Embrittlement Kinetics of N 80 Steel in H_2S Environment

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The kinetics of hydrogen embrittlement of an N 80 steel have been studied in a Na_2S-CH_3COOH solution. Determination of hydrogen content, metal density and embrittlement degree, together with acoustic-emission measurements have shown that the hydrogen distribution within the metal lattice is time-dependent and strongly influenced by non-metallic inclusions. The inclusions cause local stress intensification, favoring hydrogen collection in the lattice around them. Fracturing of charged specimens at different times evidences a mechanism of crack inactivation. An explanation of crack inactivation in terms of plastic deformation around inclusions due to hydrogen-dislocation interaction is suggested.

THE entry of hydrogen into a steel structure from a sulfide environment leads to mechanical failures at stress levels well below the UTS, even in medium strength steels (400 to 900 MN/m^2 Yield Strength).[1] The phenomena causing crack initiation and propagation to failure are known to be dependent on applied stress,[2] metallurgical structure[3] and time.[4] The influence of time is generally related to hydrogen diffusion or to crack nucleation via dislocation movement and coalescence.[5]

Assuming that the main process is the transport of hydrogen to critical zones of the metal structure (dislocation pile-ups, regions of high triaxial stress, subcritical cracks or, generally, "traps"), much attention has been paid to hydrogen mobility within the metal, *i.e.*, to the hydrogen-diffusion coefficient.

The evaluation of steels as to their embrittlement sensitivity has often been made through measurements of hydrogen uptake or effusion,[6] while mechanistic studies generally relate crack propagation to hydrogen diffusion to the crack tip.[7]

The experimentally observed times to failure, however, are hardly deducible from a diffusion-based mechanism. Actually, the surface conditions, controlling the rate of hydrogen entry, and the internal morphology of the alloy, providing sites for hydrogen accommodation, seem to be more important than the transport process itself.[8]

The discrepancy between diffusion-based mechanisms and actual behavior is clearly evident in medium strength steels which do not exhibit intergranular fractures.

In this work, some evidences of a time-dependent distribution of hydrogen inside a medium-strength steel are presented.

Fractographic observations, metal density, total hydrogen content determinations, together with acoustic stress-wave-emission (SWE) analysis, have been carried out to follow the phenomena conducive to steel embrittlement.

EXPERIMENTAL

Material

As representative material for medium-strength steel, an N 80 tube steel was chosen (C = 0.41, Mn = 1.55, Si = 0.31, P = 0.010, S = 0.010, Cu = 0.12, Ni = 0.08, Cr = 0.07, Mo = 0.27).

In order to eliminate the banded structure (due to Mn segregation) which is often found in commercial materials, the following heat treatment was applied: a) Annealing 3 h. at 1250°C; b) Austenitizing at 910°C and air quenching; c) Austenitizing at 910°C and furnace cooling; d) Tempering at 600°C for 60 min.

Step a) is meant to level Mn and Mo concentrations in the bands and in the intermediate zones: this treatment reduces the alloying element segregation to a small percentage.[9] Because grain growth occurs in step a), step b) is included to refine the grain size. The last two treatments restore the initial structure, *i.e.*, upper bainite and acicular ferrite (UTS = 800 MN/m^2, YS = 550 MN/m^2).

Cylindrical specimens were machined from the as-received tube with a 4 mm diam, heat treated and thinned to 3.8 mm diam to eliminate any surface modification. Each specimen was wrapped in a Teflon tape except for an area of 3.2 cm^2 to be exposed to the test medium.

Test Procedures

The specimens were stressed at a constant load, with or without applied cathodic current in a 0.5 M CH_3COOH + 0.01 M Na_2S solution at room temperature. The solution pH was buffered at the value of 4, so that the chemical equilibria between $H_2S - HS^- - S^=$ were completely shifted towards the associated acid. Times to failure were recorded versus current intensity for specimens stressed to 90 and 100 pct of the yield strength.

To follow the embrittlement kinetics, a number of specimens were maintained at 90 pct of yield strength under -1 mA applied current and removed at suitable time intervals; the hydrogen content, metal density and degree of embrittlement were determined. Hydrogen analyses were performed according to a modified vac-

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uum extraction method at 650°C;[10] metal densities were measured by the Mohr-Westphal method.

The degree of embrittlement was evaluated in terms of the area pct of embrittled zones observed on the fracture surface of specimens mechanically ruptured after test. Measurements of the number of inclusions per unit area and the inclusion size distribution were performed with automatic image analyzing instrumentation. The SWE tests were performed with a commercially available acoustic emission apparatus. The basic information recorded was the total number of acoustic signals emitted by the loaded specimen (80, 90 and 100 pct of the yield strength) while subjected to cathodic charging. The signals were picked up with a PZT-5A transducer (155 KHz resonance frequency), amplified by a factor of 10^4 (80 dB) and filtered (HP filter 0.1 to 2 MHz).

RESULTS

The electrochemical conditions under which hydrogen enters the metal have been changed through the change of the applied cathodic current at two stress levels, namely 100 and 90 pct of the yield strength. The curves of Fig. 1 show a constant time to failure up to a value of cathodic current which depends on the applied stress. Then the time to failure falls rapidly by two decades to a minimum, followed by a steep rise at a cathodic current of 30 mA independent of the stress.

In the current range where the times to failure were independent of the applied current, the embrittlement kinetics of the steel were followed on specimens stressed for 3, 30, 50, 120 and 284 h at 90 pct of the yield strength under a 1 mA cathodic current. The results, which are summarized in Fig. 2, reveal an embrittling process which is not a simple function of the hydrogenation time. Contrary to what would be expected, metal density and percentage of embrittled area do not increase steadily with time but, rather, show the attainment of maxima at relatively short times and then decrease with longer charging times, while hydrogen content remains constant after some 50 h.

The fracture surface of a specimen mechanically ruptured after hydrogen charging shows a distribution of brittle fracture zones (Fig. 3). These zones generally surround an inclusion-containing cavity (Fig. 4). Microprobe analyses always indicated the presence of aluminates at the center of cavities. When embrittled specimens were ruptured at liquid nitrogen temperature (*i.e.*, under brittle conditions), the cavities were again observed, indicating that the cavities did not derive from the plastic processes occurring during tensile rupture but they originated directly from the embrittlement process. However, the actually embrittled areas were not pre-existent to the tensile test but appeared as such only when the specimen was fractured.

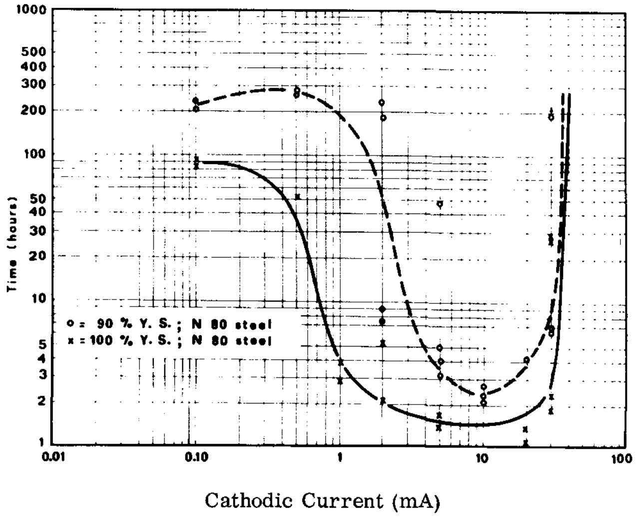

Fig. 1—Time to failure vs applied cathodic current at two levels (90 and 100 pct of the yield strength).

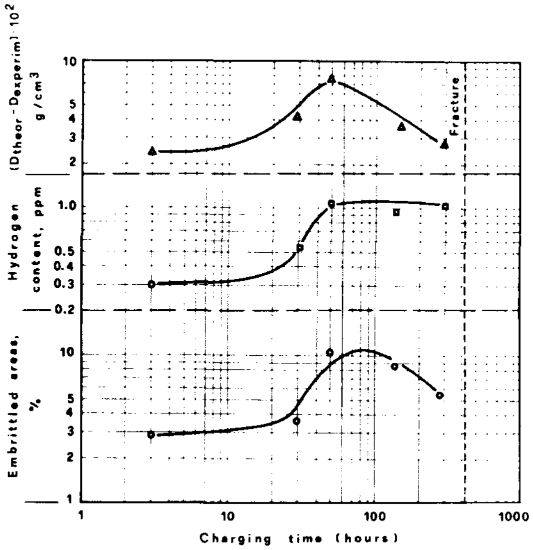

Fig. 2—Pct embrittled area, H total content and metal densities during embrittling test (applied cathodic current 1 mA, load level 90 pct yield strength).

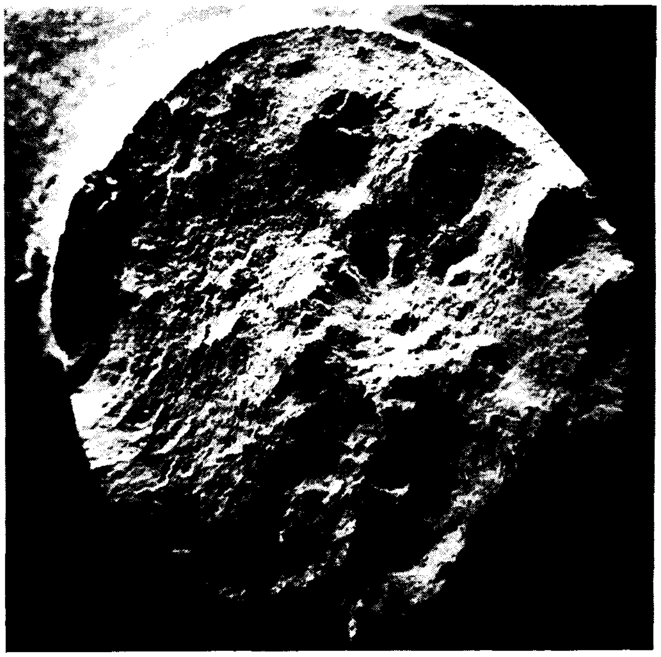

Fig. 3—Distribution of the brittle fracture zones of an embrittled specimen. Magnification 38.25 times.

Thus, it was possible to follow the actual hydrogen distribution by mechanically rupturing the material after different charging times since the brittle fracture zones represent the regions rich in hydrogen at the time of tensile rupture.

The growth of the embrittled areas is sketched in Fig. 5 and their total number is plotted as a function of the hydrogenating time in Fig. 6. It is interesting to observe that, while the number of embrittled areas increased steadily with time, their mean dimensions first increased and then decreased at longer times. The presence of inclusions at the center of the embrittled areas evidenced the importance of these particles on the hydrogen distribution inside the metal structure. To relate the inclusion dimensions and the embrittled areas a dimensional distribution has been performed with the Quantimet and the results are reported in Table I.

In Fig. 7 typical plots of the total number of acoustic signals emitted during the embrittling tests are shown. It is apparent that the phenomena leading to brittle fracture were discontinuous in nature, as has been shown previously by other techniques.[11]

DISCUSSION

The conditions controlling the entry of hydrogen into steel in a sulfide environment are essentially electrochemical, as evidenced by the peculiar dependence of the times to failure on the applied cathodic current. The decrease of the time to failure is caused by an increase of hydrogen discharge in the presence or under the control of absorbed HS^- anions.[12,13] When the electrode becomes sufficiently negative to desorb the sulfurized anions, brittle fracture is no longer observed in a medium-strength steel. This behavior is at variance with what is generally observed on high-strength steels, which suffer brittle fracture also at high current densities. In the range of currents from the inflection point to the minimum of the curve plotted in Fig. 1, it is clear that the times to failure are essentially determined by the rate of atomic-hydrogen uptake as a function of the electrochemical conditions established at the metal-solution interface.

Diffusion coefficients apparently do not play any role in the embrittlement mechanisms. Indeed, the depth of penetration, as derived from Fick's diffusion equations for room-temperature conditions at the observed failure times, assuming complete surface saturation, can be very small in comparison with the specimen diameter. Also in the lower current range, the embrittlement kinetics do not seem to be limited in any way by transport processes driven by hydrogen-concentration gradients: times to failure, indeed, are independent of the cathodic current, *i.e.*, the hydrogen flux. Under such conditions, the brittle fracture should be related to local oversaturation of hydrogen. At least for the specimens charged at a cathodic current of 1 mA, the total hydrogen content reached a constant value after

Fig. 4—Inclusion-containing cavity in the middle of an embrittled area. Magnification 1060 times.

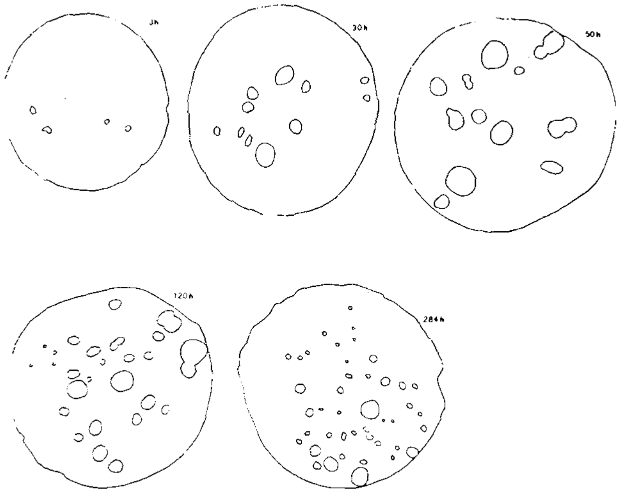

Fig. 5—Variation of embrittled areas as a function of hydrogenating time (specimen mechanically fractured after charging).

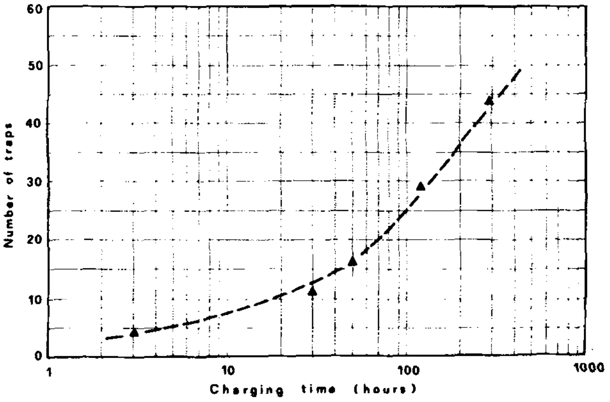

Fig. 6—Increase in the number of cavities during embrittling test (applied cathodic current 1 mA; load level 90 pct yield strength).

1/6 of the specimen life, as is shown in Fig. 2. It has been found that the hydrogen content of similar medium-strength steels shows a well-defined maximum under continuous cathodic charging.[14] The variation with time of metal density and the number of embrittled areas suggests an embrittlement mechanism which involves a time-dependent distribution of hydrogen around the entrapping cavities. From the observation of fractured surfaces it can be deduced that, for short charging times, hydrogen is mainly collected in the lattice around the largest inclusions and produces few, but relatively large, embrittled areas. With increased charging time, however, more inclusions with smaller diameters become active, apparently sucking hydrogen from the previously high concentration regions. As is shown in Fig. 5, the embrittled areas grow in number but decrease in size with increased charging time: as a result, the percentage of embrittled area first increases and then decreases.

Table I. Dimensional Distribution of the Inclusion Contained in N 80 Steel

Number of Inclusions	Dimensions
10	>6.5μ
80	>3.2μ
200	>1.6μ
500	>0.4μ

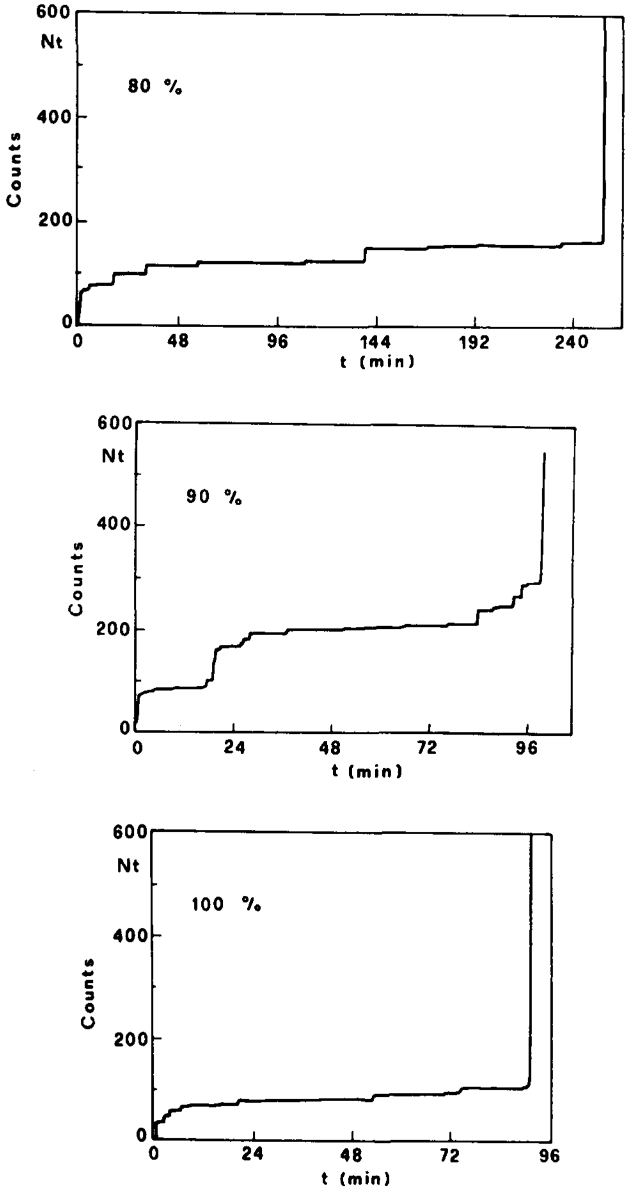

Fig. 7—SWE and hydrogen embrittlement under cathodic current (5 mA).

In order to explain such results, the assumption is made that the lattice-dissolved hydrogen is distributed according to the local intensity of the externally applied stress. If the transport processes are not limiting, *i.e.*, if diffusion occurs swiftly, then the local hydrogen concentration (C) can be derived thermodynamically by equating in every point of the stressed structure the partial molar free energy of hydrogen:

$$RT\,d\ln C = \overline{V}\,d\sigma \qquad [1]$$

from which

$$\frac{1}{C}\frac{dC}{d\sigma} = \frac{\overline{V}}{RT} \qquad [2]$$

where $\overline{V}$ is the partial molar volume of hydrogen in the metal lattice, σ is the local hydrostatic stress, R is the gas constant and T is the absolute temperature. The resulting hydrogen concentration is an exponential function of the local hydrostatic stress level. As the inclusions are of different dimensions and shapes, they will induce a different local intensification of the external stress. The local variation of the hydrostatic stress (σ) produces a consequent variation of the hydrogen concentration.

The hydrogen distribution, however, is not steady because, at longer charging times, not only are smaller inclusions capable of collecting hydrogen (which could depend on the increase of hydrogen concentration inside the lattice or on the saturation of the stress fields associated with the largest inclusions), but the maximum size of the observed embrittled areas decreases (Fig. 5), thus suggesting that hydrogen diffuses away from the neighborhood of the largest inclusions. These latter traps then have to become oversaturated, in order to let hydrogen diffuse away, and this is possible only if the local stress intensification is decreased by a morphological modification of the inclusion-matrix interface.

A decrease of stress intensification is evidenced by the SWE analysis. From Fig. 7, a decrease of the count rate $\dot{N}$ (counts/s) with time is observed. If it is assumed[15] that $\dot{N}$ is proportional to some power (>1) of the stress-intensity factor K, the decrease of $\dot{N}$ must be understood as a decrease of the K values associated with the largest inclusions. It has already been evidenced[16] that the count rate ($\dot{N}$) of the acoustic activity of a specimen containing defects of different sizes and of different K under an applied stress, is associated with the K value of the largest defect. The mechanism which permits the stress intensification to decrease must imply a plastic deformation of the matrix so that the inclusion-containing cavity can become more nearly round. It is often assumed that high pressures exist inside metal cavities because of the precipitation there of atomic hydrogen and its recombination to molecules. The results of Fig. 2, however, cannot support such a pressure theory in the case under discussion. When all the hydrogen present in the metal is supposed to be precipitated within the void volumes (which can be calculated from the density variation) and any absorption at inclusion and matrix interfaces is disregarded, the maximum resulting pressure, calculated from the ideal gas equation, is lower than 100 atmospheres, *i.e.*, less than 10 MN/m^2. Thus, the rounding out of the cavity cannot occur as a consequence of pressure buildup at the metal-inclusion interface; this fact leaves out the influence of molecular hydrogen collected on the inclusion surface.

The experimental picture presented in this work is more consistent with mechanisms which take into account the interaction of dissolved hydrogen with lattice defects. It must be emphasized, however, that the assumption often made that only one crack propagates inside the hydrogenated metal is not generally correct, at least insofar as subcritical propagation in medium-strength steels is concerned. Actually, the largest cracks, or traps, which initially collect most of the dissolved hydrogen, can be inactivated at longer times. It must be stressed, therefore, that the embrittlement mechanism proceeds via activation and inactivation of hydrogen traps with ever smaller dimensions as the time increases. The mechanism of inactivation can be hypothesized to be due to hydrogen-dislocation interactions which increase the dislocation energy or induce dislocation multiplication in the plastically deformed zones around inclusions. If an increase of dislocation density is produced, then the probability of interaction among dislocations of opposite sign increases. The resulting annihilations reduce the highest local stresses at the inclusion tip. This allows migration of dislocations from surrounding edges and thus the rounding out of the void tip.[17] This mechanism can explain the trap inactivation as a consequence of a lowering of the local stress intensification. The conditions for failure should result from a trap distribution such as to hinder the inactivation mechanism. The critical parameter could be the mean distance among the embrittled areas (referred to the mean area diameter) which decreases with time as the number of active traps increases.

CONCLUSIONS

Medium-strength steels corroding in sulfide-containing environments exhibit an embrittlement mechanism which is hypothesized to be related to hydrogen-dislocation interaction around non-metallic inclusions. When the rate of hydrogen entry is low, as in the case of freely corroding steel, the hydrogen distribution inside the metal is controlled by hydrostatic stresses around inclusions. The process leading to brittle fracture is described, not as a subcritical growth of only one crack, but as activation and inactivation of hydrogen-collecting traps, where the trap is to be understood as the zone of high triaxial stresses at the tip of an inclusion-containing cavity. The mechanism of traps inactivation is thought to be the lowering of the stress intensification at the cavity tip caused by the rounding out of the cavity tip as a result of hydrogen-dislocation interactions, rather than by pressure-induced deformation.

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