MASTER

HYDROGEN ATTACK OF STEEL

Progress Report

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Introduction

Avoiding the hydrogen attack of large steel pressure vessels is one of the main factors in alloy selection, and/or choosing operating conditions for proposed coal gasification plants and many chemical processing plants. Simply put, you wish to hydrogenate the carbon in the feed stock without hydrogenating the carbon in the steel thereby forming methane bubbles inside the steel.

There is substantial scatter in the conditions which give hydrogen attack (HA) for different heats of the same steel and fair scatter for different pieces from the same heat. Our aim has been to study the earliest stages of HA in plain carbon steel made with different deoxidation processes in an effort to identify the basic process leading to methane bubble nucleation, and the processes limiting their growth into cracks.

The first year of this contract was largely devoted to setting up high pressure hydrogen vessels for work in the range of interest (100-4000 psi, and 250-550°C), getting materials, and getting equipment operating. In the second year we've obtained results in studies using density change, fractography, microscopy, and a sensitive capacitance dilatometer to follow kinetics during attack.

This work has been primarily in the higher temperature, lower pressure domain where the rate of attack increases rapidly with hydrogen pressure. There is some problem with metallographically finding and following the early stages of attack even at several thousand magnification with the SEM. However, results are accumulating at a reasonable rate now. One Masters candidate will write up his work in the Winter Quarter. The other student, who's in his second year, is working toward a Ph.D. and will probably not write up

his thesis for another year. A new student is building a second capacitance cell to study the kinetics of HA at high pressure and lower temperature.

Progress to Date

Four carbon steels of approximately equivalent carbon content and varying mainly in the method of steelmaking, i.e. semi-killed, fully-killed, REM-treated, and electroslag refined (ESR), are being studied to determine the effect of deoxidation practice and inclusion morphology on the hydrogen attack of carbon steel. To date tests have been run on a cold-rolled steel (to develop experimental techniques), the semi-killed, and REM-treated materials. Heat treatment for the latter two steels consisted of 60 minutes at 890°C and air cooling to give an average grain size of ASTM No. 8.

Significant results are: 1) HA results in substantial (factor of ten) greater growth normal to the rolling plane than in the rolling plane; 2) metallography and fractography show a few areas with many microscopic bubbles in the REM-treated steel indicating high bubble nucleation rates on some boundaries and much lower on most boundaries; 3) incubation times, t_i , are on the order of 4-5 times that predicted from Weiner's equation.¹

The anisotropy relative to the rolling plane occurred in all three steels tested. Thus it would seem reasonable that such variables as inclusions or segregation tend to determine the local extent of hydrogen attack. This anisotropy will be examined further in the next series of experiments by comparing all four steels. Of especial interest will be the results of the ESR steel, in which the inclusion content and solidification segregation is significantly reduced.

1. See P. Shewmon, Met. Trans. 7A (1976) 279.

The tensile testing of the semi-killed steel was done at room temperature. The REM-treated and the cold-rolled steel were fractured at liquid nitrogen temperature to give less deformation before fracture. The REM steel gave a large amount of plastic deformation before fracture even at temperatures approaching 78°K. Figure 1a shows the fracture surface of the REM steel exposed for 225 hours ($5t_1$) at 450°C and 950 psig. The ledges on the surface results from the anisotropic nature of the attack evidenced in this sample. That is, as shown in Figure 1b, the fissures tended to align themselves along the same direction as the rolled out inclusions. In an unattacked steel there are none of the elongated fissures of Figure 1 though a small volume of elongated inclusions are visible. As stated previously there were areas on the fracture surface which appeared to be dense regions of small microscopic bubbles (Figures 2a and 2b). Further work is needed to confirm this.

For the experiments currently in progress, sharply-notched (60°) tensile specimens will be exposed in addition to the standard 1/2" gage length specimens. It is hoped that the increased triaxiality at the root of the notch, in conjunction with the low temperature testing, will facilitate the opening up of any microscopic holes which may have resulted from the early stages of hydrogen attack. Also, based on the results to date, the tensile bars (excluding the semi-killed steel) are oriented such that the tensile axis is perpendicular to the rolling plane. It is expected that the fracture surfaces generated in this way will show the largest amount of hydrogen attack, or alternatively, show the effect of hydrogen attack after the shortest period of time.

Kinetics and Mechanisms

During the past year, a sensitive capacitance bridge dilatometer has been completed which follows growth during attack. To date the dilatometer has been used to study HA in annealed AISI 1020 bar stock of ASTM grain size 7.

The dilatometric measurements indicate that after an extended incubation period the sample expands at a rapidly accelerating rate, more rapid than one would predict by assuming that growth results from the grain boundary transport of iron atoms away from a constant number of bubbles.² Metallographic work has also shown that HA does not initiate uniformly throughout a material; rather, the attack first appears as a few small, clusters of thin cracks and loosened inclusions. Both this clustering and the rapidly accelerating kinetics suggest that the nucleation of methane bubbles in HA may be autocatalytic, that is the stresses set up by the first bubbles quickly nucleate others around it. It is certainly true that when nucleation occurs on an interface it does so quickly over the entire length of grain boundary or inclusion. However, such nucleation occurs on only a small fraction of the boundaries.

Figures 3 and 4 show the dilatometer results for a sample at 382°C for 373 hours.

Figure 3 shows that when measurable expansion occurs the rate of linear expansion accelerates rapidly. In Figure 4 this rapid increase is approximated empirically by the equation:

$$\frac{\Delta L}{L} = 3.5 \times 10^{-6} \exp (3.7 \times 10^{-5} t^2)$$

2. P. G. Shewmon, loc. cit.

where t again represents the hydrogen exposure time in hours. Shewmon's analysis of HA predicts that during the early stages the rate of expansion of a sample will be limited by grain boundary transport of iron atoms away from growing bubbles. Using this model (assuming a constant bubble density) and adjusting the number of boundaries with bubbles to fit the value of $\Delta L/L$ at 130 hour, one can predict how the volume of the sample should vary with time. The results of this calculation is also shown in Figure 4. Note that the rate of expansion of the two curves is initially the same. However, the curves then rapidly diverge, the sample expanding much more rapidly than one would predict from the model. This may suggest that the bubble density on a given boundary increases rapidly with time, or that the bubbles are combining into a crack along the boundary. It is hoped that in going to lower values of $\Delta L/L$ we can see if there is indeed an initial period when a fixed number of bubbles grow independently of one another.

After exposure, this sample was examined using optical and scanning electron microscopy. It was observed that the initial hydrogen attack seen in the sample was localized rather than uniformly distributed. These localized regions of attacked material generally contained small bubbles and hair-line cracks along grain boundaries in addition to small fissures and loosened manganese sulfide inclusions. A typical region of attacked material is shown in Figure 5. Careful microscopy of such regions suggests that the fissures may form by coalescence of methane bubbles.

In the future, the author hopes to continue studying both the kinetics and the morphology of the early stages of hydrogen attack. Work is currently under way to improve the electrical shielding and mechanical rigidity of the dilatometer assembly to increase sensitivity. Additional theoretical and experimental work is also planned in order to learn why a hydrogen attack sample expands more rapidly than predicted.

Fig. 1

REM-treated steel exposed for 225 hrs. ($5t_i$) at 450°C and 950 psig, $\frac{\Delta L}{L} = 1.6 \times 10^{-2}$. (A) SEM fractograph, 40x; (B) section along tensile axis, 100x.

Fig. 2

REM-treated steel exposed for 225 hrs. ($5t_i$) at 450°C and 950 psig, $\frac{\Delta L}{L} = 1.6 \times 10^{-2}$. (A) SEM fractograph, 1050x, arrows indicate areas of microscopic bubbles; (B) areas indicated by arrows in (A) at 2100x.

Fig. 4

Fig. 3

Fig. 5

Unetched, 1400x

Initial stage of fissure formation in 1020 steel. Sample was exposed for 373 hours (3.3 t_i) at 950 psig hydrogen at 382°C. $\frac{\Delta L}{L} = 7 \times 10^{-4}$.