

porting this conclusion is the fact that the rate of permeation of a diatomic gas is generally proportional to the square root of the pressure. This would be expected if the diffusion were due solely to atoms, in view of the equilibrium relation

$$K = \frac{\sqrt{p_H}}{p_H} \quad [4]$$

where K is the equilibrium constant of the dissociation reaction and p_H and p_{H_2} are partial pressures of atomic and molecular hydrogen, respectively.

The importance of dissociation into atoms is also indicated by the exponential effect of temperature which is the effect that would be expected if the rate controlling the permeation were an activated adsorption on the surface resulting in some dissociation. Another bit of evidence is the fact that nascent hydrogen will diffuse in a metal against a high pressure of hydrogen.

The equation that is usually accepted as expressing the effect of pressure and temperature is as follows

$$J = \frac{L}{K} (p_1^{1/2} e^{-E/RT} - p_2^{1/2} e^{-E/RT}) \quad [5]$$

where

- J = rate of permeation per unit of area
- K = constant depending on metal and probably on several factors related to state of metal
- L = thickness of metal membrane through which gas is permeating
- p_1 = pressure on high-pressure side of membrane
- p_2 = pressure on low-pressure side
- E = an activation energy
- R = gas constant
- T = absolute temperature

In a paper of this broad scope it is not possible to present the results in any detail but a few general conclusions of the work so far accomplished may be interesting and will be enumerated. Before doing this, however, it is desirable to explain the basis for them. If the specimen exposed to hydrogen had, within reasonable limits of reproducibility, the same tensile properties as the unexposed control sample, it was concluded not to have been attacked. If these properties have been lowered in value but the microscope reveals no fissuring or if heating in the absence of hydrogen restores to a considerable extent the original properties, the sample is concluded to have been embrittled but not attacked. Finally, if the tensile properties have deteriorated and assuming is clearly revealed by the microscopic examination, it is concluded that the metal has been attacked:

- 1 Plain-carbon steels, even those of low carbon content, were severely attacked at 400 C in a relatively short time. This, of course, was to be expected from the literature. At 300 C the attack was inappreciable.
- 2 Some alloy steels were attacked severely, others were embrittled, and others not appreciably affected. Not enough results are available to establish any definite pattern but contrary to expectations some Cr-Mn steels with as much as 5 per cent Cr were definitely attacked at 2000 atm even though they were low in carbon (about 0.10 per cent). There was some evidence, but not conclusive, of attack on a Cr-Mn steel containing 10 per cent Cr.
- 3 High-nickel alloys such as K-Monel, Inconel, and Hastelloy B were either attacked or embrittled.
- 4 Some embrittled samples had their original properties restored by heating to somewhat higher temperatures in the absence of hydrogen.
- 5 Results on high-chromium alloys such as chromax, nichrome, and nichrome V are somewhat inconclusive in that specimens of nichrome and chromax were unaffected but nichrome V was attacked severely.
- 6 Tentatively it appears that 2000 atm was a considerably more severe condition than 1000 atm. Some metals that were not affected appreciably at 1000 atm were attacked severely or embrittled at 2000 atm.
- 7 No effect was observed on any stainless steels either of the 300 or the 400 series (only one of the latter was tested).

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The relation between rate of permeability and practical effects well known and the effect of variables on K is not at all established. Although this law of pressure and temperature dependence is supposedly general, the limits within which it applies are not known. It also will have application to the selection of liners for steel vessels.

4 The retention or occlusion of gases by metals may be of importance in some applications but as yet we have not had an opportunity to study the considerable literature on the subject. It is mentioned here only to call attention to a part of the general subject of interaction between gases and metals which may bear study and which may have an important relation to the other three aspects that we have considered.

In passing, it may be worth mentioning that the retention of gases by metals once they have penetrated beyond the surface is generally believed to involve not only solid solution, i.e., a penetration of the crystal lattice by atoms of the gas, but also an accumulation of gas at grain boundaries and in imperfections or pits within the crystals.

Experiments on Hydrogen Attack. Our work in this field will now be reviewed briefly. The question of hydrogen attack by decarburization or other chemical reaction could be approached from a fundamental angle. The two basic factors in dealing with any chemical reaction are (a) chemical equilibrium and kinetics of the reaction. One could investigate the equilibrium and kinetics of the reduction of various metal carbides by hydrogen but the situation

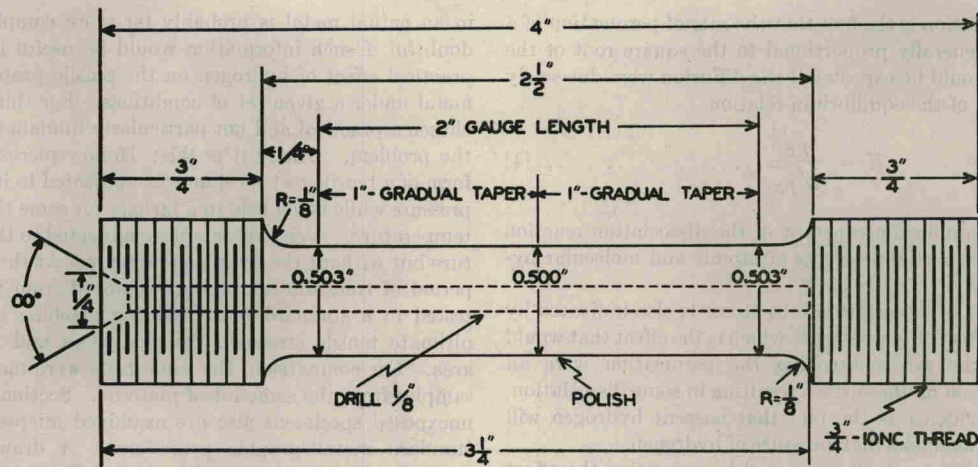


FIG. 8 TENSILE TEST SPECIMEN FOR EXPOSURE TO HYDROGEN

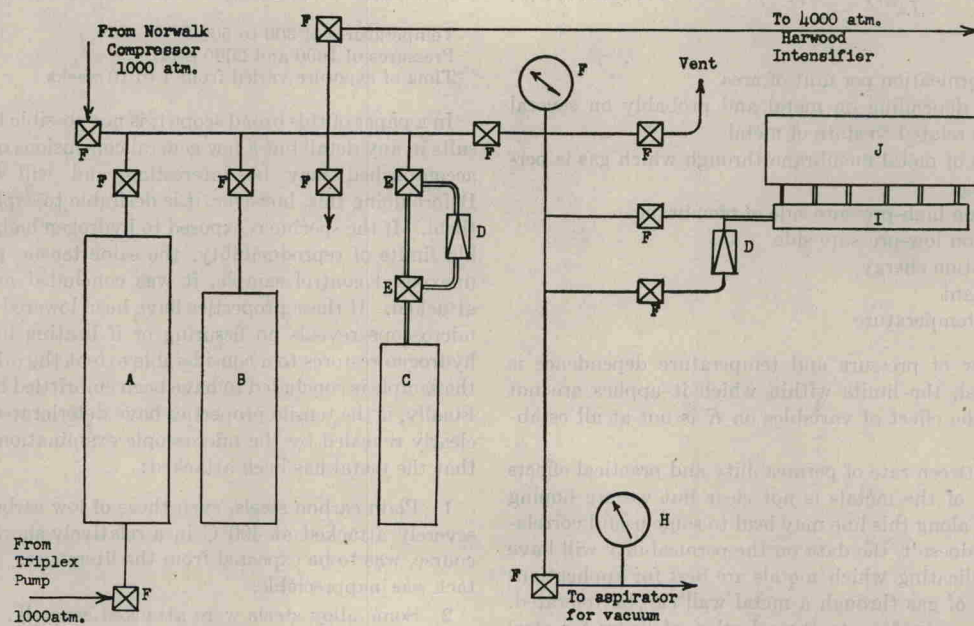


FIG. 9 DIAGRAM OF APPARATUS FOR EXPOSING TENSILE SPECIMENS TO GAS AT ELEVATED PRESSURE AND TEMPERATURE

- A, $\frac{1}{4}$ cu ft, 1000 atm storage
 B, $\frac{1}{8}$ cu ft, 1000 atm storage
 C, 200 cc, 4000 atm storage
 D, Check valves
 E, Harwood 3-way 100,000 psi valves
 F, Aminco 60,000 psi valves

- H, Vacuum gage
 I, Manifold
 J, Furnace

- Aminco $\frac{1}{4} \times \frac{1}{16}$ in. 60,000 psi tubing
 — Harwood $\frac{3}{16} \times \frac{1}{16}$ in. 100,000 psi tubing

Experiments on Embrittlement at Room Temperature. In addition to the tests at elevated temperature, other tests were made at room temperature on specimens consisting of strips $\frac{1}{2}$ in. \times 4 in. \times 16 gage, designed to yield information on the second aspect of the general problem. The strips were exposed to the gas in a vessel shown diagrammatically in Fig. 10. This is so constructed that the outer vessel of alloy steel which withstands the pressure is not exposed to hydrogen under pressure. The specimens rest on a shelf inside the inner stainless-steel vessel, above the level of the oil which is used to compress the gas from 1000 atm to higher pressures. Since the head of the vessel will be indirectly in contact with high-pressure hydrogen though its solubility in the oil, it was constructed of beryllium copper which was believed to be

unaffected by hydrogen and could be heat-treated to give a yield strength of the order of 150,000 psi. The outer vessel and the intensifier could only be exposed to high-pressure hydrogen by virtue of diffusion of dissolved hydrogen through the oil. This is a very slow process and could never proceed very far in short-time tests because the process is interrupted frequently by venting the dissolved hydrogen to the atmosphere.

The exposed specimens were given a bending test in a simple, homemade, hand-operated bending device designed to give 180-deg bending. Several specimens of a given metal were exposed together and then tested to obtain an average number of bends before breakage. This figure then could be compared with a similar average obtained with unexposed specimens.