

Catalytic Dissociation and Stress Corrosion Cracking

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When a structural metal is stressed in a hydrogen environment, the metal may crack at stress levels much lower than its normal strength. Hydrogen assisted cracking in 4340 steel was studied. The specimens were normalized austenized, oil quenched, and tempered to give a hardness of $R_c 47$. All specimens were compact tension type. The overall width, height and thickness is 5.0, 4.8 and 0.25 inches respectively. The overall crack length is $1 \frac{7}{8}$ inches. The same load of 4100 lbs. was applied to all the specimens. The specimen was contained in a sealed plastic bag. Specimens were tested in pure hydrogen as reference and also in mixtures of hydrogen with CO , NH_3 , H_2S or SO_2 . Fifty cc each of one or two of these gases were added to the bag (estimated volume of 5 liters): the nominal concentration of the added gas was approximately 1%. The relative displacement of the pin holes was measured by a linear voltage differential transducer (LVDT). Under constant load, the output of the LVDT is a measure of the crack length. A more detailed description of the experimental setup is given in Ref.1.

The LVDT output was recorded as a function of time and shown in Figs. 1-4. Two specimens tested in pure hydrogen failed in approximately 4 and 8 minutes after incubation. A specimen was loaded in pure hydrogen, and the crack grew a half inch in 3 minutes, Fig. 1. At that point, 50 cc of CO was added with a hypodermic syringe. The cracking rate was drastically reduced, and remained so for 45 minutes. At that point the load was cycled once, crack grew immediately and the specimen failed in 4 minutes.

In Fig. 2, the crack grew $\frac{1}{4}$ inch in pure hydrogen in 2 minutes.

At that point 50 cc NH₃ was added, and the cracking rate was greatly reduced for the next 59 minutes. At the 61st minute, 50 cc H₂S was added, and the crack grew to failure in 9 minutes.

Throughout this investigation, it has been observed that the effect of hydrogen on the cracking rate may vary considerably from one specimen to another, even though, the specimens were heat treated identically. In Fig. 3 the specimen did not show any indication of crack growth during the first 31 1/2 minutes; at that time 50 cc H₂S was added and the crack started to grow immediately. H₂S gas enhances cracking. This has also been observed by others. After the addition of H₂S, the crack grew 1/4 inch in three minutes. At that moment 50 cc SO₂ was added. The crack continued to grow to fracture in 6 minutes.

For the next specimen, Fig. 4, 50 cc SO₂ was added after the crack grew 1/4 inch in 2 1/2 minutes. The cracking rate was greatly reduced. At the 9th minute, 50 cc H₂S was added, the cracking rate came to a complete halt. At the 31st minute, the system was cleaned and the bag was filled with pure hydrogen. The crack stayed dormant. At 36th minute, 50 cc H₂S was added. The crack grew immediately.

It is generally concluded that hydrogen exists in a metal as atoms or ions. The presence of atomic hydrogen increases the cracking rate by several orders of magnitude from what was observed in the presence of molecular hydrogen². Perhaps the dissociation of molecular hydrogen is the first step of hydrogen embrittlement. The dissociation energy of hydrogen molecule is 103.66 kcal/mole. At STP the partial pressure of atomic hydrogen is 10^{-17.8} atm. This concentration is too low to cause any observable cracking. A model of catalytic dissociation at defect sites on a metal surface was suggested as the first of the many steps in the long process of hydrogen assisted cracking¹. Hydrogen

molecules are dissociated at defect sites such as dislocations. Hydrogen atoms or ions cause cracking. Crack growth generates dislocations. This cycle of catalytic dissociation, cracking, and defect generation is shown schematically in Fig. 5.

Catalytic dissociation must take place at local high energy sites, e.g., lattice defects on metal surface. The defects include dislocations, grain boundaries, twins, second phases, point defects, and surface steps. A grain boundary is a network of dislocations. A twin boundary is a location of high energy. The energy of a coherent boundary is mostly elastic. The elastic effect is long range and is not highly localized. The non-coherent twin boundary consists of dislocations. Certain interphase boundaries can also be viewed as a collection of dislocations. The energy of interstitial or substitutional atoms or surface steps is not high enough to cause a significant amount of dissociation. We therefore think the likely sites for dissociation are dislocations and vacancies, the dislocations being the more probable ones.

Once a hydrogen molecule impinges at a dislocation terminus on a metal surface, it is dissociated into atoms or ions, which diffuse to the crack tip through the dislocation lines, causing cracking. The energy of a dislocation can be divided into elastic and electronic parts. The region above the slip plane of an edge dislocation is compressed and it is positively charged, the region below is tensile and negatively charged. A foreign atom or molecule can be bound to a dislocation elastically and/or electronically. If the foreign atom or molecule is firmly bound to a dislocation, the hydrogen dissociation process and thereby the cracking is stopped. Such are the cases with the additions of CO, NH₃, and SO₂.

When a load cycle was applied, after the cracking was stopped, a fresh new metal surface is exposed with numerous uncovered dislocation termini: hence hydrogen dissociation and cracking were resumed, see Fig. 2. When a metal surface is exposed to an ambient atmosphere, the dislocations are bound with atoms or molecules, some strongly and some weakly. Perhaps, the incubation period is the time necessary to "clean" up enough dislocation sites through the thermal kinetic process so that enough hydrogen molecules are dissociated to cause crack growth.

Not all the gases will stop the dissociation process and cracking. A clear exception is H_2S . It seems that H_2S helps to "clean" up those covered dislocation termini but may also facilitate the dissociation of molecular hydrogen causing accelerated cracking.

The bonding of atoms or molecules to dislocation sites and its effect on the hydrogen dissociation depends on the electric dipole of a dislocation, the dipole moment of the molecule, the dissociation energy and the relative sizes of the atoms and the lattice of the metal surface. If these surface interactions were known then the control of catalytic dissociation and stress corrosion cracking would be possible.

REFERENCES

1. H. W. Liu, Ya-lung Hu, and P. J. Ficalora, "The Control of Catalytic Poisoning and Stress Corrosion Cracking," to be published in Journal of Engineering Fracture Mechanics (1972).
2. H. G. Nelson, D. P. Williams, and A. S. Tetelmann, "Embrittlement of a Ferrous Alloy in a Partially Dissociated Hydrogen Environment," Met. Trans, 2 953 (1971).

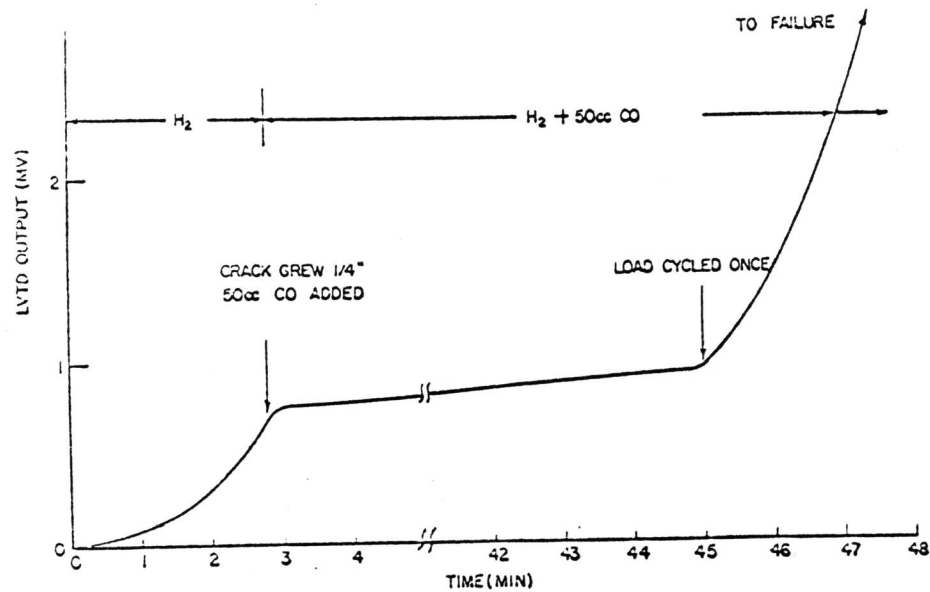


Fig. 1

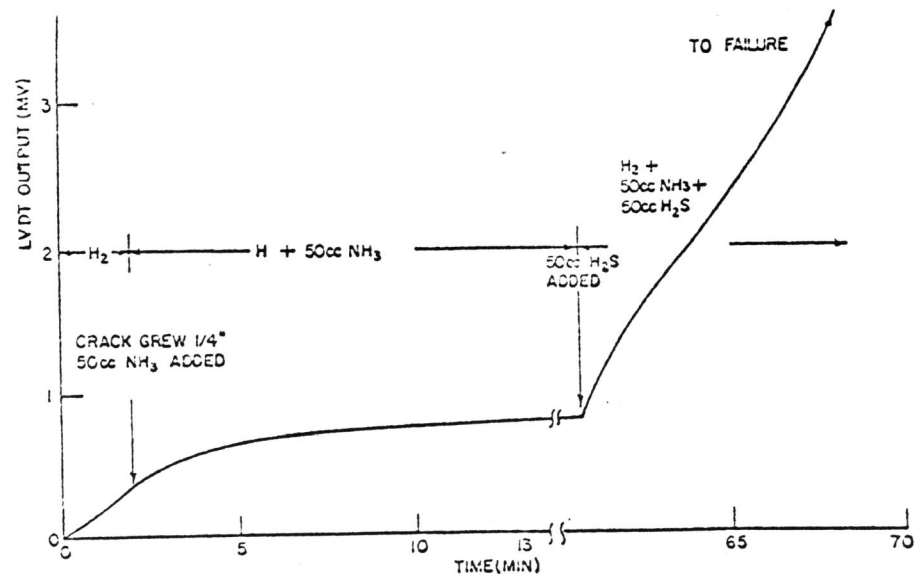


Fig. 2

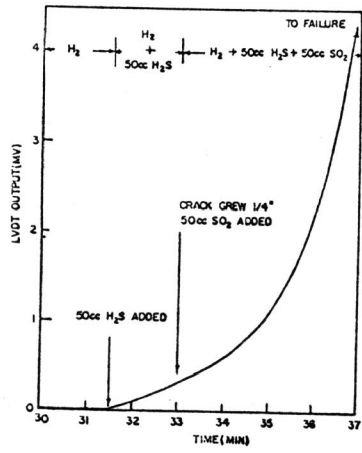


Fig. 3

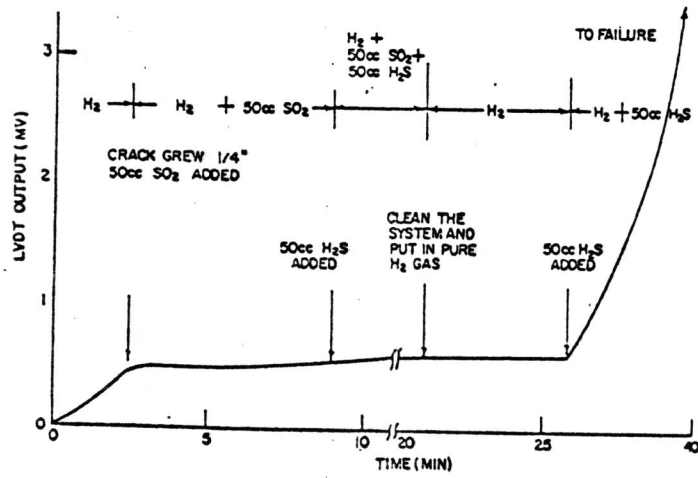


Fig. 4

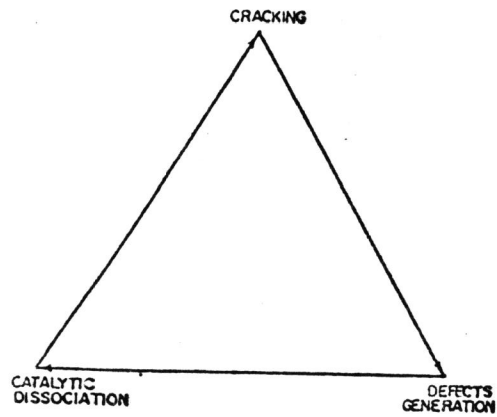


Fig. 5