STEEL DETERIORATION IN HYDROGEN

A REPORT ON CORROSION RESEARCH
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FOREWORD

From July 1959 to July 1966, the American Petroleum Institute sponsored two projects at the University of Wisconsin to evaluate the mechanisms of hydrogen deterioration of steel at high temperatures and the mechanisms of failure of steel under stress in hydrogen environments. The findings were given in eight technical papers, published in the API *Proceedings,* and fourteen progress reports issued during the investigations.

The Subcommittee on Corrosion of the Division of Refining engaged G. A. Nelson, metallurgical consultant of Berkeley, Calif., to summarize and evaluate the data. The ensuing paper was presented at a session on corrosion during the 32nd Midyear Meeting of the American Petroleum Institute's Division of Refining, Los Angeles, Calif., May 16, 1967.

Nelson's comprehensive review, "Steel Deterioration in Hydrogen," also indicates promising areas for future investigations.

Statements contained herein, although prepared for the American Petroleum Institute, represent the expressed opinions of the author.

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Introduction

The research at the University of Wisconsin sponsored by the API Subcommittee on Corrosion has been reported in eight technical papers published in the *Proceedings* of the American Petroleum Institute.[1a-8] The work at the University was directed by F. H. Vitovec. The first project was aimed primarily at explaining the incubation period, during which initial hydrogen exposure does not appear to damage steel, and also the effect of various factors on the incubation time and on the rate of deterioration of properties after observable attack has begun. The second project sought to explain the effects of hydrogen on creep rate and creep rupture strength of alloy steels under conditions that produce little or no attack on the same steels when they are not stressed. In the course of experimental work many data on effects of pressure, temperature, steel composition, and other variables were obtained, and many were published in the papers by Dr. Vitovec and his colleagues. These new data made it possible for the present writer to develop and publish a set of curves supplementing those in his previously published "Operating Limits for Steels in Hydrogen Service." [9] The new curves [10] showed the time for incipient attack on carbon steel and on carbon 0.5 percent molybdenum steel at temperatures and pressures exceeding the limits of the curves previously established as guides for indefinitely long, safe operation. The research has also produced invaluable information on the effects of strain in promoting attack. The loss in strength of carbon and low-alloy steels when exposed to hydrogen while in the temperature range of creep will be of importance to engineers and code-writing bodies when they are specifying steel for this service. Thus practical applications have been made of the Vitovec work, and more are indicated.

Theoretical Considerations

From the results of initial work an Arrhenius type of equation, here equation (1), for hydrogen attack was developed empirically: [1]

$$t=\frac{K}{p^n}\exp.\frac{Q}{RT} \qquad (1)$$

Where:

t = hydrogen exposure time for a 50 percent property change.
K and n = constants.
p = hydrogen partial pressure.
Q = an activation energy.
R = gas constant.
T = absolute temperature, in degrees Kelvin.

[a] Refers to REFERENCES on p. 14.

For SAE 1020 steel the numerical values were as follows:

K = (4.11)(10^3); for pressure, in pounds per square inch.
n = 2.
Q = 15,200 cal per mole.

Later this equation was found to agree well with equation (2) on the assumption that the time, t, is proportional to the methane pressure developed in internal voids by reaction of hydrogen gas and iron carbide: [2]

$$t = \frac{p_{CH_4}}{k_o}\left(\frac{1}{p^2_{H_2}}\right)\exp.\frac{Q}{RT} \qquad (2)$$

On the basis of these and additional considerations Dr. Vitovec and his colleagues assigned a considerable importance in the kinetics of the overall process of hydrogen attack to the carbide-hydrogen-methane reaction and its rate-controlling factors. Carbon diffusivity and carbide solubility were indicated as important in the stages following the incubation period. For the incubation period itself, however, surface phenomena appeared to be controlling. It was theorized that the initiation of the voids in which the methane reaction is to occur is a process of activation of existing nucleation sites that are internal interfaces of high energy.

Following further work on effects of stress on hydrogen attack and some experiments with specific gravity changes with different cycles of hydrogen exposure and vacuum annealing, Dr. Vitovec developed a comprehensive theory [5] on growth of fissures during hydrogen attack which indicated the methane reaction plays a significant role even during the incubation period. Pressure of the methane formed in submicroscopic voids was theorized to first build up against surface tension. Cavities then grow by vacancy diffusion and later by dislocation creep mechanisms. The theory was summarized in a table, presented here as Table 1.

The experimental procedures used by the investigators and the chemical composition of the test materials have been covered in the papers;[1,4-6] however, the treatment of samples that were machined from steel has been summarized in Table 2.

Most of the specimens were exposed at 1,000 F and at hydrogen pressure of 900 psi. It was considered that this exposure condition would not cause attack of the sensitive steels so rapidly as to mask effects but would produce attack of the more resistant molybdenum steels within a reasonable time.

The 900 psi hydrogen pressure at 1,000 F standard made it possible to define the benefits to be derived from additive elements. However, this standard was too severe to clearly define and separate such effects as true