'$ . The relation between the adsorption theory<sup>3)</sup> of hydrogen embrittlement and the decohesion mechanism has been outlined<sup>1)</sup>, and it has been shown that the adsorption theory describes a necessary but not sufficient condition for hydrogen-induced crack propagation, whereas the decohesion mechanism is sufficient.

Though the theory remains implicit at present because of our ignorance of the required functional relationships, nevertheless some qualitative predictions have been made. These are that there should be a threshold stress intensity factor,  $K$ , at a given temperature and hydrogen fugacity for a given steel below which a crack will remain stationary indefinitely. Similarly, there should be a threshold hydrogen fugacity, for a given steel, temperature, and stress intensity factor, below which a crack will remain stationary indefinitely. It also follows from the theory that a crack which has been allowed to stop propagating either by lowering the stress intensity or by lowering the hydrogen fugacity, or both, should be immediately restarted by a slight increase in the environing hydrogen fugacity at constant  $K$  and temperature. The validation of this prediction depends on the

absence of mechanisms that would appreciably increase the mean radius of curvature of the crack tip during the time interval prior to increasing the hydrogen fugacity, and on the absence of contaminants in the source of the hydrogen that may impede its ingress. Preliminary experiments designed to test this last prediction are described.

#### Experimental Technique

In order to avoid as much as possible blunting of the crack tip when at zero crack velocity, a steel of very high yield strength and of relatively low ductility was chosen; this is 18-Ni maraging steel having a yield strength of 250 ksi ( $1.7 \times 10^9$  N/m<sup>2</sup>). One-inch thick wedge-opening-loading specimens<sup>4)</sup> constructed of this steel were employed\* because in such specimens it is easy to insure that the crack will self-arrest at constant hydrogen fugacity since for a fixed crack-opening displacement the plane-strain stress intensity factor decreases continuously as the crack lengthens. In such a specimen the force by which the crack is pried open is applied by torquing a bolt. The force exerted by the bolt was measured by a calibrated load cell, consisting of a loading tup and two strain gauges wired as a full bridge, the output of which was continually recorded. A computer program made it possible quickly to calculate the stress intensity and the crack length from the measured bolt force at any stage of the experiment. In addition, the bolt force could be changed during the experiment whenever the crack was stationary and the new K calculated from the new bolt force.

A simple stainless steel chamber having an O-ring gasketed lid was constructed to contain the specimen within an atmosphere of hydrogen. The loading

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\* The authors are grateful to A. W. Loginow of this Laboratory for making these specimens available to us.

bolt of the specimen could be turned from outside the chamber by means of a socket wrench the shaft of which protruded through a rubber O-ring. Suitable posts and valves were provided for hydrogen gas and air, and connection to vacuum pump, mercury manometer and bourdon-type gauge. Contamination of the specimen surface by mercury vapor from the manometer was prevented by interposing a dry-ice cooled U-tube containing gold foil. The hydrogen gas of 99.95% purity was in one set of experiments (specimen 1) passed through a trap cooled by liquid nitrogen in order to trap out moisture, and in another set of experiments (specimen 2) through a molecular sieve trap, containing  $\sim 300$  gms of Fisher-type 5A 1/16" pellets, cooled in liquid nitrogen. The only source of vacuum used was a simple mechanical pump.

The experiment was gotten under way by repeated evacuation and hydrogen filling of the specimen chamber after which the chamber was left with nearly one atmosphere of hydrogen gas. In this environment the bolt of the WOL specimen was turned to load the crack until propagation began, as observed from the load-cell output. Initiation of propagation began in the first specimen at  $K = 69.4 \text{ ksi-in}^{1/2}$  ( $76.6 \times 10^6 \text{ Nm}^{-3/2}$ ) and in the second specimen at  $K = 55.5 \text{ ksi-in}^{1/2}$ . Immediately upon initiation the hydrogen pressure was quickly reduced, thereby lowering the velocity,  $v$ , of crack propagation, after which  $v$  could be easily controlled by varying the hydrogen gas pressure,  $p$ , or by changing  $K$ . At the conclusion of the room-temperature experiments on  $v$  as a function of  $K$ ,  $p$ , and air contamination the specimen was withdrawn from the environmental chamber, cracking was completed under liquid nitrogen, and the crack surfaces were examined by optical and by scanning-electron microscopy.

#### Results and Conclusions

Once cracking had been started and brought under control as described above attention was directed to testing the theoretical inference that a crack which

had come to a halt at a certain value of  $K$  and of  $p$  could be restarted by simply raising the hydrogen pressure by a small increment. Towards this end, the crack length of a moving crack was followed as  $p$  was lowered by small decrements until the crack length became stationary ( $v = 0$ ,  $K = \text{constant}$ ) and remained so for some minutes, ranging from one to 38 minutes. Then  $p$  was raised by small increments until the crack length was observed to begin to increase ( $v > 0$ ). This process was repeated at different values of  $K$ , which were obtained either by the relaxation of the bolt force produced by the lengthening of the crack or by adjusting of the bolt force by turning the bolt at  $v = 0$  and calculating the new  $K$  from the known crack length and measured bolt force.

Fig. 1 shows the results of this type of experiment for both of the specimens used. The open symbols represent the values of  $p$  and  $K$  at which the crack self-arrested after small decrements of hydrogen pressure and, necessarily, of  $K$  by virtue of the specimen being of the WOL type. The filled-in symbols show  $p$  and  $K$  values at which the crack restarted after small increments of hydrogen pressure at stationary  $K$ . The fine, vertical lines link self-arrest and re-starting values of  $p$ , at one value of  $K$ , which are sequentially related as described above. The data points not so linked represent equally valid measurements except that they are not sequentially related, usually because  $K$  was changed after a self-arrest point was established. Small arrows are used to indicate that those points are probably too high because overly large pressure increments were applied.

The most important result is that indeed a self-arrested crack can be made to move again by only raising the hydrogen pressure, as demanded by theory<sup>1)</sup>. The magnitude of the necessary  $\Delta p$  needs consideration, however. It was noticed that the  $\Delta p$  tended to increase with increasing duration of the stationary state of the

crack prior to incrementing the hydrogen pressure. For example, the re-start point of the linked pair at  $K = 52.3 \text{ ksi} - \text{in}^{1/2}$  was obtained after 38 minutes at  $v = 0$ , rather than after 12 minutes or less for the other re-start points of linked pairs. This observation may be explained either by a time-dependent blunting of the crack tip, or by increasing contamination from the gas phase, or by both together.

That the magnitude of the  $\Delta p$  was in fact controlled mostly by contamination may be deduced from the results of willful contamination with 6 torr of air into 209 torr of  $\text{H}_2$  after the crack had been allowed to self-arrest. The  $\text{H}_2$  pressure then was slowly increased to 1200 torr ( $\approx 1.6 \text{ atm.}$ ) and left at that value during an overnite period. The crack remained stationary under 1200 torr  $\text{H}_2 + 6 \text{ torr of air.}$  The next morning the mixed gas was evacuated and the system was flushed several times with clean hydrogen. During the last refilling with clean hydrogen the crack restarted when  $p_{\text{H}_2} < 1 \text{ atm.}$  Clearly, crack blunting could not have been the reason for the failure to have restarted at  $p_{\text{H}_2} = 1.6 \text{ atm.}$  since after repeated flushing (no change in  $K$  at any time) the crack did restart at a much lower hydrogen pressure. In addition this experiment, and others of a similar nature that were carried out, shows that air (probably the oxygen content, in line with Hancock and Johnson's<sup>5)</sup> observations) produces a barrier that strongly impedes the access of hydrogen to the Elliott region, and that clean hydrogen needs time to reduce the barrier. We conclude therefore that the  $\Delta p$ 's shown in Fig. 1 are not intrinsic characteristics but are the result of adventitious contamination and would have been smaller in its absence. The smallest  $\Delta p$ 's that were observed, 12 and 13 torr at 165 and 176 torr, respectively ( at  $K \approx 43.8 \text{ ksi} - \text{in}^{1/2}$ ), are therefore to be taken as more representative of the intrinsically necessary pressure increments for restarting, though contamination is also suspected to contribute to these values.

The curve for the self-arrest pressures as a function of  $K$  probably approaches, within its relatively large scatter, the intrinsic functional between the threshold hydrogen pressures and the stress intensity factors inferred to exist from the theory. This is because a barrier layer arising from contamination can only slow down the attainment, but not change the nature, of the equilibrium between the gas phase and the Elliott region. On the other hand, the kinetics by which a barrier layer builds up will certainly affect the relationship between crack velocity and hydrogen pressure as the latter is decremented towards the threshold value. We made such measurements in these experiments and found variability in the functional relationship  $v(p)$ ; because of the variable effect of contamination and because  $K$  was not (of necessity) held constant during the approach to the threshold value, these measurements will not be reported. It is clear that careful measurements of  $v(p)$  at constant  $K$  and in the absence of contamination are of critical value in assessing the nature of the major kinetic impedance in hydrogen-induced crack propagation.

The present preliminary experiments, though vitiated to some extent by the effects of contamination, are consistent with the demands of the decohesion theory. In effect, this theory says that at the threshold value of hydrogen pressure at a given  $K$  one has not only a mechanical but also a chemical (unstable) equilibrium between the specimen and its mechanical and chemical environment. This means that a very slight increase in  $p$  should produce a finite crack velocity. It is therefore very important to repeat the present measurements under such conditions that contamination is rigorously excluded. The restarting of a self-arrested crack by very small hydrogen pressure increments, is a natural consequence of the decohesion theory but it cannot be understood in any other terms, such as dislocation dynamics

affected by hydrogen, since at room temperature one can expect only a slightly enhanced pinning<sup>6)</sup> of a static dislocation distribution to result from the small  $\Delta p$ .

Optical and scanning electron microscopy showed the crack surfaces to be very rough, giving the appearance of intergranular cracking. No distinction could be observed between regions of the crack surfaces which had parted at different values of velocity and/or of  $K$ .

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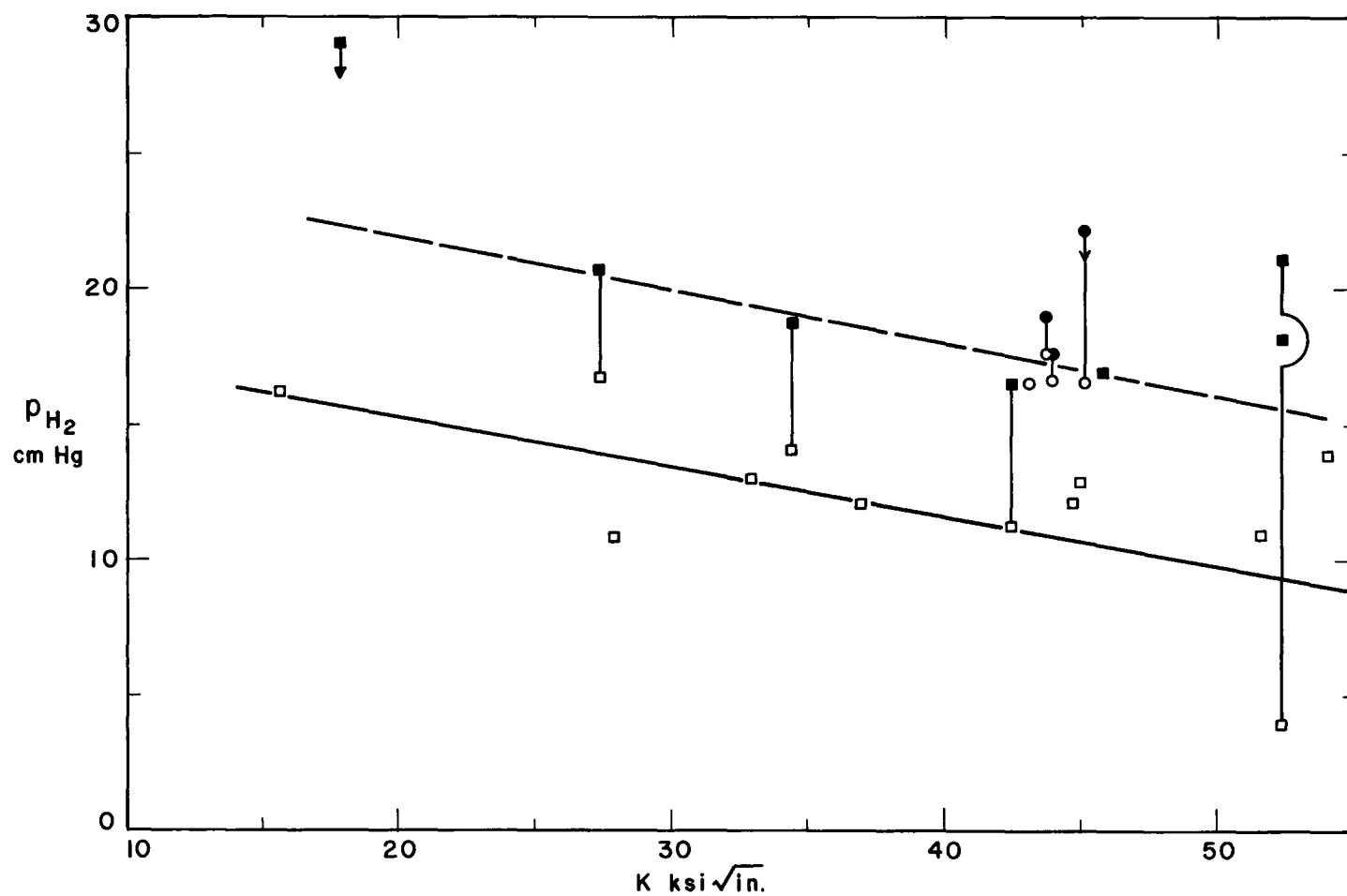


Fig. 1. Pressure of hydrogen gas at which crack self-arrests (open symbols) and pressure at which self-arrested crack restarts (filled-in symbols) as function of the stress intensity factor,  $K$ . Vertical lines interconnect sequentially related data points. Circles, first specimen; squares, second specimen.