HYDROGEN ATTACK OF STEEL

Progress Report
for period April 1, 19~~79~~⁷⁹-March 31, 1980

MASTER

Paul G. Shewmon
Department of Metallurgical Engineering
The Ohio State University
Columbus, Ohio 43210

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

January 2, 1980

prepared for
Department of Energy
Contract No. EY-76-S-02-2872

REA

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PROGRESS REPORT

Hydrogen Attack of Steel
DOE Contract No. EY-76-S-02-2872
April 1, 1979 - March 31, 1980

Objective and Scope

The objective of this work is to establish the atomic processes by which the hydrogen attack of pressure vessel steel occurs. The approach is to follow the growth kinetics using an exceptionally sensitive dilatometer and to compare these data with the predictions of models based on the postulated mechanisms. This is supplemented by scanning electron microscope (SEM) studies to establish the geometry and location of the growing methane bubbles. The steels used have been various commercial alloys because of our now confirmed suspicion that trace impurities, e.g. from deoxidation practice, play a central role in determining the nucleation and growth geometry of the bubbles or fissures.

Summary

Our efforts to understand the basic processes accompanying hydrogen attack in low alloy steels dealt with three areas:

Kinetic studies - Our sensitive dilatometer has allowed us to study the earliest stages of bubble growth in a low alloy steel. Variation of rate with temperature, hydrogen pressure, and time indicate that the bubbles grow by the interfacial diffusion of iron, driven by close to an equilibrium pressure of methane. The data are not consistent with the suggestion of several that growth occurs by creep at a rate determined by methane production.

Nucleation - A silicon killed steel was the first one studied (out of four) in which we could observe inclusions significantly aiding nucleation (others had often reported this). The role of plastic deformation appears to be more one of setting up local distortions at boundaries than one of opening microcracks. Plastic deformation gives earlier fissure nucleation at an appreciably larger fraction of the boundaries than in annealed samples. This leads to early venting of gas to the surface along continuous grain boundary paths in a manner similar to gas release in nuclear reactor fuel elements.

Alloying Effects - Our work on the relatively low rate of HA of some low carbon, high strength low alloy steels has been accepted for publication. Our novel approach to measure directly the equilibrium methane pressure, and thus the carbon activity, has made progress, but slowly.

Work Accomplished

Kinetics - During the past year we have completed a study (Ph.D. thesis by Marvin McKimpson)⁽¹⁾ which for the first time measured the kinetics of hydrogen attack during the early stages when discrete bubbles form and grow. Several authors have speculated about the rate controlling mechanism in this stage, but the instruments they had were not sensitive enough to follow the process in this early stage. The rate limiting process is clearly not controlled by creep or methane production. A model which fits the data adequately, but not precisely, presumes the methane pressure in the growing bubbles approximates the

(1) Marvin G. McKimpson, "Initial Hydrogen Attack Kinetics in a Carbon Steel," Ph.D. thesis in the Metallurgical Engineering Department of OSU, 1979.

equilibrium value, and that the bubbles grow (iron atoms are moved away) by the grain boundary diffusion of iron. The abstract of McMimpson's thesis reads as follows: (we are working on an appropriate publication from it).

The kinetics of the initial stages of hydrogen attack in a commercial 0.3% C steel (grade A516) were investigated using an in-situ dilatometer. The time, temperature and hydrogen pressure dependences of the rate of sample expansion were measured at hydrogen pressures from 1 to 20 MPa and temperatures from 350 to 475°C for sample strains of 10^{-6} to 10^{-3} . Hydrogen attack induced expansion was observed to begin shortly after hydrogen exposure and then to proceed at a nearly constant rate throughout the "incubation period" preceding rapid attack. At high temperatures and low hydrogen pressures, this nearly constant rate was proportional to $P_{H_2}^{0.9 \pm 0.2}$, and had an apparent activation energy of 115 ± 9 kJ. At high pressures and low temperatures, the initial expansion rate was proportional to $P_{H_2}^{0.62 \pm 0.07}$, and showed an apparent activation energy of 210 ± 13 kJ. These results indicate that bubble growth during the incubation period occurs predominantly by grain boundary diffusion and suggest that this growth is driven by near-equilibrium internal methane pressures. Sample expansion in the subsequent stages of accelerating growth studied by various investigators probably is controlled by creep and methane generation.

The model used to predict growth rate has been developed successively by Sagues, Hall and Wiedersich,⁽²⁾ Shih and Johnson,⁽³⁾ and most recently by Oldfield, Odette and Vagarali,⁽⁴⁾ The most important contribution of these last authors was their emphasis on the effect of the non-ideality of the methane in bubbles. This does three things:

(2) Sagues, Hall, and Wiedersich; Scripta Met. 12 (1977) 319-26.

(3) H. M. Shih, Chapt 3, Ph.D. Thesis in Department of Metallurgical Science and Engineering, Cornell University, 1978 (Prof. H. H. Johnson, advisor).

(4) Oldfield, Odette, and Vagarali, DOE Contract No. ET-78-S-01-3153.

1) limits the pressure in the bubbles to roughly 10^5 psi when the methane fugacity is 10^6 or 10^7 psi, thus favoring grain boundary diffusion over creep;

2) reduces the rate of increase of methane pressure with rising P_{H_2} so that in the equation $P_{CH_4} = K P_{H_2}^n \exp(-Q/RT)$, n decreases rapidly from 2 at 1 atm of H_2 to around 0.5 above about 1000 psi (7 MPa) of H_2 ;

3) reduces the magnitude of Q in the above expression for P_{CH_4} from -110 kJ at one atm. of H_2 to roughly -20 kJ at ≥ 10 MPa of H_2 .

These changes are all in the direction needed to give agreement between our data and the boundary diffusion, gas pressure driven model.

Nucleation - The factors determining the nucleation of methane bubbles is probably the biggest unknown in explaining the variability of attack between different regions of a given steel and different heats of the similar steels. Of the four steels originally studied by Pishko, two (ESR - electroslag refined, and REM - rare earth treated) showed myriad fine grain boundary bubbles at both high and low hydrogen pressure, one (Al-killed) showed fine bubbles at low pressure ($P_{H_2} = 940$ psi), and the growth of discrete tears at high pressure ($P_{H_2} = 3000$ psi). None of these showed significant bubble nucleation on inclusions. A copy of the paper describing this work is attached to this report. (5) It is the first published paper under this contract

Reprint
removed

The fourth steel (Si-killed) showed only grain boundary fissures, with no fine bubbles, and frequent nucleation on inclusions. An M. S. thesis completed this year (6) studied this Si-killed steel in more

(5) R. Pishko, M. McKimpson, and P. G. Shewmon, "The Effect of Steel-making on the Hydrogen Attack of Carbon Steel," Met. Trans. 10A (1979) 887-94.

(6) Mark H. Ransick, "A Microstructural Investigation of the Effects of Cold Work Upon Hydrogen Attack," M. S. Thesis in the Metallurgical Engineering Department of OSU, 1979.

detail, with particular emphasis on the way plastic deformation accelerates the attack. Plastic deformation does not open up visible microcracks but "conditions" the grain boundaries so that fissures open up on a much larger fraction of the boundaries than is observed in the absence of cold work. This leads to the opening of continuous paths for the methane to vent to the surface. The fissures on grain boundaries are very thin ($0.5\mu\text{m}$), presumably because they grew rather rapidly to the free surface, and vented their trapped gas rather grow into a more bulbous form due to the pressure of trapped gas.

Another striking feature of this silicon killed steel is the high frequency with which bubbles nucleated on MnS and manganese silicate inclusions. Such behavior was not found in any of the other steels we've worked with (the more fully deoxidized, e.g. Al killed or rare earth treated). This steel also showed numerous surface blisters which we've shown were due to the nucleation and growth of bubbles along one side of small ($10\text{-}20\mu\text{m}$) inclusions near the surface. These bubbles then raised a plug of material out of the surface until the gas vented, relieving the pressure. Internally, bubbles frequently nucleated and grew along inclusions.

Our work over several years now leads to several clear but relatively unexplained differences in the nucleation of methane bubbles in low alloy steels.

- 1) In silicon killed steels MnS and manganese silicate inclusions are quite effective in nucleating bubbles. In more fully deoxidized steels bubbles do not nucleate on them.

2) In the more fully deoxidized steels myriad small bubbles nucleate and grow on a small fraction of the grain boundaries. Inclusions play no role, but segregated impurities may.

3) Plastic strain well below that which causes fracture greatly enhances rate of fissure nucleation and the fraction of boundaries along which fissures form. This is true both for ferrite/cementite and ferrite/inclusion interfaces.

Alloying Effects - Equilibrium Methane Pressure - The best way to stop HA is to add alloying elements to decrease the activity of carbon. The first kinetic study completed on this project was a comparison of several high strength low alloy steels. These were chosen to have quite low carbon (0.03-0.05%C) yet relatively high strengths. A paper describing this work has been accepted in Met.

Trans. (7) The abstract reads as follows:

Three HSLA steels with extremely low carbon contents and varying alloy contents were exposed to 21 MPa (3000 psi) hydrogen pressure in the temperature range 350 to 510°C. The resulting sample expansion rate was measured using a highly sensitive capacitance dilatometer.

In all three HSLA steels, the early expansion rate was found to be independent of exposure time, but a function of exposure temperature and pressure. The temperature dependence of the sample expansion rate was very similar for all three HSLA and the reference carbon steels, and corresponded roughly to an activation energy of 190 kJ/mole.

Though the sample expansion rates exhibited the same temperature dependence, they varied by as much as two orders of magnitude among the three HSLA and the carbon steels. This marked variation in rate was proportional to the estimated carbon activity in each steel.

(7) G. Sundararajan, and P. G. Shewmon, "The Attack of HSLA Steels," accepted for publication in Met. Trans.

Comparison between the API curves for 1/2 Mo steel and the experimental curves constructed for HSLA steels indicated that these steels should provide comparable or better resistance to hydrogen attack than the 1/2 Mo steel.

As a follow-up on this work we designed a small cylindrical specimen with which we hope to measure the equilibrium methane pressure. The sketch shows a cross section of the sample. All parts are made of the

steel to be studied. The welds create a gas tight internal cavity. By putting this specimen in our dilatometer and equilibrating it at low but successively higher P_{H_2} , the internal equilibrium methane pressure could be inferred from the elastic elongation of the shell holding the two end plugs together (the shell is crosshatched in the sketch).

We have been trying to do this all year and haven't any results yet. The welded joint is a problem, or more precisely, getting someone with a reliable electron beam welder to make the weld is a problem. After we finally got them welded once, it turned out we had solid state welded the two plugs together by not allowing enough clearance for solidification shrinkage of the weld. We have make another set with a larger gap between the plugs. The larger gap means that a much greater depth of the low carbon steel must be decarbed to fill the gap with the equilibrium P_{CH_4} , but sticking is less likely. These are being welded at Sandia Lab and should be back with the new year. We have our fingers crossed.

If this technique works, we would hope to get two things out of it. The relative activity of carbon in the various steels, at 400-500°C.

Also, it may be possible to measure the kinetics of methane formation at much lower temperatures than before. Thus, we feel it is worth the effort.