



Steels for Seamless Hydrogen Pressure Vessels

W. T. Chandler¹ and R. J. Walter.¹ Loginow and Phelps have made a considerable contribution to our knowledge of the effect of high-pressure hydrogen on sustained-load crack growth in steels. However, we believe that the data on threshold stress intensity for sustained-load crack growth in hydrogen (K_H) for the so-called resistant steels and possibly some of the moderately susceptible steels must be applied with caution to pressure vessels. In service, pre-existing cracks in hydrogen pressure vessels will be loaded in the hydrogen during pressurization. In the tests conducted by Loginow and Phelps, precracked specimens were loaded in air and thus the crack surface was covered with oxide prior to exposure to hydrogen. We have performed tests in which precracked specimens were loaded in hydrogen to determine K_H . Loginow and Phelps found no crack growth in type 304 stainless steel in 10,000 psi (69 MN/m²) hydrogen at a stress intensity of 62 ksi $\sqrt{\text{in.}}$ (68 MN m^{-3/2}). In tests on a similar stainless steel, type 321, in 5000 psi (34.5 MN m^{-3/2}) hydrogen, we noted crack growth on loading in hydrogen at a stress intensity of 28 ksi $\sqrt{\text{in.}}$ (31 MN m^{-3/2}). The crack growth was small, since the crack soon arrested because of blunting due to rounding of the crack front. Crack growth can be reinitiated by loading to a stress intensity higher than previously, after which the crack grows for only a few minutes and again arrests, but at a stress intensity higher than the previous arrest stress intensity. This process of crack growth initiation and arrest at succeeding higher stress intensities was continued up to a stress intensity of 111 ksi $\sqrt{\text{in.}}$ (122 MN m^{-3/2}). A similar behavior was found for the nickel-base alloy Inconel 625, except that rapid crack arrest resulted from crack branching rather than crack rounding. We suggest that crack growth did not initiate in the steels called resistant steels by Loginow and Phelps because of the presence of the oxide on the crack surface. In light of our results, granting that we tested different materials, did Loginow and Phelps see any correlation between K_H and the stress intensity at initial loading for the moderately susceptible steels? It should be noted that as a crack grows through a pressure vessel wall, the stress intensity is continually increasing. It is possible for materials in which cracks tend to blunt or branch in hydrogen that although cracks will arrest at a relatively high stress intensity in a decreasing stress intensity test, a crack may begin to grow at a lower stress intensity when loaded in hydrogen, and the crack may continue to grow when the stress intensity is continually increasing. Tests of this nature are required.

The authors' observation that blunting was not a factor in preventing sustained load crack growth was based strictly on formation of the plastic zone ahead of the crack. It is our observation from microscopic examination of surface cracks in tensile specimens and the crack fronts in WOL specimens that crack blunting

occurs because of a combined environmental-microstructural effect. As a result, a rounded crack tip is preferred over a sharp crack. Have the authors performed microscopic analysis of the crack tips on the lesser embrittled steels?

The K_H determined by Loginow and Phelps is, of course, the threshold stress intensity for crack growth in hydrogen under a sustained load. Many service conditions involve cyclic loading—for example, pressure vessels are subject to cyclic loading due to pressurization-depressurization. Cyclic crack growth rates are affected by hydrogen environments at stress intensities below K_H . We have recently performed tests to determine the influence of 15,000 psi (103.4 MN/m²) hydrogen on cyclic crack growth rates in ASME SA-105 Gr. II steel, which had a yield strength of 39 ksi (269 MN/m²). Cyclic crack growth rates for a cyclic frequency of 1 Hz ($R = 0.1$) ranged from approximately 100 times as fast in hydrogen as in helium at a stress intensity of 20 ksi $\sqrt{\text{in.}}$ (22 MN m^{-3/2}) to approximately 10 times as fast in hydrogen as in helium at a stress intensity of 40 ksi $\sqrt{\text{in.}}$ (44 MN m^{-3/2}). We also performed tests in hydrogen at a cyclic frequency of 0.1 Hz. The 1-Hz tests were performed with a sinusoidal wave contour, and the 0.1 Hz tests were performed with a 0.5 second ramp to the maximum load, a 9-s hold at the maximum load, and a 0.5 second ramp to the minimum load. Thus, the basic difference between the two cyclic rates was the 9-s hold period during the 0.1-Hz cycle. The crack growth per cycle in hydrogen was 2–3 times greater for the 0.1-Hz cycle than for the 1-Hz cycle. Thus, under these conditions in which the crack was being continually resharpened by cycling, crack growth occurred under a sustained load and at stress intensities as low as 13 ksi $\sqrt{\text{in.}}$ (14 MN m^{-3/2}).

The results of our measurements (reference [3], Loginow and Phelps) on HY 100 and ASTM A-302 steels also emphasize the importance of considering cyclic, as well as sustained, load crack growth during hardware exposure to hydrogen. The cyclic load crack growth rates in these steels were considerably enhanced in high pressure hydrogen at stress intensities as low as 10 ksi $\sqrt{\text{in.}}$ (11 MN m^{-3/2}). Sustained load crack growth was restricted to the inner plane strain region for ASTM A-302 steel at stress intensities above 58 ksi $\sqrt{\text{in.}}$ (64 MN m^{-3/2}).

Preliminary tests on HY 100 showed that hydrogen-induced sustained load crack growth occurs only at stress intensities above 100 ksi $\sqrt{\text{in.}}$ (110 MN m^{-3/2}). Thus it is exceedingly dangerous to predict susceptibility to hydrogen-enhanced crack growth from sustained load crack growth data if the hardware is cyclically loaded in hydrogen.

The authors have made valuable observations regarding the crack path in the more susceptible steels, which has led them to postulate a mechanism for hydrogen-induced sustained load crack propagation. We would like, however, to offer another interpretation of their results. It is believed that the apparent discontinuous crack growth at low K levels can be correlated with the crack branching observed at these stress intensities. These branches can interweave to give the illusion of a discontinuous crack front.

The discontinuous nature of the fracture near crack arrest differs greatly from our observations of tensile and fracture mechanics specimens tested in hydrogen. In all instances, there is a sharp demarcation between the brittle subcritical hydrogen-induced crack growth and the ductile fast fracture critical crack growth. Beachem² also examined numerous WOL specimens tested in hydrogen environments, and observed that the fracture appearance was increasingly more brittle with decreasing K . Crack growth in low alloy steel specimens immediately prior to crack arrest was brittle intergranular without indication of discontinuous crack growth. The lack of discontinuous crack extension was noted by Beachem to be in apparent conflict with Troiano's model for crack extension.

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² Beachem, C. D., "A New Model For Hydrogen-Assisted Cracking (Hydrogen "Embrittlement"), *Trans. AIME*, Feb. 1972, pp. 437–451.

A possible explanation for the authors' fractographic observations is that K_H differs for the microstructural constituents, and the difference in fracture appearance near crack arrest is a reflection of the differences in K_H for these constituents.

As a final note, it appears that the authors monitored the load from strain gages located at the ends of the loading pins. At these locations, the strain measurements lie outside of the major load path. Would the authors comment on the accuracy of these measurements?

L. M. Dvoracek.³ The authors are to be commended for their excellent paper on the susceptibility of steels to cracking in high-pressure hydrogen. They have shown, as other investigators have, that susceptibility of steels to cracking increases with the yield strength. Since the cracking process is one of hydrogen embrittlement, the size of the plastic zone at the crack tip is very important. This discussor wonders, since the fatigue cracking was not done in the presence of hydrogen, whether the larger size of the plastic zone of the lower strength (resistant) steels made them immune. If the fatigue cracking has been done in the presence of hydrogen in either a gaseous form or in a sulfide solution, the critical stress intensity factor would have been decreased and the plastic zone size would have been smaller. A smaller plastic zone would promote cracking. The authors' proposed cracking mechanism by steps at areas of high triaxial stress could then proceed, thereby causing cracking in the lower strength resistant steels.

W. F. Brown, Jr.⁴ The authors are to be congratulated for presenting data that is of importance to the users and fabricators of gaseous hydrogen storage vessels. NASA has, in the past, encountered failures in using large welded vessels to store hydrogen gas at high pressures. These failures, in many cases, were associated with the propagation of weld cracks which existed when the vessels were placed in hydrogen service. These cracks propagated along weld paths and eventually caused leaks. It was considered desirable to reduce the hydrogen pressure for those vessels in service with the thought that the cracking rate would be reduced. However, no data was available on crack growth rates in hydrogen, and decisions on pressure reductions were purely arbitrary. The type of data presented by the authors is directly useful in establishing the effects of reduced hydrogen pressure on the crack propagation rates for seamless vessels. I hope that this investigation will be extended to include the effects of hydrogen on weldments in pressure vessel steels because experience has shown that the failure problem is mainly associated with welded vessels.

I would appreciate further explanation of several points in the authors' paper: (1) Why was a 10-percent secant used to determine the air-fracture toughness measurements? ASTM E-399 has always specified a 5-percent secant. (2) Which of the materials listed in Tables 1-4 are tubular? (3) Was the hydrogen analysis significantly different after a run as compared to its analysis before a run? (4) Were the K_I values as determined from direct measurement of the final crack length (equation (1)) different from those calculated on the basis of load measurement (equations (2) and (3)). (5) Could crack closure be responsible for the light parts of the heat-tinted hydrogen crack? If closure forces were sufficient, the heat tinting atmosphere might not have reached these areas.

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Authors' Closure

The comments of Chandler and Walter are especially appreciated because of the commentators' extensive experience with testing in high-pressure hydrogen. With respect to the effect of an oxide film on crack propagation, it is recognized that in WOL specimens, precracked in air, crack growth begins only after the film at the crack tip has been penetrated or reduced by hydrogen. However, once crack propagation has initiated in hydrogen, the crack tip remains free of any oxides. This condition pertains to all moderately and appreciably susceptible steels listed in our paper. For these steels, spontaneous crack arrest occurred in absence of an oxide film at the crack tip. Thus, the K_H values, obtained under conditions of crack arrest, represent the lower limit of stress intensity for crack initiation. The nature of the oxide film that formed on the resistant carbon and alloy steels before exposure to hydrogen is considered to be similar to the film on the low-alloy steels which showed moderate or appreciable crack growth in hydrogen. Therefore, it is believed that hydrogen did penetrate the oxide film of the "resistant" steels and would have caused crack propagation if these steels had not been resistant. Therefore, the data obtained, although not promising that the lower strength steels are immune, are considered to indicate strongly that the steels are very resistant to hydrogen crack propagation. In this respect, it is noteworthy that the maximum yield strength of the resistant steels is at about the level that separates resistant from nonresistant steels in other environments (e.g., H_2S solutions) that produce cracking by hydrogen embrittlement.

The results by Chandler and Walter obtained on Type 321 stainless steel could be explained by nonelastic effects. Decrease in load on a WOL specimen can result not only from crack growth, but also from yielding at the crack tip during and immediately after loading, and extreme care must be exercised in interpreting load-cell indications. The increase in "arrest" values on successive loading steps is possibly the result of work hardening, which is very pronounced in austenitic stainless steels.

In our tests, we did not see any systematic effects of initial stress intensity on K_H .

With respect to crack blunting, we would like to mention that metallographic examination was performed on all steels that showed crack propagation, and that blunting of crack tips was not observed at magnifications up to 1000X.

With respect to dynamic loading, it was recognized in our paper that dynamic loads could alter the level of K_H , which in our tests was obtained under static conditions, and that cycling frequency could affect the results as well. Most hydrogen pressure vessels are operated at essentially constant stress during most of their service life. Superimposed are very low frequency stress changes resulting from filling and discharging operations. In instances of high-frequency stress changes, the critical K values must be determined for the specific service conditions.

The alternate mechanism for crack propagation in hydrogen proposed by Chandler and Walter is plausible. However, detailed examination of many fracture surfaces suggests that crack interweaving occurs less frequently than the discontinuous propagation. This view is supported by the presence of many shear ridges separating areas of crack propagation by the hydrogen mode.

With respect to the accuracy of load-cell measurements, the load cells were calibrated under geometrical conditions identical to those existing in WOL specimens. Comparison of measured crack length with those calculated from load cell measurement showed very good agreement.

In regard to Mr. Dvoracek's discussion—the precracking of the WOL specimens was accomplished by fatigue loading the specimens to a level well below their K_{Ic} values and also appreciably below the K_o levels used in subsequent exposure to hydrogen. Since the plastic zone size is a function of the applied K and the yield strength of the steel, the plastic zone at the inception of exposure to hydrogen was larger than during precracking. Our observations indicate that hydrogen cracks initiate within the plastic

zone. Thus, we do not expect a large plastic zone to present an impediment to cracking. Furthermore, two of the steels tested (HY-80 and A372, N&T) had the same plastic zone size because they have the same yield strength and were tested at the same K_0 . Yet, the results show that HY-80 resisted crack propagation but A372, N&T showed moderate susceptibility in our tests.

Concerning Mr. Brown's discussion—in welded pressure vessels, flaws are more likely to occur in the weld metal and the weld heat affected zone (HAZ) than in the base metal. In hydrogen service, such flaws can propagate if the weld metal or HAZ is susceptible to crack propagation in hydrogen. Thus, information obtained from tests on base metal cannot necessarily be used to predict the behavior of weldments. In seamless vessels, there are no welds and such complications do not exist.

The following are answers to Mr. Brown's specific questions:

- 1 The 10-percent secant method was chosen arbitrarily, since a valid K_{Ic} value could not be obtained on the materials of interest.
- 2 Of the materials tested, the following were taken from tubular stock:

ASTM A106 Grade C
ASTM A372 Class IV
AISI 4145
AISI 4147

The other steels were from plate stock. In the context of the subject paper, tubular and plate materials of the same steel can be considered as being similar. Although currently most of the plate materials tested are not used in tubular form, they were included in the test as possible candidates for the manufacture of seamless pressure vessels.

3 The analyses of hydrogen conducted before and after each test did not indicate any significant changes.

4 In several but not all instances, the final crack lengths obtained by direct measurement were slightly greater than those calculated from load cell measurements. These differences were dependent upon the amount of unfractured ligaments present, and did not exceed seven percent of the crack length. We believe that a small part of the load was supported by the unbroken ligaments. Since the elastic compliance function C_6 in equation (2) is based on a relationship between load and a continuous crack, any unbroken ligaments would tend to interfere with the experimentally determined compliance function.

5 Metallographic examination of specimen cross sections and fractographic examination by means of scanning electron microscope of fracture surfaces indicated that cracks in hydrogen do not progress in a continuous uninterrupted manner. These findings are in agreement with the heat-tinting pattern and indicate the presence of ligaments unbroken during crack propagation in hydrogen.