MASTER

HYDROGEN ATTACK OF PRESSURE-VESSEL STEEL

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by

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SUMMARY

The nucleation and growth of methane bubbles in the hydrogen attack of pressure vessel steel has been shown to obey models developed to describe the growth of bubbles limiting the creep ductility of metals. This has been done through studies of the effect of prior deformation on bubble nucleation as well as the effect of methane pressure (stress) and temperature on growth kinetics. A comprehensive model of the factors limiting growth has been developed. Its application to the hydrogen attack of a 2 1/4 Cr - 1 Mo steel leads to several interesting predictions.

INTRODUCTION

From its inception the work of this project on hydrogen attack (HA) has followed two paths, studies of nucleation and growth kinetics. The nucleation work started by searching for chemical effects. These were found in the differences between nucleation sites in silicon killed (normal sulfur content, $\approx 0.2\%S$) and fully killed (low sulfur $\leq 0.08\%S$). However, we have never been able to explain the nucleating heterogeneity or develop a model, beyond saying that in going from silicon killed to the fully killed steel nucleation at sulfides becomes more difficult, and nucleation on grain boundary, or α/Fe_3C interface, more common. In the past year work on the effect of cold work has led to a significant enhancement in nucleation rate and clear model which will be followed up next year in a new study of the enhanced rate of HA of welds.

We have completed our first study of the growth kinetics of HA in a carbon steel (an electroslag refined A516). This clearly shows that:

- 1) The equilibrium pressure of methane is maintained in the bubbles over a large part of the growth period.
- 2) The accurate correction for the non-ideality of this high pressure methane gas in the bubbles is essential for valid modeling.
- 3) Iron diffusion along interfaces (gas/metal or grain boundary) limits bubble growth over the majority of the incubation time.
- 4) Dislocation creep plays an important role in bubble growth only in the final stages of HA as the bubbles become large and link up into fissures.

Work in progress has combined several models developed to describe the growth of boundary voids in creep ductility to develop maps that indicate the dominant bubble growth mechanism as a function of bubble size and hydrogen pressure. HA provides a better way to check these models than does creep ductility since in HA all specimen strain results from bubble growth so the growth rate can be followed throughout the range of growth experiments. In creep experiments one can only measure the total strain and infer bubble growth from strain to fracture or fractography.

Nucleation - Effect of Plastic Strain

The earlier Nelson Diagram published by the API showed two branches on the carbon steel line in the low pressure region⁽¹⁾. They indicated that HA occurred at a lower pressure for welded and/or cold worked steel than for annealed steel. I know of no systematic work on the effect of welding though several authors have studied the effect of cold work. They showed that cold work significantly increased the fraction of grain boundaries over which bubbles nucleated and decreased the time for loss of ductility (the so-called incubation time).

In Ransick's M.S. thesis work we deformed our samples by three point bending to a maximum strain of 15%. (Pub. 1 and 2)* The results of this work are described in two papers accepted for publication. This confirmed that deformation significantly enhanced the fraction of boundaries on which methane bubbles nucleated, as well as the density of bubbles nucleated. This leads to the formation of an interconnected set of grain boundary channels which vented to the surface and lead to complete decarburization of the deformed layer. The undeformed regions of the same material exhibited HA on some boundaries, but little decarburization since the equilibrium methane pressure built up in the bubbles retarded the formation of methane.

*See list of this year's publications at end of text. *Removed*

The predominant orientation of the fissures formed in the deformed and hydrogen attacked region was parallel to the elongation on the tension side and perpendicular to the strain vector on the compression side. This is of particular interest because Dyson and coworkers^(2,3) have found that a few to ten percent strain of Nimonic 80 followed by heating to below the recrystallization temperature leads to the development of a high density of submicron voids along grain boundaries. These decorated boundaries are oriented primarily parallel to the tensile strain and perpendicular to compressive strain, that is, the same orientation of boundaries that showed preferential HA in our samples. Voids of this size could easily be expanded by the equilibrium methane pressure for the conditions studied by Ransick (460°C. 950psi H₂). We feel confident that the cold work lead to the formation of submicron voids along many boundaries in our steel which in turn lead to rapid HA. Whether or not carbides always played a role in enhancing the nucleation along these deformed boundaries is unclear. Since strains of a few percent can occur locally in constrained welds, it is quite credible that in thick multipass welds, the same type of submicron voids could develop at grain boundaries and lead to an enhanced rate of HA.

A related more subtle change in the bubble nucleation lead to publication 3. There it is shown that in an aluminum killed 1020 steel an increase in the hydrogen pressure from 6.4 MPa to 17 MPa changed the bubble morphology from many discrete bubbles at low pressure to thin fissures along the boundary segment at high pressure. The ESR 1020 steel (also fully killed) showed only discrete bubbles at both pressures. In both cases only a small fraction of the boundaries developed bubbles. The transition from round bubbles to fewer long thin ones at higher methane pressures can be rationalized by using an analysis of Rice

and coworkers⁽⁴⁾. However, the marked difference in morphology between the various 1020 steels requires several ad hoc assumptions, and remains unexplained.

Kinetics

The main effort this year has been devoted to acquiring data on the kinetics of methane bubble growth during the very early (pre-incubation) stage of hydrogen attack. This is primarily embodied in Marvin McKimpson's Ph.D. thesis work (Pub. 4). This data has provided the principle data base for the model building of Professor G. R. Odette under DOE Contract ET-78-S-01-3153 (Fossil Energy Res.)⁽⁵⁾. This data also has played a key role in our studies of the mechanism (Pub. 5).

McKimpson's data is of particular value because it measured the P_{H_2} and temperature dependence of bubble growth during the early stages when the bubbles are small and discrete. This stage makes up the great majority of the incubation time for HA, but has not been studied in the past due to the small volume changes involved. Fig. 1 shows a plot of the rate curves he obtained on a temperature/hydrogen pressure diagram. From the relatively low hydrogen pressure dependence and the observed time (radius) independent growth rate it is clear that dislocation creep is not rate-controlling during this initial stage of bubble growth. After a linear expansion of 10^{-4} to 10^{-3} the rate rapidly accelerates and we believe dislocation creep becomes the predominant growth mechanism.

The significant change in the slope of the constant rate curves in Fig. 1 in going from low to high P_{H_2} stems entirely from the increasing deviations from ideality of the methane in the bubbles as the P_{H_2} rises and the temperature falls. (This was first suggested by Odette, Vagarli and Oldfield⁽⁶⁾ and makes a profound difference in the calculation of the methane pressure.) For bubble growth limited to the grain boundary diffusion of iron, the expansion rate is:

$$\frac{dv}{dt} = \frac{2\pi D_{gb} \delta \left(P_{CH_4} - \frac{2\gamma}{r} \right)}{kT} f(r/\ell) \quad (1)$$

where the symbols represent:

D_{gb} - grain boundary diffusion coefficient

δ - grain boundary thickness

γ - solid/vapor surface tension

r - bubble radius

ℓ - interbubble spacing along boundary

$f(r/\ell)$ - a function roughly equal to unity

At low methane pressures P_{CH_4} is proportional to $P_{H_2}^2$ while at high methane pressures the exponent on P_{H_2} drops from two to below unity. The overall activation energy for this process Q , is the sum of the positive Q_{gb} and a negative contribution from the decrease in P_{CH_4} with rising temperature at constant P_{H_2} . Q_{gb} is independent of P_{H_2} , and for high hydrogen pressures P_{CH_4} becomes less dependent on temperature so the apparent Q rises (Fig. 1).

The temperature and pressure exponents predicted by eqn. 1 fit McKimpson's data only moderately well. Sundararajan (Pub. 5) has shown that better agreement is obtained if one used the equation of Chuang et al. (4) which predicts that both surface and grain boundary diffusion are limiting and the rate of bubble growth varies as $(D_{gb} P_{CH_4})^{3/2}$ not the power of unity as in eqn. 1.

This paper (Pub. 5) treats the various limiting cases of growth in HA much more completely than that of any previous workers. The various processes which limit bubble growth are shown in the "bubble growth map" of Fig. 2, representing carbon steel, and Fig. 3, representing something closer to 2 1/4Cr - 1 Mo. The principal new ingredient in the 2 1/4 Cr steel is the importance of lattice creep

in relieving the stresses that are built up due to bubbles only nucleating and growing on a small fraction of the grain boundary segments. (This is termed constrained cavity growth in the creep literature.) Thus in Fig. 3 the lattice is assumed to be 10^3 times more creep resistant ($C_0 = 1000$) and the carbon activity, a_C , 100 times lower than for the carbon steel of Fig. 2.

To explain these diagrams consider the plain carbon steel (Fig. 2). Small bubbles in the Bubble Sinter Regime will sinter shut since $P_{CH_4} < 2\gamma/r$. To nucleate and grow the bubble radius must become greater than $10^{-2} \mu m$ for $P_{H_2} = 10 \text{ MPa}$ (1400 psi). Once nucleated the bubbles grow at a slow constant rate limited by surface and grain boundary diffusion of iron out of the bubble. When the radius has grown enough to cross into the "Powerlaw Creep" region the growth rate is limited by dislocation creep. The rate of bubble growth increases steadily and rapidly with radius here so this region is crossed more quickly. As the bubbles get larger, and perhaps merge into fissures, the growth rate may become limited by the formation of methane.

Turning now to Fig. 3 one can see that the methane pressure is an order of magnitude lower for a given P_{H_2} . This raises the critical radius for nucleation by a factor of ten. The lower methane pressures and much stronger matrix leads to the restraint of the growth of the inhomogeneously distributed bubbles by the strong matrix. This leads to the region labeled "Accommodation Process Control." Our preliminary results confirm that this is indeed the limiting process and that the field extends to even higher pressures than shown on the figure.

Two types of predictions come out of this concerning the behavior of 2 1/4 Cr - 1 Mo steel:

- 1) Nucleation must depend on preexisting voids the order of $0.1 \mu m$ in diameter. Any creep deformation or welding/process that created submicron voids

on grain boundaries could remove this nucleation barrier and greatly accelerate the slow rate of HA.

2) The code allowable stresses are comparable to the methane pressures inside the bubbles, thus an applied load could substantially increase the rate of HA. Since the accommodation creep varies as roughly the fifth power of the stress, if the stress due to the applied load equals that of the P_{CH_4} the rate of growth increases by 2^5 .

Work in Progress

This report has dealt primarily with the studies completed during the past year. Here we mention two projects that got well underway in this year. The aim of both is an exploration of the relation between the kinetics of HA and models developed to treat grain boundary void (bubble) growth in solids. One studies the HA kinetics in an aluminum killed carbon steel, the other the growth of steam bubbles in oxygen bearing (tough pitch) copper.

Though McKimpson's data on one carbon steel fits the models well one should have some concern about all carbon steels fitting this model. The variable between steels would be primarily in the nucleation of microscopic bubbles. The aluminum-killed steel differed from McKimpson's in that it develops long thin bubbles at higher hydrogen pressures and fewer bubbles at all pressures. Reproducible steady state "creep" data is being obtained and the kinetic exponents differ measurably from that found by McKimpson. For example, it appears that the low bubble density leads to creep constraint of bubble growth at low pressures. Kinetic work will also be done on the silicon killed steel studied by Ransick. This work is the Ph.D. thesis of Mr. Panda.

The work on tough pitch copper was started in an effort to apply our kinetic models to a different alloy system in which the diffusion data and driving

pressures were better known. This is the M.S. thesis of Mr. Chun-Sien Lin.

Reproducible expansion data is being obtained but in a temperature range below the critical temperature. This means that the pressure inside the bubbles depends only on temperature and cannot be varied by changing the hydrogen pressure.

Reproducible kinetic data is being obtained. Metallography and interpretation are in progress.

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