HYDROGEN ATTACK OF CARBON AND LOW-ALLOY STEELS

The mechanism of attack is believed to involve the absorption of hydrogen at the outer surface with establishment of an equilibrium between the molecular and atomic hydrogen

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The term "hydrogen attack" is used to describe the damage to the microstructure of steel due to exposure to hydrogen. This damage can be very extensive and can markedly reduce the tensile strength of the metal and result in failure under moderate stresses. This is in contrast to the reversible embrittlement which has been the subject of much more study. In that case, the hydrogen is dissolved in the metal, either due to exposure to high-pressure hydrogen or to electroplating, and upon heating to moderate temperature or standing for a long time the hydrogen leaves and the metal returns to its previous condition.

It has been established that attack by hydrogen involves reaction with the metal carbides to form methane, and tests have been showing that the amount of methane formed corresponds to the amound of carbon lost. This reaction is accelerated by increased pressure, particularly at higher temperature, and it is approximately proportional to the length of the time of exposure.

Some carbides are more stable

It has long been known that certain carbides, especially chromium and molybdenum, are thermodynamically more stable than the iron carbide, Fe_3C, or cementite. Additions of these metals to carbon steels permit services involving hydrogen at higher temperatures and pressures.

Most equipment design has been guided by the plot prepared by George A. Nelson of the Shell Development Co. which is shown in Figure 1. This plot is revised from time to time, a recent one May, 1966. (1) Nelson has kept in touch by correspondence with a large number of plant people in the petroleum and chemical industry and has recorded on this plot the cases where failures have been observed and the cases in which there have been apparently no failures. These are plant observations and they have very great value in being typical of the service conditions. On the other hand, they probably include some cases where the operating conditions were not well controlled, and particularly where there have been periods away from the reported operating conditions.

Figure 1 shows that the temperature for which a plain carbon steel can be used ranges from 600 to 700 F at low pressure up to about 450 F at pressures above 300 atmospheres. The addition of ½% of molybdenum considerably raises the temperature limits. Addition of chromium further increases the permissible temperature.

Higher pressure studies limited

The research studies at the higher pressures have been limited pretty much to some very extensive pioneering work, done by Naumann (2) in Germany in the '30's, and, then in the last decade or so, several different research problems carried out in the laboratory of Barnett Dodge (3) at Yale. In these tests, the extent of decarburization has been measured by three ways that tend to average the effect.

One is the loss in tensile strength, simply by measuring the tensile strength as related to the exposure conditions. Second, by finding the average carbon content by analysis. Third, by measurement of the expansion which accompanies the exposure. We find in some cases as much as a 25% volume expansion in the metal resulting from the decarburization.

There is a fourth way, which does not merely average, and which indicates better the nature of the decarburization. This is the microscopic examination of the structure.

More on decarburization

We felt that we wanted to get more information on the nature of the decarburization. Particularly, we would like also to know more about the service conditions for the low-alloy steels—that is, with no more than about 3% chromium. Chromium contents in this neighborhood correspond to the A-387 Grade C and Grade D steels, which are less expensive than the higher chromium steels and also more machinable and workable; it is therefore important to know what are their service limits.

We began our studies with plain carbon steel. Figures 2 through 5 show the nature of the attack at a hydrogen pressure of 10,000 lb./sq.in.

Figure 2 shows at 1000 times magnification an unexposed steel containing 0.95% carbon. This is a ferritic steel with the alternating bands of ferrite and of pure iron saturated with dissolved carbon. The irregular shape of the grains is shown here.

Figure 3 shows an attack region. The attack has taken place at the grain boundaries, and fissures have opened up. The hydrogen dissolved in the iron has reacted with the ferrite band, and the methane formed has escaped back toward the fissure. As long as the methane is contained in the fissures it tends to oppose the reaction, and the equilibrium pressure at ordinary service temperatures has been calculated as very great. It is therefore possible to develop a very high pressure and still be producing methane, that is, still continuing the attack.

Completely decarburized steel

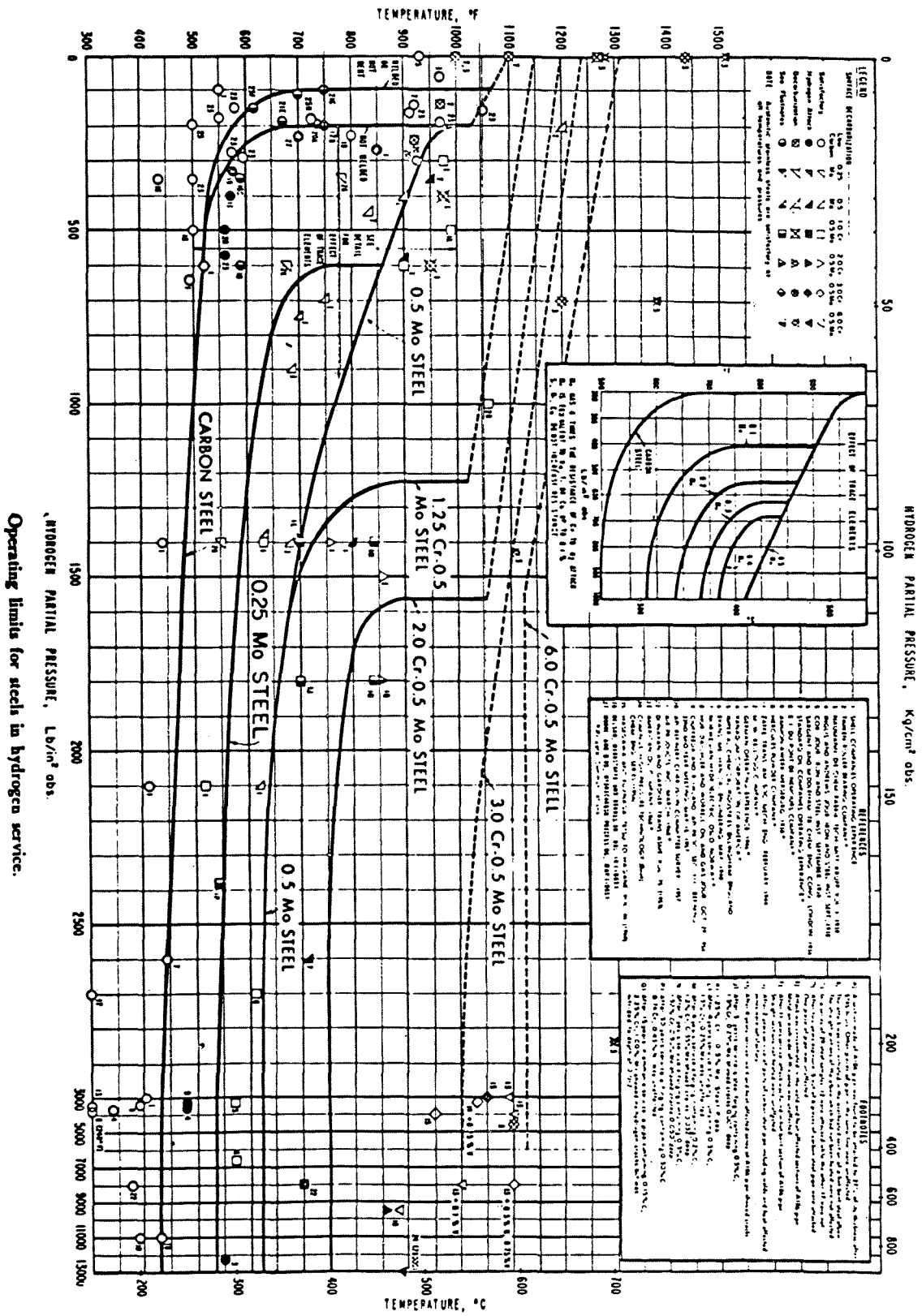Figure 4 shows a completely decarburized steel. All of the ferrite

Figure 1. Nelson's operating limits for steels in hydrogen service.

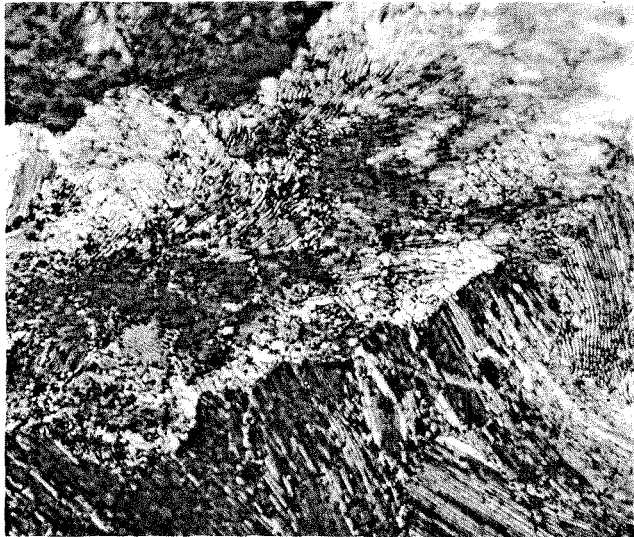Operating limits for steels in hydrogen service.

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Figure 2. Microstructure of 1095 vacuum melted steel before exposure to hydrogen. 1000X etched 1% Nital.

Figure 3. Fissure in 1095 vacuum steel after exposure to hydrogen for 3 hours at 10,000 psig and 930 F. 1000X etched 1% Nital.
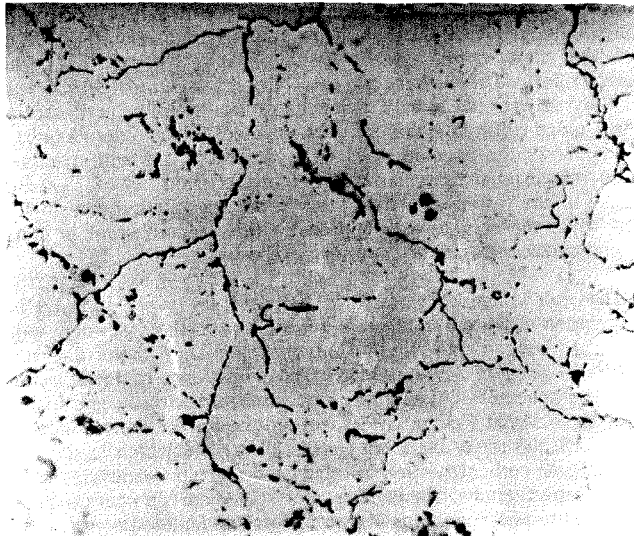

Figure 4. Completely decarburized zone of 1095 vacuum steel after exposure to hydrogen for 3 hours at 10,000 psig and 930 F. 1000X etched 1% Nital
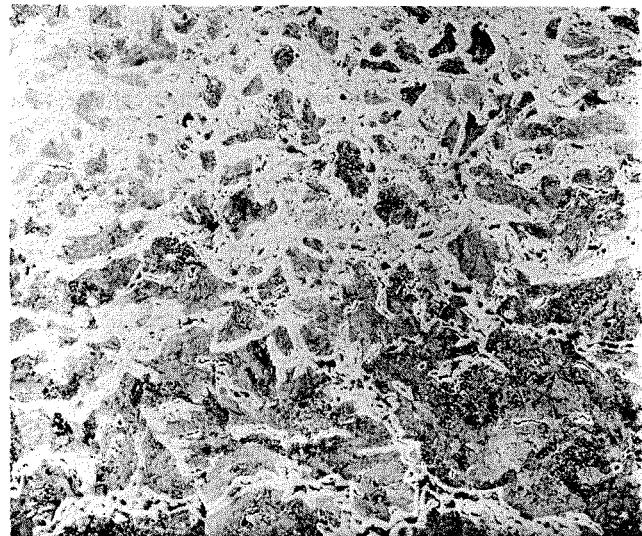

Figure 5. Transition zone between attacked and unattacked material in 1095 vacuum steel after exposure to hydrogen for 3 hours at 10,000 psig and 930 F. 100X etched 1% Nital.

bands have been reacted and the appearance of the boundaries is the result of the grinding compound used for smoothing the specimen.

Figure 5, at 150 times magnification, shows at the lower part a region of nearly completely decarburized steel. The upper part is a region that has been only partially decarburized. This figure then shows the transition between the decarburized slightly attacked regions.

Figure 6 shows a plot of the carbon contents. The tests are made with specimens 3/8 in. in diameter which are exposed to temperatures ranging from 750 to 1,100 F. and at a maximum pressure of 10,000 lb./sq.in. Some of our earlier work (4) went up to 15,000 lb./sq.in. The right side of the plot is the outside of the specimen and the left side is the axis of the specimen. These data are obtained by carefully turning down the specimens on a lathe, keeping the turnings from different diameters separate and getting the carbon content versus the position. We see in this figure that decarburization has removed something like a third of the carbon from the outer layer. The attack then progresses inward and we have quite a sharp gradient at about the depth where one-half of the specimen has been decarburized, whereas all of the specimen at the left of this line shows pratically no loss of carbon.
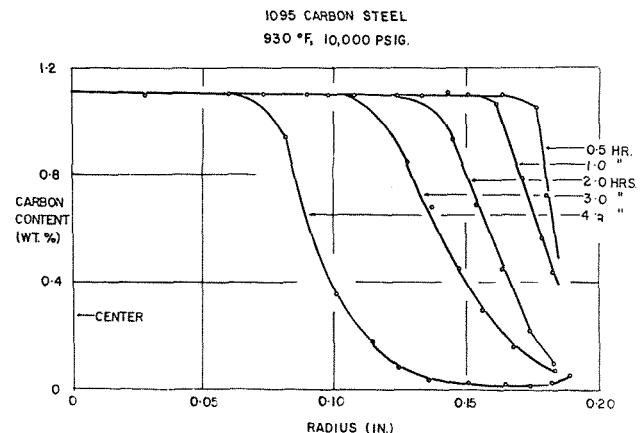

Figure 6. Effect of time on the attack zone of a 1095 carbon steel exposed to hydrogen at 10,000 psig and 930 F.

Figure 7 shows the fraction of the original carbon lost for three different steels with carbon contents of 0.95%, 0.45% and 0.18%.

The carbon removal is almost a straight line relationship, and with the 1018 and 1045 the rate of removal is substantially proportional to the amount of carbide there to react, as one might expect.

Figure 8 shows the effect of temperature. A three hour exposure has moved the carbon gradient to a depth about half the radius, with the outer half seriously decarburized.

Figure 9 shows the extent to which that rate of decarburization is increased by pressure. We have also exposed very pure vacuum steels kindly provided by the Research Laboratory of the U.S. Steel Corp. Figure 10 shows the data obtained at one, two, and three hours.
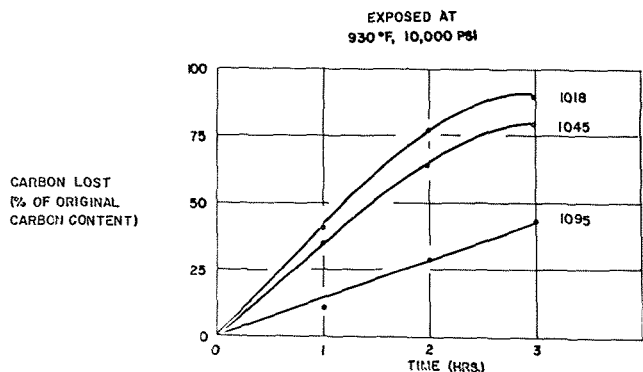
EXPOSED AT
930 °F, 10,000 PSI

Figure 7. Fraction of carbon lost for three different steels with carbon content 0.95%, and 0.18%. Exposed to hydrogen at 10,000 psig and 930 F.
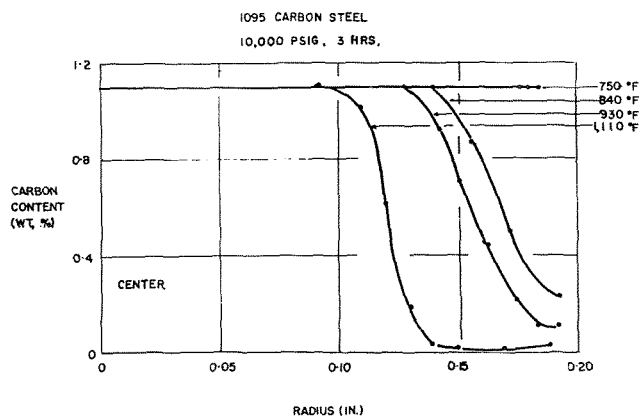
1095 CARBON STEEL
10,000 PSIG, 3 HRS.

Figure 8. Effect of temperature on the attack zone of a 1095 carbon steel exposed to hydrogen at 10,000 psig for 3 hours.
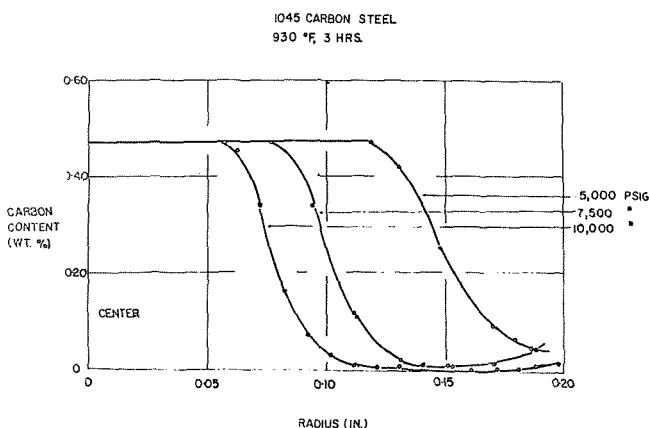
1045 CARBON STEEL
930 °F, 3 HRS.

Figure 9. Effect of pressure on the attack zone of a 1045 carbon steel exposed to hydrogen at 930 F. for 3 hours.
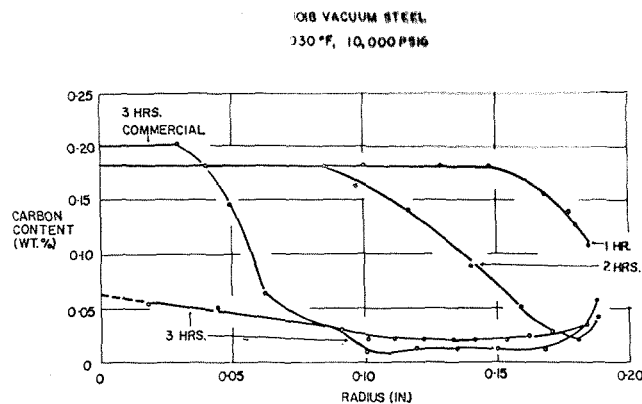
1018 VACUUM STEEL,
930 °F, 10,000 PSIG

Figure 10. Effect of time on the attack zone of a 1018 vacuum steel exposed to hydrogen at 10,000 psig and 930 F. with a comparison to the attack zone of a 1018 commercial steel.

Commercial steels most resistant

It was our belief that the commercial steels, containing small amounts of chromium and molybdenum due to the use of scrap, might have a somewhat greater resistance to decarburization than the high purity vacuum steels. We have found, however, that at the shorter periods of one hour and two hours the vacuum steel was less rapidly decarburized; only at longer exposures is the commercial steel more resistant than the vacuum steel. Microscopic examination shows the vacuum steel to have a more uniform structure with less foreign material included in the grain boundaries. Because of the fewer imperfections, the attack starts more slowly, but when the structure is opened up the vacuum steel is more rapidly attacked than the commercial steel.

The mechanism of attack is believed to involve, first, the absorption of hydrogen at the outer surface of the specimen, with establishment of an equilibrium between the molecular and atomic hydrogen. Since atomic hydrogen diffuses rapidly through iron the specimen quickly becomes saturated with atomic hydrogen. Even at 750 F., our lowest test temperature, the hydrogen reacts with the most available source of carbon, which is the iron carbide, or cementite, precipitated in the grain boundaries or at other imperfections. The elemental dissolved carbon near the grain boundaries also reacts, as shown by carbon-depleted areas in the microphotographs.

The reaction forms methane, which accumulates in any void spaces, such as at the grain boundaries. The pressure of methane causes the steel to creep and eventually to rupture. The outer surface of the specimen, where the metal is not confined, is ruptured first. The metal near the surface, being weakened, is less able to confine the metal below the surface so that the ruptured zone moves inward.

Also the network of fissures provides easier access of hydrogen and easier escape of methane. In the case of the 1095 steel, the amount of carbon is great enough to react with the hydrogen as fast as it is supplied from the outside of the specimen. There is therefore a narrow zone in which most of the reaction is taking place. With the steels of lower carbon content, the 1045 and 1018, the reaction proceeds almost uniformly throughout the specimen. With these two steels sufficient hydrogen is present at all depths to support the reaction. However, the restraint opposing the creep of the metal increases as the axis is approached. The variation in the amount of attack with depth is therefore primarily due to this physical mechanism.

It should be emphasized that our specimens were unstressed during the exposure to hydrogen. Naumann (2) and others have found that a tensile stress can considerably increase the rate of decarburation. This supports our view of the part played by the creep of the metal as postulated above.

Literature cited

1. Nelson, G.A., Hydrocarbon Proc. & Pet. Refiner, 45, 201-4 (1966).

2. Naumann, F.K., Tech. Mitt Krupp, 1 (1938).

3. Dodge, B.F., Ind. Eng. Chem. 48 (5) 885-93 (1956).

4. Thygeson, J.R. and Molstad, J.C., J. Chem. and Eng. Data 9 (2) 309-15 (1964).

Discussion

Q. Was a high-purity hydrogen used?

Molstad: It was ordinary cylinder hydrogen which we did not dry or purify. It was compressed from cylinder pressure, initially at 3,000 lb./sq.in. by a piston actuated by a high-pressure oil pump.

Q. Have you done any work with ammonia synthesis gas containing ammonia?

Molstad: No, but I recall reading that decarburation proceeds more rapidly with a nitrogen-hydrogen mixture than with pure hydrogen at the same conditions.