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THE STATUS OF THE HYDROGEN PROBLEM IN STEEL

by

R. D. McDonald*

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ABSTRACT

Hydrogen problems in steel are described, with particular emphasis on the problem of embrittlement of ultra-high strength steels as manifested by delayed failure. Ways are described in which hydrogen enters steel and is recognized by tests. Theories that have been developed over the years of research are related and explained briefly in order of sequence up to the most recent proposals advanced. These theories serve to explain many of the observations concerning hydrogen, although gaps in the knowledge still exist.

Alleviation of embrittlement still depends heavily upon diffusion treatments at baking temperatures, although many ways of preventing entry of hydrogen are being tried with moderate success.

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ÉTAT DU PROBLÈME DE L'HYDROGÈNE DANS L'ACIER

par

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RÉSUMÉ

L'auteur décrit les problèmes que pose l'hydrogène dans l'acier et tout particulièrement celui de la fragilité des aciers à très forte résistance qui se manifeste par une défaillance à retardement. Il décrit les façons dont l'hydrogène s'infiltre dans l'acier et comment on le reconnaît lors des épreuves. Les théories qui ont été mises au point au cours des années sont mises en relations et expliquées brièvement par ordre chronologique jusqu'aux plus récents travaux. Ces théories servent à expliquer plusieurs des observations faites au sujet de l'hydrogène, mais il existe encore des lacunes.

Le correctif de la fragilité entre en action lors des traitements de diffusion aux températures de cuisson, bien que l'on tente de plusieurs façons avec plus ou moins de succes de prévenir l'infiltration de l'hydrogène.

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INTRODUCTION

The primary function of this report is to present a current picture of developments concerning the general problem of hydrogen in steel. It is the intention of the author to deal most specifically with certain special problems related to the occlusion of hydrogen in high to ultra-high strength steels. However, to ensure that the scope and complexity of the general problems are appreciated, some of the general information relating to hydrogen in steel will be briefly described.

HYDROGEN AND PROCESSING METHODS

There are several processing operations during which hydrogen may enter into steel. These are:

1. Melting
2. Pouring ingots and castings, especially castings, in green sand moulds.
3. Welding
4. Electrochemical processing when the steel is cathodically polarized.
5. Corrosion processes (which are electrochemical in nature).
6. Processes in which hydrogen is present under conditions of high temperature or pressure, or both.

The first three of these operations during which hydrogen may enter steel are associated with the molten metal stage of production. The remainder are associated with the solid metal state and represent surface phenomena by which hydrogen may be occluded in the steel.

During melting operations in an arc furnace, water vapour is dissociated at the arc and hydrogen can enter the steel. Its entry into the steel probably shows the greatest tendency to occur during the reducing period of a basic electric two-slag melting process. Also, hydrogen can enter the melt from moisture or hydrogen present in additive materials. In castings the moisture present in green sand moulds can also be a source.

Hydrogen present in ferritic steels in quantities of one to two ppm can be associated with low ductility. This is manifested in a standard tensile fracture by low percentages of reduction in area and elongation.

Hydrogen introduced during electrochemical processes may cause poor ductility, plating defects, and -- probably most important -- delayed failured of high to ultra-high strength steels under static loading conditions. Studies have indicated that steels at a strength level of 270,000 psi may be more sensitive to hydrogen embrittlement than steels in the 200,000 to 230,000 psi range.

In welded joints, hydrogen is one of the main factors responsible for cracking in the heat-affected zone, and may also cause other flaws such as weld-cracking and weld porosity.

EMBRITTLEMENT THEORIES

Manifestations of hydrogen in steel, revealed in mechanical behaviour and fracture appearance, have been studied and recorded by Hobson, Sykes, Hewett, Burton, Zapffe, Frohmberg, Troiano, and others. The theory of embrittlement most widely accepted until recently was the "Planar Pressure Theory" by Zapffe et al (1). This theory proposed that molecular hydrogen could be formed in voids by atomic hydrogen in the steel diffusing to these voids. It could be shown, by gas laws and kinetic theory, that this process could result in the building up of very high pressures in voids that are sufficiently large for kinetic theory to be applicable. Hydrogen concentrations may be produced in the steel by supersaturation of the lattice or by electrochemical action, thus resulting in diffusion to areas of lower hydrogen content. It was believed that the pressures in voids could either exceed the tensile strength (2) or provide high residual stresses that abetted brittle failures.

Attempts to improve on this theory, to help explain some observations not satisfied by the planar pressure theory, were made by Bastien and Azou (3). They suggested that hydrogen is concentrated around dislocations as a Cottrell atmosphere. A dislocation is a defect inherent in a crystal lattice that might be briefly described as a localized mismatch resulting from the atoms being out of registry in the crystal. These authors suggest that hydrogen-laden dislocations can be moved through the lattice and can discharge hydrogen atoms into voids in which they combine to form molecular hydrogen, thereby creating pressure and causing embrittlement. Kazinczy (4) postulates that the contribution of the hydrogen gas in the void to the crack propagation energy is due to the release of energy caused by expansion of the gas during crack growth.

The adsorption theory recently developed by Petch and co-workers (5) is quite different. They suggest that a crack forming ahead of an array of dislocations, which can be piled up at a grain boundary by applied stress, progresses to fracture because of the adsorption of hydrogen on the surface of the crack as it forms.

A still different mechanism has been developed at Case Institute of Technology as a result of studies by Troiano and co-workers (6) on brittle delayed failure of high-strength steels. A very brief explanation is given here.

In order to explain certain observed phenomena not adequately covered by previous theories, a dual stress/hydrogen role was evolved. This theory requires a triaxial stress region that occurs just below the root of the notch in a stressed specimen and creates an activity gradient. Hydrogen then diffuses, during what is described as an incubation period, into the triaxially stressed region. Local stress concentration at the sharp notch results in plastic flow at its root. Plastic flow then generates blocked dislocation arrays, which, in turn, can respond as embryo cracks or as microcracks. Fracture normally will not occur until a critical concentration of hydrogen has diffused into this triaxially stressed region. Although the manner in which hydrogen embrittles is still left somewhat in doubt, it is suggested that the fracture or cohesive strength of the iron lattice is lowered by the segregation of an uncondensed atmosphere into the lattice near the tip of the embryo crack.

The crack will propagate, then stop, indicating that it has passed beyond the influence of the hydrogen-rich region. The process is then repeated in a step-like way until catastrophic or sudden failure occurs. Aging tests after straining have shown that ductility first increases with aging. The reverse can be predicted from pressure theories. As a result, the aging/ductility curve (Figure 1) shows a double instead of a single reversal. This phenomenon can be explained by a logical analysis of the hydrogen distribution in the region of a notch (7); this analysis supports the explanation for brittle delayed fracture and discontinuous crack propagation.

DETECTION OF EMBRITTLEMENT

Before considering methods of detection, a brief summary of observations concerning the characteristic mechanical behaviour of steel that contains undesirable amounts of hydrogen is in order. One of the most significant effects is the sensitivity to strain rate and temperature. That is, embrittlement is enhanced by slow strain-rates and moderately elevated temperatures. The high-temperature limitation is dependent on the rate of outgassing. This observed characteristic points to a relationship between the degree of embrittlement and the diffusion rate of hydrogen. Consequently, embrittlement detection tests have been devised to take advantage of this relationship.

There are several mechanical tests that will demonstrate hydrogen embrittlement. The principal ones are:

(a) Slow bend tests.

(b) Standard dynamic tensile tests.

(c) Static load (delayed fracture) tests.

Because failures due to hydrogen are related to diffusion rates, the presence of hydrogen cannot be demonstrated by an impact test or any test wherein a too rapid rate of fracture is accomplished. The slow bend test, when compared with the standard bend tests, will demonstrate this quite effectively. The quantitative value obtained from this test is the degree of bend to failure. The qualitative evidence may be the presence of "fish eyes" on the surface of the fracture. The standard tensile test frequently will also show fish eyes on the surface of the fracture, and these will be accompanied by low ductility, as determined by measurements of the elongation and reduction of area. This may show on the stress/strain curve merely as a reduced strain and a reduced fracture stress (Figure 2). However, the tensile test is usually not sufficiently sensitive. Although the finite fatigue life may be reduced by hydrogen, the fatigue test is not usually used to demonstrate hydrogen embrittlement.

The static load or delayed failure test is conducted by applying a constant tensile load on a notched specimen, usually by means of a simple beam loading device. Although the presence of hydrogen may sometimes be revealed on a smooth bar specimen, in general it has been demonstrated that its presence is manifested more intensely as the notch is made sharper. This test is applied to high strength steels in order to detect their susceptibility to delayed failure. Usually the source of hydrogen is from electroplating or some cathodic polarizing process.

The three principal test methods, listed above, may be carried out in a variety of ways. This applies particularly to the static load test that has recently been conducted on a notched bend specimen loaded as a cantilever beam. Specimens having both circular and rectangular cross sections have been used for these tests.

The constant or sustained load tests usually have the disadvantage of requiring complex and expensive testing equipment, and often require lengthy test periods.

Constant strain tests require less complicated equipment, are credited with giving sufficiently reproducible results, and, generally speaking, require shorter testing time. Two important specimen designs of this type, which are now in use, are the Douglas stressed ring and the NAEC notched C-ring. One disadvantage is the necessity of having material in tubular form.

Direct hydrogen measuring methods have been devised to measure the actual hydrogen produced during chemical processing. Of these, only two show much promise for general use. The first of these is the Lawrence Hydrogen Detection Gauge. This is an electronic device sometimes called the "hydrogen probe". It employs a metal-walled tube, which is placed in a processing solution. The hydrogen atoms pass through the tube wall, recombine to form molecules, and are reionized by a beam of electrons.

The ions migrate to a charged plate and the flow of current is read from an arbitrary scale called the "hydrogen index". This instrument has been used to monitor cleaning and plating operations and has been adapted to correlate with the results of sustained load tests. Reproducibility is not as good as might be desired, although improvements are being made.

The second method was devised at the University of Pennsylvania. It consists of two glass cells separated by a membrane made of the steel that is being investigated, or of Armco iron. When plating solutions are being tested, the plating solution is on one side of the membrane and a sodium hydroxide solution is on the other. The metal membrane is cathodic with respect to a platinum electrode on the measuring (NaOH) side. This is accomplished by means of a potentiostat. Hydrogen diffusing through the membrane from the plating side is ionized on the measuring side, and the current flow is recorded. Because of its sensitivity, skilled personnel are required to operate this device;this hampers it in becoming a tool for general use.

ALLEVIATION

The alleviation of hydrogen embrittlement is attained (a) by preventing the entry of hydrogen into the steel, (b) by reduction of the amount of hydrogen present, (c) by its redistribution, or (d) by the use of alloys that are less susceptible.

Prevention of entry requires close control of furnace practice, foundry practice, and certain processing operations. As previously described, hydrogen can be added with moisture-containing steelmaking materials such as slag and alloying materials, or it can enter from contact of molten steel with moisture-containing moulding materials. During basic electric melting operations, nascent hydrogen is produced at the electric arc and enters steel very rapidly during the reducing period of a two-slag process.

In metal arc welding, the main source of hydrogen is moisture in the electrode covering. The new AWS: A5. 5-1964 specification for low alloy steel electrodes permits maximum moisture of 0.6% for E70XX, 0.4% for E80XX and E90XX, and 0.2% for E100XX and stronger low-hydrogen classes, so recognizing the increasing sensitivity to hydrogen with increasing tensile strength from 70,000 psi to 100,000 psi and above. Pick-up of moisture can occur on exposure to the atmosphere, especially if the humidity is high, and baking at temperatures up to 425°C (800°F) may be necessary to restore electrodes after exposure.

Traces of hydrogen may also result from rust, organic and foreign matter on the base metal, or directly from moisture in the air. Even with inert-gas-shielded arc processes, hydrogen pick-up can occur from moist dirt or condensation in the equipment, from impure argon, or from improper shielding. Alleviation remedies, in addition to correct shielding, are implied by the causes.

Removal of hydrogen has for many years been accomplished mainly by long diffusion treatments at temperatures where the optimum advantage could be taken of high diffusion rates and low solubilities. Hydrogen can be diffused out of steel at temperatures in the ferritic field, and soaking at temperatures just above the Ms (martensite start) is frequently used. Also, advantage is taken of the abrupt reduction in solubility when austenite transforms to ferrite. This is accomplished by cycling the temperature through the critical range once or several times, until experience shows that ductility is improved or that "flake" cracks will not form during rapid cooling or hardening treatments.

New developments to alleviate this problem have been made and studies continue. Two of the outstanding developments that have come to practical fruition during the past decade are the vacuum melting and vacuum pouring techniques. Much of the high quality steel is now produced by these methods. Vacuum melting may be a double, or sometimes triple, melting process whereby in the final stage a previously cast ingot is used as a consumable electrode and recast, under vacuum, as a new ingot. Vacuum induction melting is another widely used technique. Gases and impurities are very effectively controlled by these methods. Vacuum pouring, or degassing, involves melting in the usual manner. However, pouring is conducted by subjecting the ladle metal to vacuum conditions as or before it is teemed into the moulds. This greatly reduces gases such as hydrogen, oxygen and nitrogen.

The above techniques are related to the steel production stage. However, the subsequent entry of hydrogen into high-strength steels, which still poses very serious problems, has not been neglected. Although much has been done to prevent the occlusion of hydrogen during electrochemical processing, the principal safety precaution remains the baking treatment at temperatures from 100°C to 200°C (212°F - 390°F) for periods of at least 5 hours. Often the time required may be 24 hours or more (Figure 3). This technique, although proving acceptable in accordance with present standards, still leaves much to be desired. Although effective in alleviating the problem, the baking treatment may not completely remove the hydrogen. Several investigators have shown that complete ductility may not be recovered by accepted de-embrittling treatments, and that, even when tensile ductility and strength have returned to normal, susceptibility to delayed failure may remain in ultra-high strength steels. To effectively remove hydrogen from cadmium deposits, it has been shown, temperatures in excess of 190°C (375°F) are required for at least 5 hours.

Prevention of entry of hydrogen during electrochemical processing has received considerable attention. Close control of plating bath impurities and of pH has been moderately successful in some cases. Certain types of plating baths may be less prone to introduce hydrogen - for example, a fluoborate bath has been favoured over a cyanide bath for cadmium. Also, additives have been used in the bath to promote the oxidation of hydrogen and thereby prevent its entry into the steel. Plating under partial vacuum by the "vacuum sputtering" technique is sometimes used, thus avoiding electrochemical action. Barrier plating (such as the electroless gold barrier technique developed and patented in Canada), and also plating a flash coating of cadmium, baking, and allowing the flash coat to act as a barrier to reduce further occlusion are two techniques that have received attention in recent years.

Another prevention technique that deserves mention is the use of hydraulic media other than aqueous for the pressure testing of high tensile steel tanks, such as missile casings. This was adopted after it was found that failure susceptibility could be introduced, during such tests, through mild corrosion attack and consequent introduction of hydrogen.

CONCLUSIONS

To generalize, the problem of hydrogen in steel, although under a reasonable measure of control, is far from solved. Many research organizations are currently studying this problem intensively for the purpose of standardizing test procedures and of finding out more about the mechanisms by which hydrogen operates to cause the mechanical problems observed. With a greater understanding of these mechanisms, prevention of entry of hydrogen, or alleviation of embrittlement, may become more effective, and perhaps development of less sensitive, or insensitive, steels may become possible.

ACKNOWLEDGEMENT

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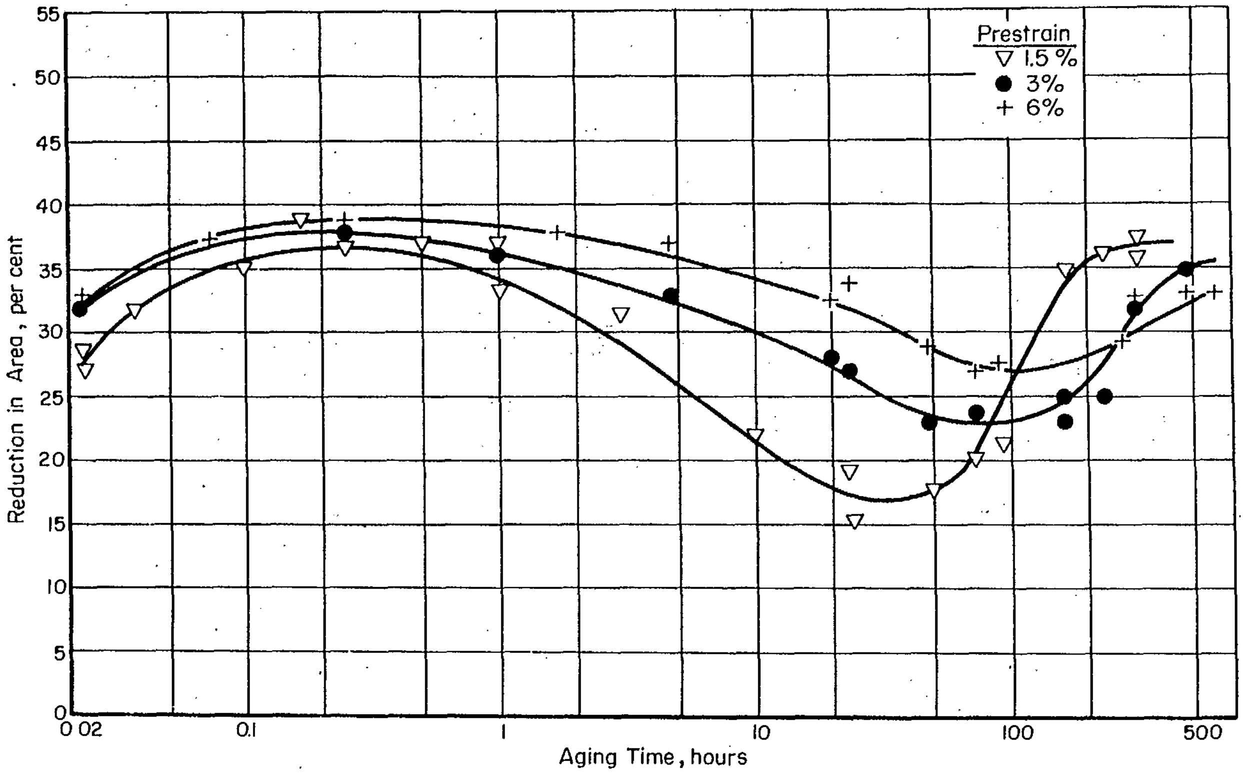

Figure 1 - Aging curves at 150°F for specimens strained different amounts in liquid nitrogen, showing the effect on ductility (7).

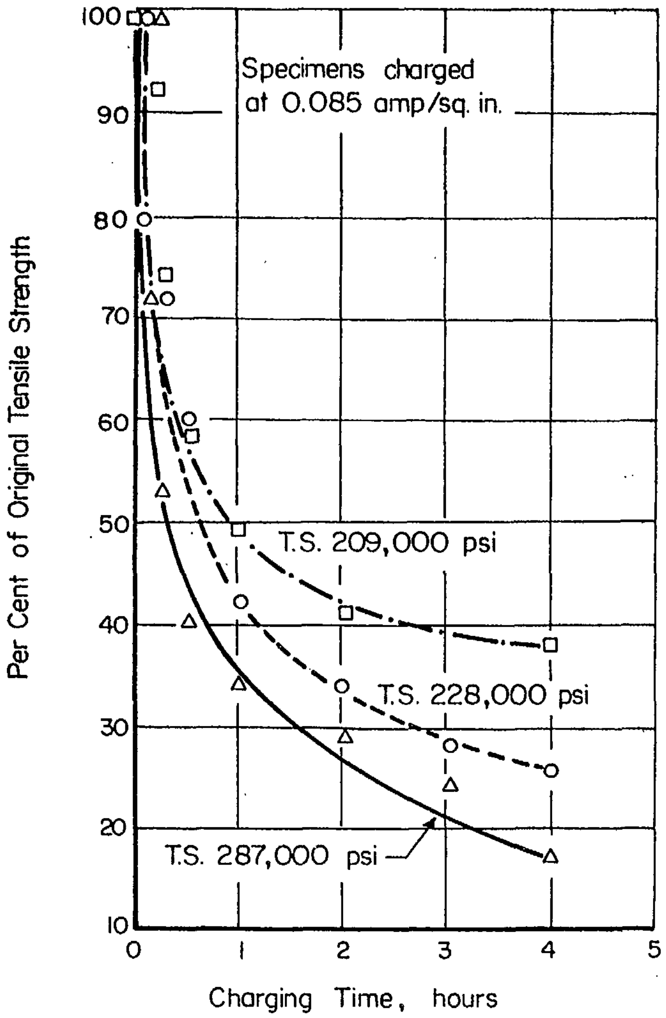

Figure 2 - Curves showing the effect of hydrogen charging time on the tensile strength of an AISI 4340 steel (8).

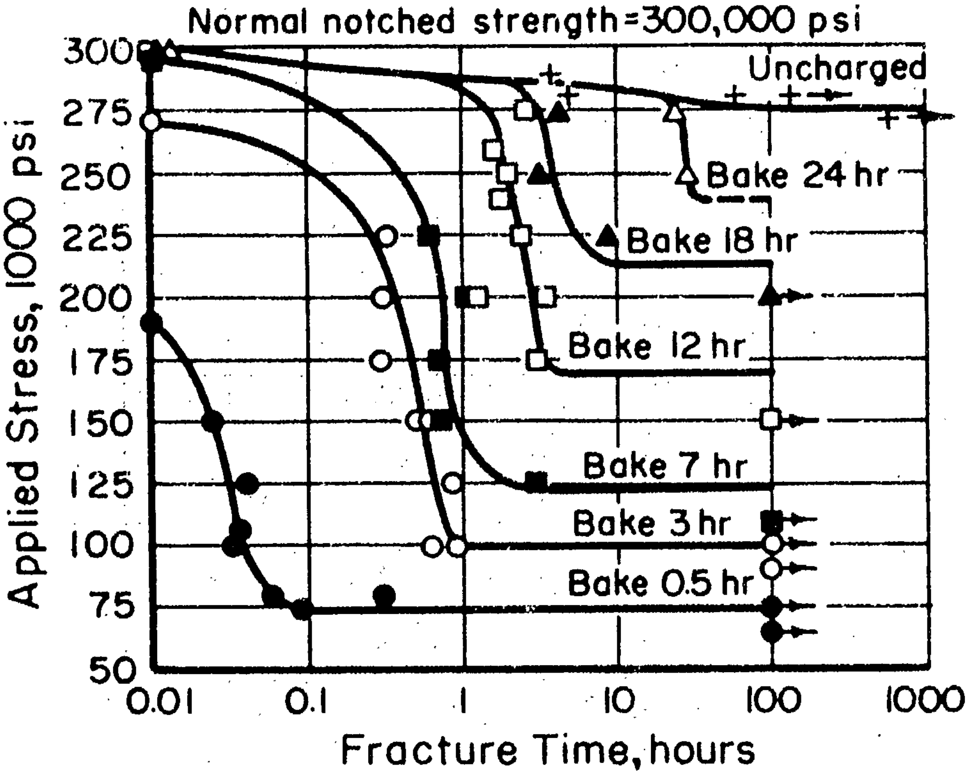

Figure 3 - Curves showing the effect of baking in reducing the delayed failure susceptibility of a hydrogen-embrittled steel (9).