EFFECT OF HYDROGEN IN PLASTIC ZONES OF SINGLE-EDGE NOTCH HSLA SAMPLES

I. R. Harvey* and J. G. Byrne

Department of Metallurgy and Metallurgical Engineering
University of Utah
Salt Lake City, Utah 84112-1183

INTRODUCTION

Hydrogen embrittlement has caused many service failures in linepipe steel. Service conditions present several avenues by which hydrogen can adversely affect the mechanical properties of such steel. Fesseler [1] reported that local mechanical damage can arise from handling and laying of pipe and that some cathodic protection schemes can in fact inject dangerous amounts of hydrogen into a steel. There can be synergism between these two aspects which can give extremely high hydrogen charging conditions resulting in failure [2]. Metallurgists in the oil and gas industries refer to this type of failure as hydrogen stress cracking (HSC). Future synthetic natural gas from coal gasification may contain as much as 50% H_2 which will be very deleterious to linepipe properties. Sulfides present in natural gas, hydrogen sulfide or carbon disulfide, tend to inhibit the recombination of $2H_{ADS} \rightarrow H_2$ and therefore favor atomic hydrogen absorption into a steel [3]. Welding of linepipe is a potential source of nearly every known hydrogen problem depending on the circumstances of the technique [4]. Thus it is apparent that NDE techniques adaptable to field use will be important to the maintenance of thousands of miles of existing and future pipelines. The particular use of positron annihilation to be described could be one such technique.

The particular focus of the current work was an exploration with positron annihilation of plastic zones at crack tips and how these are or are not affected by hydrogen. It had been established some time ago [5,6] that hydrogen can temporarily screen defects such as vacancies and dislocations from detection by positrons. This is a consequence of the trapping of the hydrogen at the defect prior to the arrival of the positron. The hydrogen then electrostatically repels a subsequently arriving positron, and the latter then usually annihilates with an electron of higher energy in a more perfect region of the lattice. If the hydrogen leaks away, positrons are again able to detect the defect type involved.

Another motive for the work was to verify a report [7] that claimed to have mapped with positron annihilation an increase in the size of a plastic zone in a steel due to the cathodic charging of hydrogen. Several aspects

*Now in the Department of Metallurgy, Colorado School of Mines, Golden, Colorado, 80401.

of this report were quite difficult to understand, especially how a sample containing a crack could be wedged open and then sectioned (with wedge in place) into 2-mm thick slices, which then were hydrogen charged and positron surveyed with astounding resolving power in view of the limitations of typical positron source sizes.

In the current work, hardness and positron Doppler shift data were taken to examine the relations between hydrogen and tensile-induced plastic zones ahead of a notch.

EXPERIMENTAL DETAILS

The basic positron Doppler broadening method used was described earlier [8,9]. A ^{68}Ge spot source of positrons was located behind each sample to be surveyed. The sample holder was traversed with a micrometer screw across the ^{68}Ge source, and annihilation gamma rays from the sample passed through a 3-mm wide gap between two one-inch thick lead blocks to a high-purity Ge detector. The sample material was machined from 18-inch OD by 0.25-inch thick API Grade 5L X-52 linepipe steel whose chemical analysis in wt. % was as follows: 0.07 C, 0.01 P, 0.43 Mn, 0.02 S, 0.02 Si, 0.027 Cu, 0.0001 V, 0.05 Nb, 0.015 Ni, 0.027 Cr, 0.001 Mo, 0.003 Ti, 0.058 Al, and balance Fe. Coupons were machined to 2 3/16 in. x 1 in. x 1/32 in. to fit an existing sample-traversing holder and with the longest dimension in the longitudinal direction of the original pipe. There was some grain elongation in this direction from the processing of the pipe. A 1/32-inch wide square-ended notch was machined 1/4 inch deep at midlength on one edge to give a single-edge notch (SEN) specimen. This notch was widened at its outer end to facilitate wedge placement later in the experiments. After machining, sample surfaces were ground through 600-grit paper, then polished through to 0.05 μm Al_2O_3 carried in H_2O. Surface damage was then removed by electropolishing in a solution of 94% glacial acetic acid and 6% phosphoric acid for 2.5 minutes at 45 volts.

In order to correlate the positron P/W parameter with the shape of a cracktip plastic zone, two samples were coated [10] with a commercial brittle lacquer that forms crack patterns proportional to the strain in the base metal and perpendicular to the applied strain. Two other samples designated CWZ and ZCWR were used to make charging and deformation comparisons. The CWZ was to be deformed, wedged to maintain the COD, positron scanned, hydrogen charged, then positron rescanned. The ZCWR was to be hydrogen charged first, then deformed, then wedged, recharged, and positron scanned.

Hydrogen charging was done in 1 N H_2SO_4 poisoned with 5 mg/ℓ As_2O_3 for 50 minutes at a current density of 10 mA/cm^2. Specimen ZCWR was deformed 20 minutes after charging. Deformation of all the samples was done in an Instron machine at a crosshead speed of 0.02 inches/min. The straining of a lacquered sample (TLB) was interrupted at crosshead displacements of 0.04, 0.055, and 0.068 inches for photographic studies of the plastic zone shape. In the CWZ sample, a crack became apparent at a displacement of 0.105 inches, and in the ZCWR sample at a displacement of 0.068 inches. Each of these two samples was then wedged and unloaded at those displacements for the subsequent steps described earlier.

Plastic zone sizes measured both with the strained lacquer, with positron scans, and with hardness agreed reasonably well with values calculated from fracture mechanics [11] as follows:

$$K = Y\sigma\sqrt{a} \qquad (1)$$

$$r \propto K^2/\sigma_{ys}^2 \qquad (2)$$

where a is crack length, σ is the applied stress on the un-notched cross-section, r is radius of the plastic zone, σ_{ys} is the yield stress, Y is a geometric constant, and K is the stress intensity factor.

EXPERIMENTAL RESULTS

In Fig. 1, one sees the load-versus-displacement traces of the samples ZCWR and CWZ. The marks 1, 2, and 3 indicate the displacements at which photos of the plastic zone of the lacquer-coated sample TLB were taken. The dips on the curves marked CWZ and ZCWR indicate the displacements at which wedges were inserted as a crack began to run. That plastic zone had a shape of a pair of open claws or "hinges" such as described by Hahn and Rosenfield [12] for plane stress in SEN samples. Such a shape is consistent with the profiles we observed in traversing other sample plastic zones both with positron and hardness measurements to be described below.

The positron scans were basically aimed firstly at examining the effect of hydrogen put into a plastic zone after it was formed, and secondly hydrogen put into the sample prior to the formation of the plastic zone. For the former, denoted CWZ, a crack with plastic zone was formed, and the notch displacement maintained with a wedge. Figure 1 shows that the early stage work hardening rate was lower for this material than for the ZCWR case where the hydrogen was charged into the sample before deformation. Only about 60% of the displacement of the CWZ sample was necessary to produce a crack when hydrogen was present initially.

While hydrogen was allowed to diffuse out of the ZCWR specimen, the CWZ specimen was positron surveyed as cracked, along three traverses perpendicular to the notch and 1/8 inch apart with the results shown in Fig. 2. As distance of the traverse from the notch root increased, a dip in the positron P/W parameter was found consistent with the "hinged" plastic zone shapes developed by etching by Hahn and Rosenfield [12]. It is of interest that the plastic zone shows increasing values of P/W in the "hinges" at larger distances from the notch and crack tip. This could be attributed to numerous dislocations emitted from the notch and crack region which pile up in the extremities of the plastic zones.

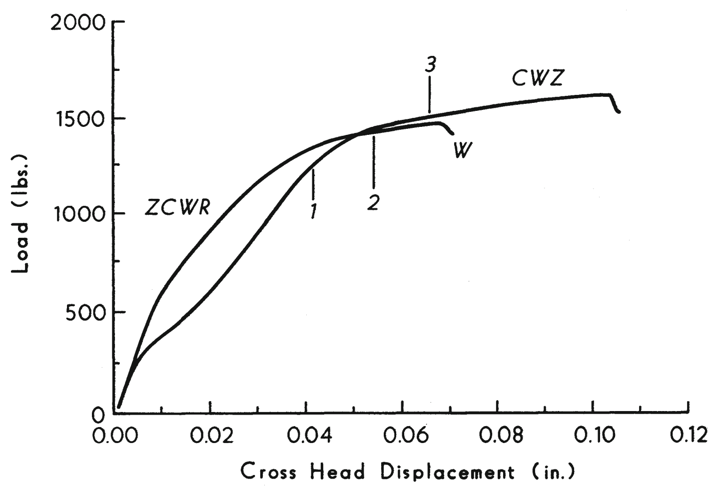

Figure 1. Load-versus-displacement traces for CWZ and ZCWR single-edge notch samples. Displacements 1, 2, and 3 refer to coated sample TLB.

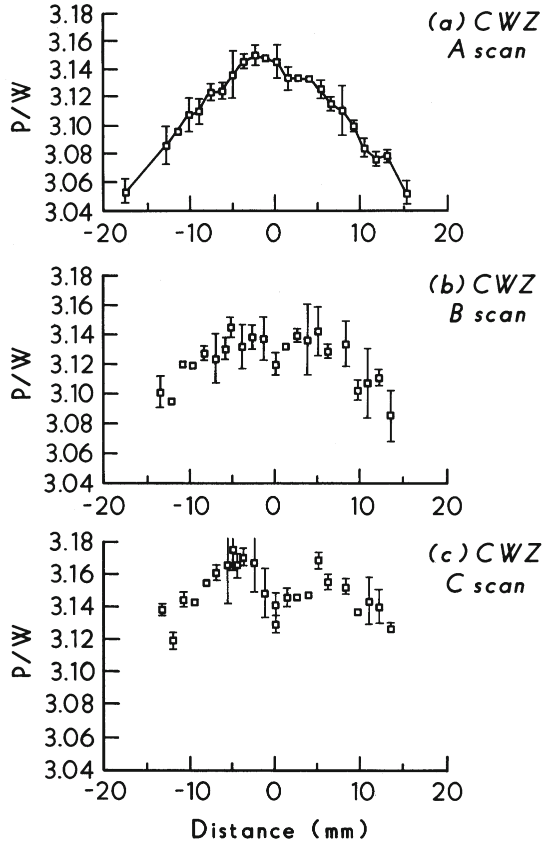

Figure 2. Positron scans across the plastic zone of the CWZ sample prior to hydrogen charging. Positions A, B, and C were respectively at 0.25 inches, 0.375 inches, and 0.50 inches away from the root of the notch. The scans were transverse to the notch direction. P/W is plotted versus position in mm to each side of the notch center.

Figure 3 shows an overlay of Fig. 2a and the equivalent scan following hydrogen charging plus a waiting period of 24 hours at rooom temperature to allow the dislocations to release most of the trapped hydrogen [13]. The two graphs are essentially the same. This and the fact that the wedged notch did not produce any additional crack propagation due to the hydrogen charging suggest that no change took place in the plastic zone.

The positron results of the ZCWR sample, which was charged, cracked, wedged, recharged, and allowed to release its hydrogen for 45 hours at room temperature prior to the positron scan, are shown in Fig. 4. Two curves are seen, one for the situation after charging, cracking, and wedging, and a second curve for the situation after final recharging and subsequent relaxation period. One notes that the P/W parameter is reduced nearly everywhere except at the peak after recharging and waiting 45 hours. This suggests that there are real differences between the type of hydrogen traps involved in the CWZ case where 24 hours was sufficient to nearly degas the specimen. In the ZCWR case, even after 45 hours, there was still enough hydrogen in the sample to give positron screening effects indicated by the lower P/W values. The charge-strain-charge sequence used with the ZCWR sample may develop traps with greater binding energies for hydrogen. These

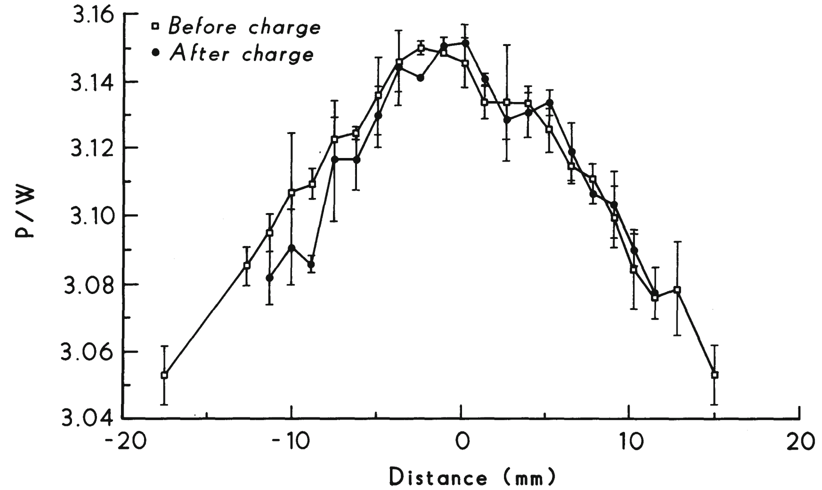

Figure 3. Positron scan of CWZ sample from Fig. 2a superimposed on a scan made after charging with hydrogen and waiting 24 hours. P/W is plotted versus position in mm to each side of the notch center.

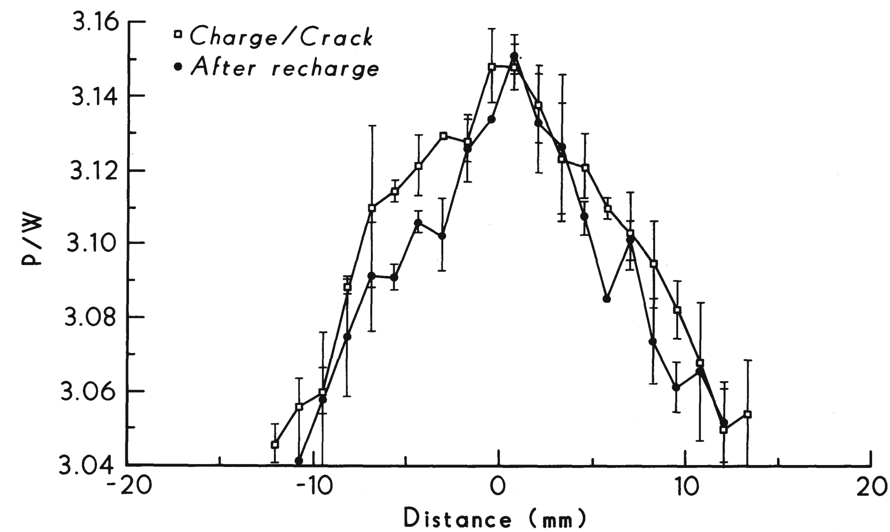

Figure 4. Positron scans of ZCWR sample before and after recharging. Recharging caused general lowering of P/W values. P/W is plotted versus position in mm to each side of notch center.

could resist the 24-hour period described by Asaoka [13] for hydrogen release. Such hydrogen would then be available for the depression of the lower P/W curve in Fig. 4 due to hydrogen screening of dislocations.

Since the initial baseline P/W values of CWZ and ZCWR were slightly different, all the values in Figs. 3 and 4 were normalized by their respective P/W baselines and replotted in Figs. 5a and 5b. In Fig. 5a, one sees that charging followed by deformation gives a higher and steeper P/W profile than does deformation alone, i.e., defect generation is predominant over proton screening in the upper curve, and defect generation is clearly stronger when hydrogen is initially present than for simple deformation alone. The faster rise and higher peak of the ZCWR curve indicates that more damage is confined in the same spatial plastic zone when hydrogen was present initially. This may mean that the hydrogen gave more resistance to dislocation motion and generation.

Figure 5b shows that the CWZ sample after charging is not much affected but that the ZCWR values after the final recharging are lowered by screening as suggested earlier.

One week after the final positron scans were run, Rockwell B hardness studies were conducted on the samples. Figure 6 shows the hardness results for a lacquer-coated and deformed TLA sample as well as the CWZ and ZCWR samples after final charging. For the TLA sample, the scan was exactly

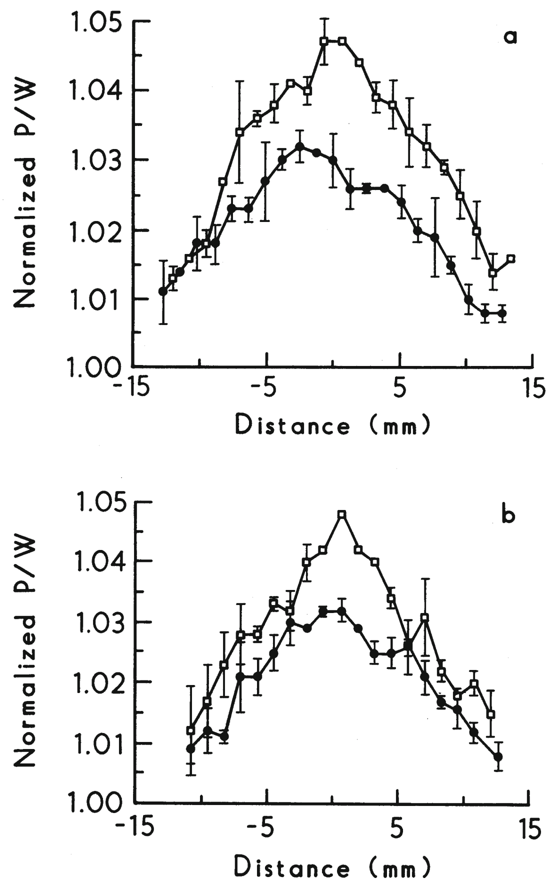

Figure 5. P/W scans of Figs. 3 and 4 divided by their respective baselines for:

a) ZCWR before recharging (upper curve) and CWZ before charging (lower curve).
b) ZCWR after recharging (upper curve) and CWZ after charging (lower curve).

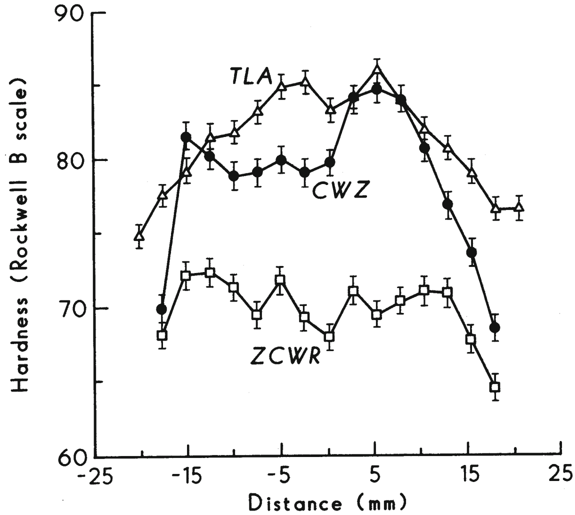

Figure 6. Rockwell B hardness values for samples TLA, CWZ, and ZCWR. Values of R_B versus position in mm to each side of notch center.

analogous to that in Fig. 2 denoted as position A for the CWZ sample before hydrogen charging. TLA incidentally is an identical sample to the TLB referred to in Fig. 1. The hardness trend is reasonable; however, the as-polished hardness for the material was R_B 82. The crossover points with the baseline hardness correspond exactly to the outside limits of the visible hinges found optically in the TLA lacquer-coated sample. This would therefore indicate a softening next to the plastic zone. A perhaps related surface-softening effect had been noted in annealed 4340 steel tensile samples at 12% elongation [14]. The latter hardness observation correlated with earlier reports of decreases in surface dislocation density [15] and positron lifetime at 12% strain in the same samples. The CWZ and ZCWR curves also indicate softening effects related to hydrogen, but here we are on firmer ground. The CWZ values show an overall lowered hardness compared to TLA, while the ZCWR is lowered still further and also seems to lose the characteristic peaking tendency. Many other workers have found hydrogen to sometimes produce softening in various steels. For example, if the charging is severe, unrecoverable geometric softening due to voids and fissures can result, whereas if the charging is mild, reversible hardness loss can come from hydrogen-enhanced screw dislocation mobility [16]. Many other hydrogen-softening reports and mechanisms are summarized by Lunarska [17], but for the present situation the suggested high fugacity or severe charging explanation of Hirth and coworkers [16] based on geometric softening due to voids and fissures would seem appropriate. The double charging of ZCWR relative to CWZ would fit this explanation as would the lower values of CWZ with respect to TLA. Another explanation of such softening which could be mentioned is that of Li et al. [18] who contend that hydrogen absorption or removal can be facilitated by the motion of dislocations where a hydrogen fugacity gradient exists. Thus dislocation motion and subsequent annihilation, and thus softening, can be caused by a gradient in hydrogen fugacity.

Finally, it is interesting to compare predicted and observed plastic zone sizes. From Equations (1) and (2) given earlier with $1/2\pi$ as the proportionality constant in Equation (2) and taking the crack length, a, to be the depth of the machined notch, and a/w (w is specimen width) as 0.26, the plot of Y versus a/w in Hertzberg [11] gives a value of Y = 2.7. Then with

σ_{ys} reported by the manufacturer as 428 MPa, one gets values of plastic zone radius of 5.1 mm for TLA, 4.6 mm for ZCWR, and 5.0 mm for CWZ. A value of approximately 5 mm for r is less than but perhaps comparable with the distance visible between the "hinges" in a photo of specimen TLB pulled to displacement 3 in Fig. 1. Further, the crossover points at R_B 82 in Fig. 6 for the TLA sample are at about ±10 mm with respect to the notch center, which is also larger than but perhaps comparable with the calculation of 5 mm.

In conclusion we find no change in plastic zone size due to hydrogen charging, which was one of the main questions prompting this investigation.

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