HYDROGEN
IN
METALS

HYDROGEN IN METALS

Proceedings of an international conference
on the effects of hydrogen
on materials properties and selection
and structural design

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Preface

The Conference described in this volume was organized in response to recent interest shown by engineers and designers, as well as scientists, on the role of hydrogen in failure of structural metals and alloys. This is actually a re-awakening of interest, for considerable experimental work was carried out in the 1950's. The pattern is the same as in many subject areas: a period of intense experimental and analytical effort, culminating in a general synthesis of understanding, followed by a period of reduced productivity. In the hydrogen field, the cycle peaked in the late 1950's with the synthesis by Troiano and his co-workers. The stimulus, which renews the upward cycle, has apparently been provided for hydrogen in metals by two somewhat unexpected experimental observations. (i) Hydrogen affects the properties of not only iron-base alloys, but titanium, nickel and refractory alloys as well. Further, there is growing evidence that its presence can affect aluminum-base alloys. (ii) Both low and high pressure hydrogen are highly effective embrittling agents, and for a wide variety of materials.

These observations emphasize how broad is the hydrogen problem, and suggest that new directions and techniques will be required to control and understand this pervasive problem. It thus seemed appropriate to convene a conference which would provide the opportunity for basic researchers, engineers, and designers working with a wide variety of materials, to intermingle and benefit from each other's experience and knowledge. It was hoped that the conference would provide to the materials community a clear statement of how well the hydrogen problem is understood, what limitations it places on material selection and design, and what future problems can be foreseen. To be truly successful, it should also lead to long term interaction among those interested in the problem.

The attainment of these goals will finally be judged by the literature of the future. However, one positive accomplishment was that the major problem areas have been identified, and these are expected to serve as the focus for research and development efforts for the next several years. Although somewhat beyond the scope of a preface, we believe it useful to list these areas primarily as markers for those reading these proceedings. They are:

1. the relationship between internal and external hydrogen embrittlement.
2. the validity of separating materials into two classes; one where there is an actual transition from ductile to brittle behavior, and one where there is only a reduction in the relative ductility.
3. the role of dislocations in embrittlement phenomena.
4. the dual and complementary effects of strength level and microstructure as a determining factor for hydrogen susceptibility.
5. the interrelationships between hydrogen embrittlement and stress corrosion cracking.
6. the development of techniques for directly identifying hydrogen effects, as well as measuring hydrogen concentrations.

As the identification of these problem areas has broadened the experimental base of hydrogen effects, it has also sharpened the need for a synthesis of understanding. In this light, the Conference was not only a summary of work done, but a call for work to come.

We greatly appreciate the organization work done by Mr. Ralph G. Dermott, Director of the Technical Divisions and Activities of the American Society for Metals, who served as Conference coordinator, and by Mrs. Jean Gibson of Carnegie-Mellon University, who handled many of the problems which accompanied the organization of the meeting. We wish also to gratefully acknowledge the financial support of the Division of Materials Research of the National Science Foundation, the Metallurgy & Ceramics Division of the U. S. Army Research Office-Durham, and the Metallurgy & Materials Program at the United States Atomic Energy Commission.

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October 1973

CONTENTS

1 INTRODUCTORY LECTURES

2 LOW AND MEDIUM STRENGTH STEELS

3 HIGH STRENGTH STEELS

4 STRESS CORROSION CRACKING

5 ALUMINUM ALLOYS

6 REFRACTORY AND NUCLEAR MATERIALS

7 TITANIUM ALLOYS

8 NICKEL BASE ALLOYS

9 CHARACTERIZATION AND ANALYSIS

10 NEW MATERIALS PROBLEMS

11 INDUSTRIAL APPLICATIONS

INTRODUCTORY LECTURES

GENERAL KEYNOTE LECTURE

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It is a pleasure to have this opportunity to keynote this conference on a subject that has intrigued me for a substantial portion of my total professional activities. The breadth of the influence of H_2 is so great that it will not be possible for me to even touch on all aspects of the problem let alone treat anything in depth. As is proper for a general keynote presentation, we shall try to keep the tone tutorial rather than to take a stand on some of the phenomena where sharp differences of opinion exist. (A rather novel position for me although I suspect most of you know where I stand). Indeed the series of review lectures to follow to-nite and during the week will certainly, as planned, fill in for my lack of depth.

It is almost trite to speak of the general ubiquity of hydrogen. It is literally everywhere from 7 or more miles below the earths crust to the upper limits of the atmosphere and available for damage in a variety of forms that are only recently beginning to be fully appreciated.

The damaging effects of hydrogen has long been recognized in ferrous materials and subsequently in other metals and alloys. It has been said that there is nothing new, ever. Of course, as scientists and engineers we do not subscribe to this: but let us take a few minutes and look back; and I quote: from a study by a Mr. W. J. Johnson from Manchester, England and reported to the Royal Society a few months short of 100 years ago.

"Some three years ago my attention was called to a remarkable change in some of the physical properties of iron caused by its temporary immersion in hydrochloric and sulphuric acids. This change is at once made evident to any one by the extraordinary decrease in toughness and breaking-strain of the iron so treated, and is all the more remarkable as it is not permanent, but only temporary in character, for with lapse of time the metal slowly regains its original toughness and strength. (Author's note: Reversible Damage)

The decrease in toughness is such that a piece of steel which, previous to immersion in hydrochloric or sulphuric acid, would stand bending on itself and back, two or three times, will break short-off like a pipe-stem when bent. So great is the influence of acid, in fact, that ten minutes' immersion in dilute sulphuric acid will cause a coil of highly carbonized tempered cast-steel wire to break of itself into several pieces while in the liquid. (Brittle delayed failure) (Environmental Degradation) (SCC).

Half an hour's immersion in hydrochloric acid will make a piece of steel containing, say 0.60 per cent of carbon so brittle that no amount of exposure to the air or heat will ever completely restore it. (Author's note: Irreversible Embrittlement) On hardened and tempered steel the decrease in toughness produced by immersion in acid is greater and more rapid than with the same steel in a soft state. (Author's note: Influence of Strength Level)

Hence it is probable that iron and steel, when placed in hydrochloric, sulphuric or other acid, absorb some of the nascent hydrogen generated by the action of the acid, thus forming what, for lack of a better term, may be called an alloy* or iron and hydrogen. (Author's note: Diffusible Hydrogen)

By way of testing the theory that occluded hydrogen is the cause of the change in the properties of iron after its immersion in acids, the writer determined to dispense with acid altogether, and endeavour to produce the same result by subjecting pieces of iron to the action of nascent hydrogen.

"With this view two pieces of iron wire were connected respectively with the zine copper plates of a battery of 80 Daniell's cells, and immersed in a vessel of Manchester town's water at a distance

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* "By the term alloy I mean a solution of one metal in another."

of one inch apart. On closing the current, bubbles of hydrogen were given off from the wire connected with the zine plate of the battery, but not from the wire connected with the copper plate, the oxygen liberated there apparently forming oxide or iron. After 24 hours the surface of the wire connected with the zinc plate was unchanged; but on moistening the fracture, bubbles were given off, just as if it had been immersed in acid. The other wire, though much oxidized and eaten away, did not give off bubbles when broken, and had not become brittle.

"The water was then replaced by an aqueous solution of caustic soda, when, after two hours, the moistened fracture of the wire connected with the zinc pole of the battery was found to bubble. Twenty-two hours' longer immersion, the battery working all the time, caused the bubbles to be more abundant; the toughness of the wire was also diminished. The wire at the positive pole was, however, unchanged, either on the surface or in toughness".

"From this we see that not only is acid not indispensable for the production of, at all events, the major portion of these changes in iron, but the latter can be equally well produced in an alkaline solution". (Author's note: Still not accepted by some)

Let us now review a few fundamental relationships which are vital to have in mind in consideration of much that is to follow at this conference, particularly with respect to ferrous materials but not exclusively so. Following this in keeping with the general tone of the conference we shall be primarily concerned with factors involving the influence of hydrogen on performance.

The solubility of hydrogen in alpha iron (ferrite) is negligible at ambient temperatures and increases in a more or less linear fashion up to the alpha-gamma transformation temperature, when the solubility approximately doubles abruptly from about 3 to 6.5 ppm and continues to increase in a more rapid linear fashion above this temperature and at the melting point will approximately double again from 14 to 26 ppm.

At any temperature, equilibrium calls for the rate of formation of nascent and molecular hydrogen to be equal.

$$H_2 \rightleftarrows 2H$$

and the mass action constant

$$K = \frac{(PH)^2}{(PH_2)}$$

where

PH = partial pressure of atomic hydrogen in the metal.
PH_2 = partial pressure of molecular hydrogen outside the metal.

Hence

$$PH = K(PH_2)^{1/2}$$
$$PH_2 = K(PH)^2 \qquad (1)$$

By Henry's Law, the concentration of hydrogen in a metal at a given temperature is proportional to the partial pressure of the hydrogen in it, or

$$C = K'PH \qquad (2)$$

where

C = concentration of dissolved hydrogen

Thus, from equations (1) and (2) above, it follows that the amount of hydrogen dissolved at a given temperature is proportional to the square root of the gas pressure outside the metal, or

$$C = K''(PH_2)^{1/2} \qquad \text{Sievert's Law} \qquad (3)$$

Because of the sharp decrease in solubility of hydrogen with lowering temperature, the steel, when cooled from saturation at elevated temperatures will be highly supersaturated. Greatly increased partial pressure of atomic hydrogen would be required to hold this excess hydrogen in solution in the crystal lattice - a situation not commonly encountered, but of vital importance in many industrial processes, such as catalytic crackers. This the natural result of the stability of hydrogen in ordinary atmospheric environments. Hence, dissolved hydrogen will diffuse out of the metal lattice and recombine to molecular hydrogen. This can occur either in the atmosphere near the surface of the steel or within the steel in voids. In the sense of dissolved hydrogen in the crystalline lattice, inclusions are voids. In this latter case, the pressure of molecular hydrogen will be built up in the voids according to the square root relationship of equation (3) above. This pressure build-up will continue until the equilibrium pressure PH_2 is attained. Under these particular conditions the driving force for the hydrogen is pressure or, indirectly concentration.

When atomic hydrogen is liberated at the surface by chemical or physical attack, no actual gage pressure (above atmospheric) of hydrogen is developed on the surface. Thus one has what must be considered to be a vitual pressure or concentration. For an ideal gas, the driving force may be considered to be the fugacity, a thermodynamic quantity which may be regarded as a virtual pressure or concentration.

Independent methods of cal culating this for hydrogen on iron immersed in acid all give values that lie between 10^5 and 10^8 atmospheres, pressures far higher than the bursting strength of steel. Such reactions as those of water vapor, corrosion, pickling in acid, or cathodic precipitation may create an atmosphere at the steel surface, which in terms of hydrogen-atom concentration, may be equivalent to a partial pressure of hydrogen gas of thousands of atmospheres at ordinary temperatures. In this way, we can account for the high concentrations of hydrogen that may be obtained in steel by chemical attack or by cathodic charging. The fugacity varies with the electrical potential developed in the environment, which in turn depends on which environment is used, and on its concentration and temperature.

Because of this high concentration, hydrogen will continue to diffuse into the steel causing it to become highly supersaturated. If this environment is removed, hydrogen will diffuse out. This diffusion and recombination to molecular hydrogen in discontinuities in steel gives rise to gas pressure just the same as in the case of a steel cooled from some high temperatures where it was saturated with hydrogen. Thus, we see that the origin of the hydrogen is of little import, once it is absorbed. At this point, I should like to remind you that high pressure will exert high stress and, in accordance with Sievert's law, high dissolved localized hydrogen. This should be kept in mind in attempting to evaluate hydrogen embrittling mechanisms.

As we have noted, it was known more than 100 years ago, that steel, after exposure to a hydrogeneous atmosphere will suffer damage which may be either temporary or permanent.

At temperatures near the ambient plus or minus several hundred degrees F^{o}, we observe the phenomena now referred to as Hydrogen Embrittlement. At elevated temperatures and pressures, hydrogen will manifest itself in the form of decarburization in steel, and intergranular fissures, blistering and general permanent damage as well as reduced stress rupture and creep ductility. Generally, we refer to this as Hydrogen Attack. It should be appreciated that these two manifestations of hydrogen are not mutually exclusive. An alloy which may have suffered hydrogen attack at an elevated temperature may be subject to hydrogen embrittlement at lower temperatures. A problem well-recognized by refineries, power plants, paper mills, etc. Let us now be more specific.

One of the most intriguing aspects of the hydrogen embrittlement phenomenon is its sensitivity to strain-rate and temperature. Briefly, the embrittlement (loss of ductility) is enhanced by slow strain-rates and moderately elevated temperatures. These are mutually dependent variables and may be perturbated over a wide range of strain-rate and temperature. This is, of course, precisely the converse of the more conventional behavior, where high strain-rates and low temperatures enhance brittle behavior and give rise to the so-called transition behavior characteristics of many B.C.C. systems. This slow strain-rate and temperature sensitivity imparted by hydrogen indicates that the phenomenon is under the control of and paced by the lattice diffusion of hydrogen which for the dynamic test conditions described here, may be supplemented significantly by short circuit paths, including atmospheres transported by moving dislocations.