A THEORY ON HYDROGEN EMBRITTLEMENT OF IRON AND IRON ALLOYS

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INTRODUCTION

Hydrogen embrittlement of iron and iron alloys is a phenomenon in which a relatively small amount of hydrogen in the solid causes a loss of ductility with no increase in hardness. Techniques have been developed for controlling or preventing it without understanding the mechanism by which it occurs.

The phenomenon also occurs in some metals and alloys that have little, if any, iron in their composition. The method by which it takes place when iron is absent or present in relatively small amounts is quite thoroughly understood. The definition given in the *Metals Handbook* is practically universally accepted and is as follows:[1]

> "Hydrogen embrittlement. In oxygen-bearing copper, silver, and similar metals, a condition of low ductility resulting from absorption of hydrogen at high temperature, internal reduction of cuprous or corresponding metallous oxide, and creation of intergranular holes or cracks by the accompanying generation of steam."

OCCURRENCE

Hydrogen, like carbon, is more soluble in the face-centered cubic phase of iron and iron alloys than in the body-centered cubic phase, There is less total void space in the face-centered cubic austenite than in body-centered cubic ferrite but the actual voids are larger. This helps to explain why austenitic steels are not susceptible to hydrogen embrittlement.

Hydrogen is stored in steel tanks with no embrittlement occurring. It has been determined that very little hydrogen from a hydrogen atmosphere will diffuse into the steel unless it is heated. At relatively high temperatures the hydrogen molecules may break down due to a catalytic action of the metal. Controlled wet or dry hydrogen atmospheres at high temperatures may be used to help induce hydrogen embrittlement. This has been done by many investigators in their attempts to determine just how hydrogen embrittlement occurs and what can be done to control or prevent it.

[1]Lyman, Taylor (ed.), **Metals Handbook** (Cleveland: The American Society for Metals, 1948), p. 7.

Hydrogen is present in high concentrations on the surface as ions, atoms, and molecules during pickling and cathodic action in some cells. The rate of diffusion into the metal is dependent on the surface concentration and the temperature.

Liquid metal, during casting or welding, may pick up hydrogen from the water vapor in the air. The method by which the water vapor breaks down is not thoroughly understood.

The presence of hydrogen in iron or iron alloys does not automatically cause embrittlement. It appears that hydrogen embrittlement does not occur until the specimen has undergone a strain and then it may also depend on the rate of straining. "Hydrogen embrittlement of metals is surprisingly sensitive to rates of strain, slow rates of strain giving brittle behavior and rapid rates of loading giving ductile fractures."[2]

One of the earliest theories suggested that a brittle hydride constituent was formed at the grain boundaries and thus lowered the cohesion.[3] No hydrides of iron are known and no precipitate has been detected at the grain boundaries.

For a long period of time it was believed that hydrogen embrittlement occurred in iron and iron alloys as it does in other metals. Stanley carried out an excellent investigation to show that the process was different.[4] Stanley vacuum melted a sample of pure iron with carbon to reduce the oxygen as oxide from 0.08%, which is in conventional iron, to 0.007%. If the embrittlement process were similar to that in copper, this should have reduced the tendency for hydrogen embrittlement to occur. After conditioning the samples in a hydrogen atmosphere, Stanley found that reducing the amount of oxygen as oxide had no effect on the embrittlement of the metal.

Many of the current theories, such as the planar-pressure theory of Zapffe, are based on the idea of pressure being built up by melocular hydrogen in tiny voids in the metal.[5] The metal becomes

[2]Queneau, B. R., **The Embrittlement of Metals** (Cleveland: The American Society for Metals, 1956), p. 19.

[3]Stanley, James K., "The Embrittlement of Pure Iron in Wet and Dry Hydrogen," **Transactions of the American Society for Metals,** 44:1103, 1952.

[4]**Ibid.,** p. 1101.

[5]Zapffe, C. A., "Written Discussion of 'Practical Importance of Hydrogen in Metal-Arc Welding of Steel'," **Transactions of The American Society for Metals,** 39:191, 1947.

embrittled when the pressure of the hydrogen reaches some critical value. The idea of high internal pressure in the voids appears reasonable for cases involving pickling or cathodic action. The concentration of atomic hydrogen on the surface would be relatively high and diffusion into the solid would continue until saturation or critical pressures in the voids would be reached. There would not be a normal case of equilibrium between the molecular hydrogen in the voids and the atomic hydrogen on the external surface. The idea of high pressures in the voids fails when one considers that a low pressure hydrogen atmosphere may also cause embrittlement. In such a case the molecular hydrogen in the voids would build up to equal the external pressure and maintain equilibrium with it. It may be possible that even the low pressures developed by such a mechanism would still be enough to reduce cohesion and cause embrittlement.

The theory I wish to present is relatively simple. Atomic hydrogen diffuses into the metal and molecular hydrogen forms in tiny voids at grain boundaries, slip planes, and along lines of imperfection between blocks in a mosaic structure. Equilibrium is maintained between the molecular hydrogen in the voids and atomic hydrogen on the walls of the voids and in solution in the crystal structure. The atomic hydrogen would be absorbed on the surfaces of the voids by a form of covalent bonding with the metal.

Before any strain occurs, the condition is that as shown in (a) of figure 1. The metal along AB is not bonded from a to b. When

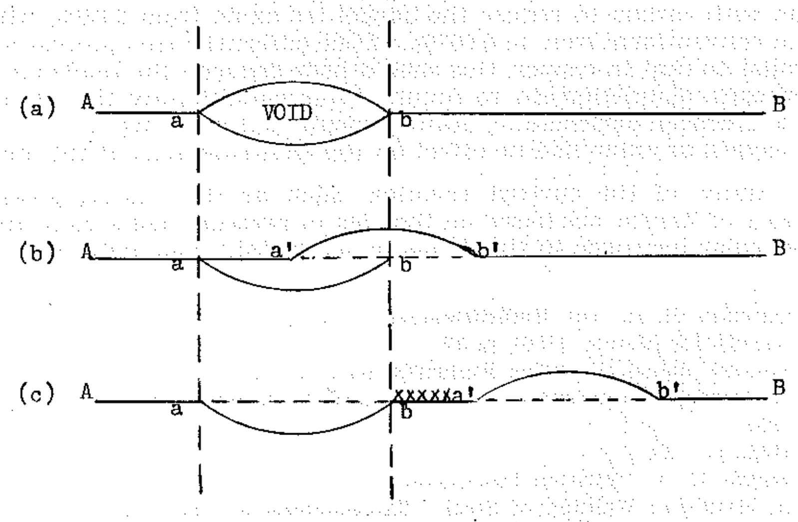

Figure 1. Strain Diagrams

straining begins to occur, the condition is that in (b) of figure 1, assuming negligible change in the total volume of the void. There is then no bonding from a to b'. But this has no great effect on the total strength of the metal since this would happen without hydrogen being present. The surfaces, aa' and bb', are in contact with the hydrogen and rapidly pick up atomic hydrogen. The metal acts as a catalyst which increases the rate of breakdown of the molecular hydrogen to maintain equilibrium. Some atomic hydrogen would also diffuse to the surfaces from its place in solution in the crystal structure. As the parts of the void separate, as in (c) in figure 1, a film of atomic hydrogen is along ba'. There is then no bonding along ab and a'b' and reduced bonding along ba' due to the presence of the hydrogen, which would reduce the number of bonds shared by the metal atoms across the interface.

The equilibrium between the molecular hydrogen and atomic hydrogen does not adjust instantaneously, although the metal acts as a catalyst. This explains why slow rates of straining result in embrittlement while faster rates do not. There would be a more complete film of hydrogen with the slower rate of straining.

The verification or disproof of this theory, as with all others, must wait until further experimentation has been carried out in this and related fields.

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