MASTER**HYDROGEN ATTACK OF STEEL, #3**

Progress Report,
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PROGRESS REPORT

The past year has seen our efforts bear fruit on two fronts:

1. The "geometry" of attack and nature of the nucleating impurity
2. Kinetics of the initial stage of hydrogen attack

Geometry and Nucleating Impurities

Our initial work on the effect of deoxidation practice on hydrogen attack (HA) has been completed and accepted for publication in *Metallurgical Transactions*. ~~The paper is attached.~~ The abstract reads:

Four normalized carbon steels made in different ways (Si-killed, Al-killed, REM-treated, and electroslag refined) were studied to determine the role of differing fine inclusions on the early stages of hydrogen attack (HA). Hydrogen exposures were made at 450°C (6.5 MPa) and 375°C (7.6 MPa). The first stage of HA is shown to be the development of a closely spaced (1-2 μ m) array of small bubbles over the ferrite/pearlite, or occasionally the ferrite/ferrite boundaries. These grew together to form tears, primarily in the rolling plane, leading to more rapid expansion normal to this plane. The planes of separation followed high solute layers in banded steel but only rarely did the fracture surfaces follow inclusions. At 450°C REM-treated steel was attacked the fastest and the Al-killed steel took two to four times as long for attack.

The most pleasing result of this is that myriad small bubbles 1-2 μ m apart were found on the fracture surface of all steels after HA as we had predicted before looking for them. They seem to be the essential first step in the development of the fissures or tears that have been observed for years in the study of HA, primarily with the light microscope, at least that is the case at this temperature (450°).

The nature of the nucleating agent needed to aid bubble nucleation in this low pressure, high temperature range remains unclear. It

clearly is inhomogeneously distributed in all steels, and the agent would appear to differ from one steel to another. Also, nucleation does not occur preferentially around the usual inclusions such as MnS as reported by Shih and Johnson at 600°C.¹ The active agent, or agents, at 450°C seems to act more on the atomic scale.

Early Kinetics of Attack

The second major thrust of our program has been the building and debugging of a capacitance bridge dilatometer which would be orders of magnitude more sensitive than any used before to follow the kinetics of HA. This has now been made operational and fractional changes in length of $\leq 10^{-7}$ hr⁻¹ can be followed at temperature and under H₂ pressure; an improvement of 10² over the last year at this time. We have operated up to 520°C and 3100 psi. Pressures up to the rated vessel pressure of 5000 psi should be attainable, but temperatures much above 520°C would require development of better seals at electrical lead throughs and gas tubing joints.

The electrical equipment consists of a General Radio Capacitance Bridge and Signal Generator, an Ortec Lock-in Amplifier and a recorder. The capacitance cell is modeled after that developed for low temperature thermal expansion work by White.² The biggest noise problem has been traced to temperature differences in the cell due to severe convection in the high pressure hydrogen. Elimination of much of this noise has made the current 10⁻⁷ sensitivity possible. With time we may develop the ability to work at sensitivity of 10⁻⁸ but there is currently no great motivation to reach this level.

The main advantage of following the kinetics of HA at such low values of expansion is that during this early stage the rate of expansion is largely or completely independent of time up to an expansion of about $1-5 \times 10^{-4}$. Beyond this "breakaway" the length increases exponentially with time as reported by Sagüés. In view of our work mentioned above (attached paper) we believe this early steady expansion rate is due to the growth of myriad separate bubbles on grain boundaries. After breakaway the bubbles have probably grown together and larger tears are making the main contribution to expansion. The expansion in this stage is probably determined by a balance of methane formation and creep as suggested to Sagüés. Our own aim has consistently been to follow the earliest stages of attack since we believe that the rate limiting process here plays a more fundamental role in establishing the nature of HA.

Two projects have been underway this year using the dilatometer. One on carbon steel aims to establish the basic pressure and temperature dependence of attack in a carbon steel. This in turn leads to curves of constant rate of attack on a plot of temperature vs pressure which should parallel those shown on a Nelson plot of HA data. The other study aims at comparing the HA resistance of various high strength steels by establishing the temperature threshold of attack at high pressure (3100 psi), as well as the pressure threshold of attack at higher temperatures. These indicate the power of the high sensitivity dilatometer both as a source of new information on rate limiting atomic processes and as a fast sensitive tool for ranking alloys for their resistance to HA.

Rate Equations for Carbon Steel

One of the basic unanswered questions in models of HA is, why the rate of attack stops at high pressure with decreasing temperature. Sagüés,³ as well as Johnson and Shih⁴ suggests it is due to the slow formation of methane. This would give a rate which increased with the bubble surface area or a rate proportional to (time)³ for a constant number of bubbles. And, following Grabke, an activation energy of 13.6 K cal/mol Shewmon suggested that carbon supply would be limiting.⁶ This would give little or no time dependence, for a fixed number of bubbles, and an activation energy of 35 K cal/mol, the sum of the heat for carbide solutions plus that for diffusion of carbon in ferrite.

One of the best established conclusions we've found is that the early attack at high pressure follows an equation of the form

$$\text{rate} \sim P_{H_2}^{1.4} \exp (47,000/RT)$$

The rate is essentially time independent up to breakaway and the Q of 47 K cal/mol applies for carbon steels (Fig. 1) as well as various high strength low alloy steels (Fig. 4). Thus we have added the new fact that the low temperature, high pressure limit of HA is clearly established by a process whose activation energy is 47 K cal/mol. The nature of this process is still unclear.

The pressure dependence of the HA in carbon steel is shown in Fig.

2. The high pressure exponent of 1.4 is fairly definite. The low pressure is certainly higher than 1.4 but its exact value is less clear. The data in Figures 1 and 2 have been combined in Fig. 3 to draw constant rate curves. These are more to indicate the ultimate

goal of our approach than to give definitive values of rate. However, the curves at high pressure are rather firmly established. The bottom line (5×10^{-8} /hr) was chosen to give breakaway in 10^4 or about the time Nelson gives to his line defining the limit of attack. This line is about 100°C above the Nelson curve given by the API.⁷ But the attached paper also indicates rates of HA an order of magnitude slower than that reported in the older literature.⁷ The reason for this variance is unclear at this stage in our work.

Low Alloy Steels

This study was initiated to examine the capability of the capacitance bridge dilatometer as a device for screening or ranking alloys. As a start we chose several HSLA steels which had particularly low carbon contents and relatively high ratios of carbide forming solute to carbon content. (See Table I.) Work was done primarily in the high pressure regime. This is the region of primary importance for engineering applications, and the area which has been least studied in the past.

Two important early results are:

1. Before breakaway the rate of expansion of a given alloy at constant pressure is independent of time, and depends only on temperature, even though the rate varies by orders of magnitude between various alloys.
2. The temperature dependence of the rate is the same for all steels, with $Q = 47 \text{ K cal/mol}$. (Fig. 4). (The 2-1/4 Cr - 1 Mo steel is the only possible exception to this, but we couldn't get consistent attack there.)

One might expect that the orders of magnitude difference in rate between different alloys reflects the variation in the activity of carbon. That assumption is attractive, but uncertain for now. The variation in the carbon activity between a carbon steel and that for 2-1/4 Cr-1 Mo, calculated by Geiger, is as great as the roughly 10^3 variation shown in rate of attack between these two steels. However, we now have no way of calculating the relative carbon activities of the other alloys.

The fact that the rate at high pressures is a function only of temperature and doesn't increase with time suggests that there are a fixed number of nuclei which preexist or nucleate very quickly. We have not done enough fractography or metallography on material attacked at high pressures to say when the bubbles form or whether the geometry differs from that found by us at low pressures. The limited work we have done indicates that only a few of the boundaries undergo attack, just as was found at lower pressures and higher temperature.

In summary, we now have the tools needed to develop new information on the atomic processes which limit the very nearly stages of HA-- the stage where HA consists of the growth of many small bubbles isolated from one another. The unique feature of our work is the ability to follow the rate of growth of these bubbles in a given specimen as the hydrogen pressure or temperature is changed. This is leading to accurate rate equations which in turn should stimulate the development of a better theoretical understanding of the rate limiting processes of HA.

The sensitive dilatometer also allows one to relatively quickly screen new alloys and rank them relative to one another in their ability to resist HA. This group of alloys which are accepted for resistance to HA in the U.S. currently seems to be closed. However, the technique would be of value for surveying the effect of process variables on these alloys, such as welding or tempering, or for heat to heat variations.

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CHEMICAL COMPOSITIONS OF TEST MATERIALS
(WEIGHT PERCENT)

STEEL NUMBER	C	Mn	Si	S	P	Cr	Ni	Cu	Mo	Al	Cb	Ce
1 EXPERIMENTAL ALLOY No. 9518 REM TREATED	0.034	3.70	0.90	0.001	0.015	0.50	0.03	0.05	0.02	0.03	0.14	0.01
2 ARMCO 787 STEEL No. 55946	0.048	0.54	0.23	0.011	0.004	0.60	0.90	1.18	0.27	0.02	0.024	-
4 SUMITO STEEL No. C10102	0.028	1.75	0.100	0.005	0.006	0.004	0.18	0.21	0.26	0.051	0.074	-
5 SA542 STEEL (WESTINGHOUSE) CLASS - 3	0.12	0.47	0.22	0.017	0.01	2.26	0.22	0.12	0.99	-	-	-
6 ARMCO STEEL No. 58011 REM-TREATED	0.17	1.10	0.24	0.009	0.01	0.08	0.11	0.15	0.03	0.066	-	0.04

Hydrogen Attack Rate vs Pressure ESR 1020 Steel

Figure-2

Hydrogen Attack Rate vs Pressure ESR 1020 Steel

Figure-2

Calculated Constant-Rate Curves for Hydrogen Attack

Figure-3

Rate of Hydrogen Attack vs Temperature Low Alloy Steels- 3050 to 3100 Psi

Figure-4