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FAILURE OF STEELS IN HYDROGEN AT HIGH TEMPERATURES AND PRESSURES

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This paper reports on a microscopic study of the changes in steels when in in contact with hydrogen at high pressures and temperatures. Hydrogen under such conditions decarburizes carbon and alloy steels [1, 2].

We have established that specimens subjected to one-sided hydrogen pressure (tubes with internal pressure) and specimens subjected to pressure on all sides (e.g. specimens put inside tubes) tested under the same conditions, do not suffer decarburization to the same extent.

The Table below shows the results of decarburization studies of the tube walls and of test specimens (i.e. put inside tubes for testing) of steel 20 (nominal 0.20% carbon) as a function of time under the action of hydrogen at 500°C (930°F) and 150 kg/sq. cm (2130 psi).

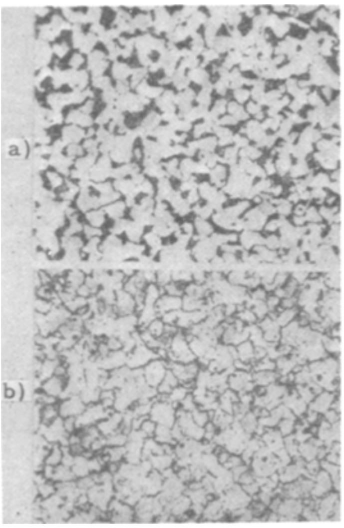


Fig. 1. Microstructure of steel 20. x 200. a = As-delivered; (annealed at 920°C = 1690°F); b = after 89 hrs. in hydrogen at 500°C (930°F) and 211 kg/sq. cm (3000 psi)

Decarburized Depth of Tube Walls and Inside of Test Specimens. **

No.	Wall Thickness, mm	Hydrogen Pressure, kg/sq cm	Duration of Test, hr	Decarburized Depth, mm *	
				Tube Walls	Test Specimens
1	2.45	150	5	None	None
2	2.48	146	20	0.2	0.7
3	2.55	144	48	0.5	Throughout Depth
4	2.56	147	198	0.9	Same
5	2.37	150	399	1.1	"
6	2.49	150	791	1.5	"

* Decarburized depth determined from microstructure and composition of metal removed layerwise.

** The test specimens (placed inside the tubes) were 20 mm long and 8 mm diam.; the tubular specimens, on the other hand, were 11 mm inside diameter.

From the data in the Table it is evident that the walls of tubular specimens are decarburized considerably less than the specimens placed inside the tubes.

That the different decarburization rates of tubes and inside specimens are not due to differences in geometry was demonstrated by special tests. Three series of tubular specimens of identical size (O.D. 16, I.D. 11, mm = 0.64 and 0.44 in) of steel 20 were exposed to hydrogen at 500°C (930°F) for 90 hours at 210 kg/sq. cm (2990 psi). The specimens of the first series were under internal pressure only, those of the second series were exposed to hydrogen on all sides while in a pressure vessel, and those of the third series were also placed in an autoclave, but exposed to the action of hydrogen only on the outside. When the hydrogen acted on one side only, the specimens were completely decarburized to a depth of 1 mm, whereas when it acted from all sides, the specimens were decarburized throughout.

The reason for the difference in rates of decarburization in the previous tests is therefore that the tubes were exposed to hydrogen only on one side, but the test specimens on all sides. In the tubular specimens the concentration of hydrogen causing decarburization of the walls decreases from the internal to the external surface [3], but in the inside specimens the hydrogen concentration, after a comparatively short time, becomes considerable over the whole depth of the specimen, at a level sufficient to cause complete decarburization. Hence the rate of decarburization with hydrogen acting from all sides will be much greater than when it acts from only one side.

Fig. 1 shows the microstructure of the decarburized and undecarburized zones of tubular specimens of steel 20, differing in grain size, and Fig. 2 shows the same effect for steel 30KhMA (0.25-0.35% C, 0.40-0.70 Mn, 0.17-0.37% Si, max 0.040% each P and S, 0.80-1.10% Cr, max 0.40% Ni). It will be seen that there are differences between the microstructures of the decarburized zone on the inside of the tube, and the undecarburized zone on the outside. This difference is revealed in microsections by ordinary etching and from the change in the decarburized zone found after repolishing previously etched specimens. The decarburized zone contains less pearlite: in the coarse-grained steel it is evident that the decarburization starts from the surface of the pearlite grains (Fig. 3). A similar phenomenon has been observed by others [4].

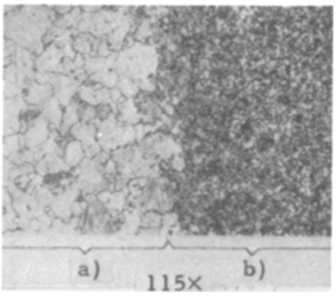


Fig. 2. Microstructure of steel 30KhMA after 2063 hrs. in H_2 at 600°C (1110°F) and 93 kg/sq. cm (1320 psi), x 115. a = decarburized zone; b = undecarburized zone.

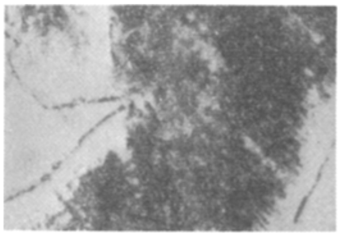


Fig. 3. Structure of partially decarburized pearlite grain in steel 20, x 1000

The changes in the decarburized zone, clearly revealed in repolishing previously etched specimens, are also interesting. Ordinary etching of the decarburized zone causes at the grain boundaries more extensive changes than in the original material. Hence after repolishing the outlines of the grain structure are preserved in the decarburized zone. Very likely the changes in the decarburized zone are due to the development of grain boundary damage by the action of hydrogen at high temperature and pressure. This is due to a 'loosening' at the grain boundaries, i.e. submicroscopic disturbances of continuity which gradually change over into intergranular cracks. The 'loosened' state of the grain boundaries in the decarburized zone results in a more extensive etching of the metal. Hence the contours of the grains are clearly revealed after repolishing, a thing that is not observed in the undecarburized zone.

The 'loosening' of the grain boundaries, changing over into clearly visible intergranular cracks, is found in the decarburized zone of different materials (technical iron, steels 20, 30KhMA and EI 579) after all-sided action of hydrogen at high temperature and pressures (Fig. 4).

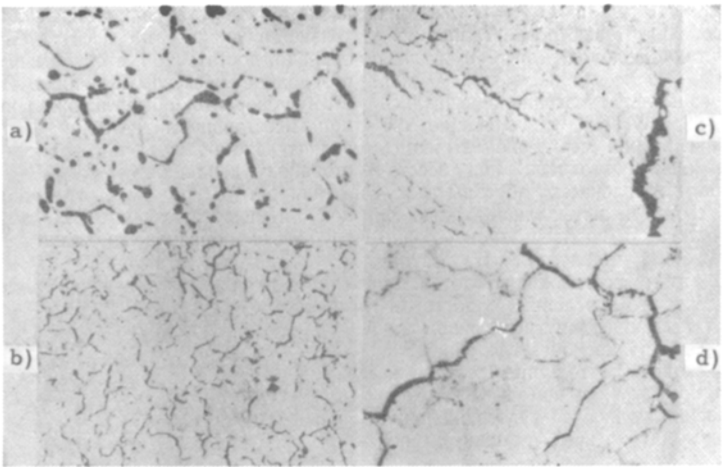


Fig. 4. Different steels after action of hydrogen at high temperatures and pressures. The microsections were repolished after etching.
a = technical iron, 220 kg/sq. cm (3140 psi) 450°C (840°F), 57 hrs. x 200;
b = steel 20, 276 kg/sq. cm (3830 psi) 500°C (930°F), 14 hours x 200;
c = steel 30KhMA, 140 kg/sq. cm (1990 psi) 600°C (1110°F), 1012 hrs x 200;
d = steel EI 579, 628 kg/sq. cm (8900 psi), 600°C, 2041 hours, x 140.

EI 579 contains 0.16-0.22% C, 0.25-0.50 Mn, 0.40 Si, 2.50-3.0 Cr, 0.25 Ni, 0.30-0.50 W, 0.35-0.50 Mo, 0.7-0.85 V, max. 0.030 P and S ea.

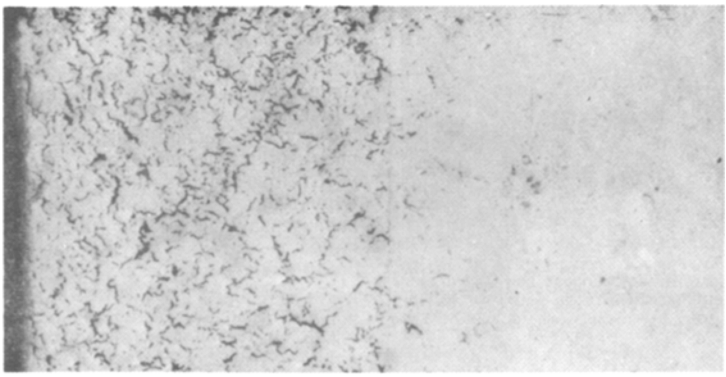
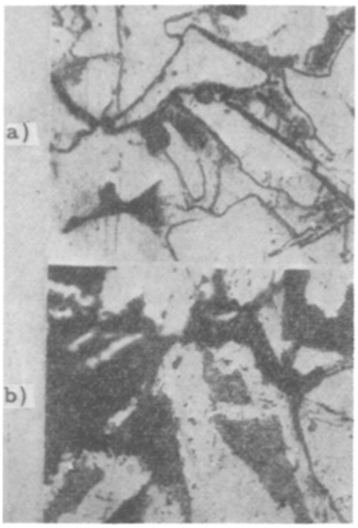


Fig. 5. Tubular specimen of steel 20 after 399 hours in hydrogen at 150 kg/sq. cm (2130 psi) at 500°C (930°F) Repolished after etching. x 70. Left hand is inside, right hand is outside of tube.

On tubular specimens of steel 20, exposed to hydrogen internally, a branched network of microscopic cracks, running along grain boundaries from the inside of the tube to the outside, can be clearly seen (Fig. 5).

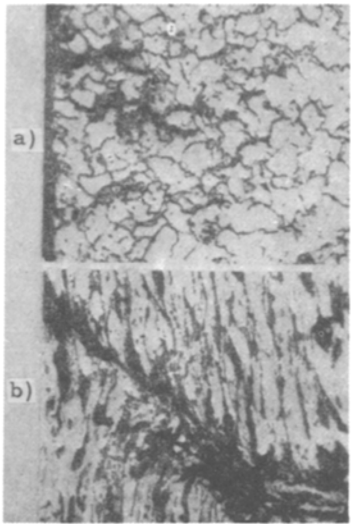
The depth to which the crack front penetrates depends on the material, the dimensions of the tube and the temperature, pressure and length of exposure to hydrogen.

During the action of hydrogen, because of the development of initially sub-microscopic, later microscopic interruptions of continuity, intergranular cohesion at grain boundaries should be lowered. It is of particular interest to find out if this is so in the earlier stages of hydrogen action, when the deterioration at the grain boundaries is revealed only after repolishing. After a tubular specimen of steel 20 had been exposed for a short time to hydrogen action, a ring was cut from it, and on this, intergranular cracking was observed on bending (Fig. 6a). Similar rings, cut from tubes exposed to nitrogen at the same temperature (internally) showed transgranular fractures (Figure 6b). We established that the deterioration of grain boundaries is not eliminated by later high tempering. That hydrogen acting at high temperatures and pressures on technical iron, steel 20 and also low-alloy steels, containing not more than 3% Cr (30KhMA and EI 579), causes 'loosening' and sets up disturbances of continuity at grain boundaries, is shown by the results of microscopic investigation of the tube metal subjected to rupture testing at high temperatures under internal hydrogen pressure. In these materials, delayed failure is not usually accompanied by appreciable macroscopic plastic deformation. Microscopic failures are characterized by the passage of the cracks along the 'loosened' grain junctions and by the absence of deformation of the crystallites. The cracks start from the internal surfaces of the specimens (Figure 7a).



Magn. 340X

Fig. 6. Cracks formed in bending of rings cut off a steel 20 tube. a = specimen after 75 hours in hydrogen at 500°C (930°F), and 135 kg/sq. cm (1900 psi); b = specimen after 204 hours in nitrogen at 500°C and 340 kg/sq. cm (4840 psi)



No Magn. Indicated

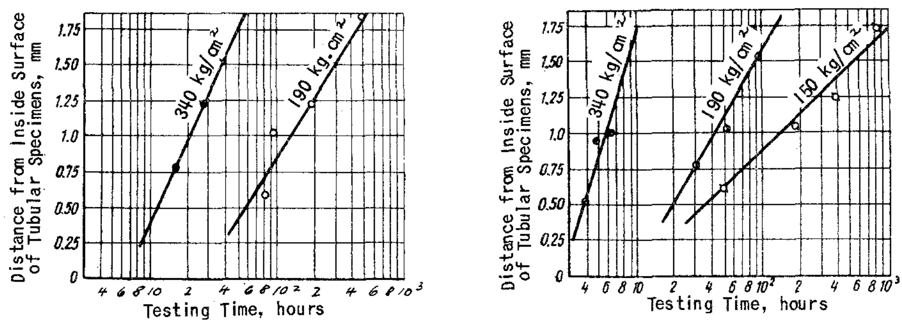
Fig. 7. Microstructure of tubular specimens of steel 20. a = specimen failed in hydrogen at 500°C and 276 kg/cm^2 (3930 psi) after 14 hrs; b = specimen failed in nitrogen at 500°C and 400 kg/sq. cm (5590 psi) after 303 hours.

Failure of tubes at the same temperature under internal pressure of nitrogen occurs with appreciable plastic deformation. The microscopic picture of failure in this case is characterized by considerable elongation of the grains and transcrystalline cracking (Fig. 7b).

The results of rupture testing correspond with the differences in microscopic failure of carbon and low-alloy steels in hydrogen and nitrogen [5]. It has been found that the rupture strength of tubular specimens under internal hydrogen pressure is below that of specimens under internal nitrogen pressure, and this is because failure occurs along hydrogen-weakened grain boundaries, the strength of which is lower than the strength of the individual crystals.

Tubular specimens of high alloy steels in which no reduction of intergranular strength is observed under internal hydrogen pressure at up to 600°C (1110°F) fail across the grains, both when tested in hydrogen and nitrogen, with micro and macroplastic deformation. It is evident that if the testing time of these steels were long enough, fracture might change from trans- to intergranular, irrespective of the medium (hydrogen or nitrogen) because it is connected with the nature of rupture at high temperatures.

To study the kinetics of crack propagation through walls of tubular specimens, a series of steel 20 tubes with a wall 2.5 mm (0.10 in) thick was held under constant internal hydrogen pressure for different periods on the assumption that under the specified conditions any cracks which appear will attain appreciable dimensions. After a definite time of testing, transverse microsections were prepared and the penetration of the crack front was measured on them.



a) (b)

Fig. 8. Relation between testing time and depth of penetration of crack front through wall thickness of tubular specimen of steel 20, under internal hydrogen pressure, (a) = at 450°C (840°F); b = at 500°C (930°F)

The results of these tests at 450 and 500°C (840 and 930°F) in Fig. 8 show that the dependence of the depth of crack penetration into the walls of tubular specimens at constant temperature and hydrogen pressure is linear in semilogarithmic coordinates. The 'incubation' period for the development of cracks depends on the sensitivity of the means used for detecting them. In microscopic investigations, the 'incubation' period will appear shorter when the magnifications are large, and this will be reflected in the thus determined rate of penetration of the crack front in the initial stage of its formation.

CONCLUSIONS

1. Hydrogen acting at high temperatures and pressures decarburizes materials such as technical iron, steels 20, 30KhMA and EI579. The decarburization is considerably more extensive when the action of hydrogen is on all rather than on one side (e.g. inside tubes).

2. In the decarburized zone, cracking develops gradually at the grain boundaries, with an appreciable lowering of intercrystalline cohesion.

3. The depth of penetration of the crack front (fromthe moment in which the incidence of a crack is observed) in tubular specimens under internal hydrogen pressure is to a first approximation proportional to the log of the time of hydrogen action.

References

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