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KINETICS OF HYDROGEN ATTACK OF 2-1/4 CHROMIUM-1 MOLYBDENUM STEEL

The Ohio State University PH.D. 1983

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KINETICS OF HYDROGEN ATTACK OF 2 1/4 Cr-1 Mo STEEL

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
T.A. Parthasarathy, B.Tech., M.S.

* * * * *

The Ohio State University
1983

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**VITA**

<table>
<thead>
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<tr>
<td>1976</td>
<td>B.Tech., I.I.T., Madras</td>
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<td>1977-80</td>
<td>Development Engineer, Welding Research Institute, India</td>
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<td>1980-81</td>
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</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS .................................................. 11
VITA .............................................................................. 111
LIST OF TABLES ............................................................ v1
LIST OF FIGURES ........................................................... vii1
INTRODUCTION ............................................................. 1
SECTION I - EFFECTS OF WELDING AND TEMPERING
ON THE HYDROGEN ATTACK KINETICS
OF 2 1/4 Cr-1 Mo Q & T STEEL

BACKGROUND .................................................................. 9
Basic Understanding .................................................. 9
Experimental Work ................................................... 13
EXPERIMENTAL STUDIES ................................................. 17
Dilatometry ............................................................... 17
Metallography ............................................................ 50
Carbon Activity Measurements ......................................... 54
ANALYSIS OF EXPERIMENTAL RESULTS
AND DISCUSSION .......................................................... 61
Base Metal and Weld Metal ........................................... 63
Tempering Effects ........................................................ 76
CONCLUSIONS .............................................................. 82
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chemical compositions of the base metal and the weld metal</td>
<td>25</td>
</tr>
<tr>
<td>2. Hydrogen Attack strain rates of the base metal</td>
<td>34</td>
</tr>
<tr>
<td>3. Hydrogen Attack strain rates of the weld metal</td>
<td>41</td>
</tr>
<tr>
<td>4. Heat Treatments of samples used for the study of tempering effects on HA behavior and carbon activity</td>
<td>42</td>
</tr>
<tr>
<td>5. Hydrogen Attack strain rates of samples XT1, XT2, XT3, XT4 and XQ measured at 823 K</td>
<td>49</td>
</tr>
<tr>
<td>6. Measured carbon contents of the nickel foils equilibrated with the different 2 1/4 Cr-1 Mo steel samples and the calculated carbon activity values with respect to graphite standard state</td>
<td>59</td>
</tr>
<tr>
<td>7. Material parameters used in the model</td>
<td>131</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sequence of mechanistic steps for bubble growth during hydrogen attack (Ref. 10)</td>
<td>11</td>
</tr>
<tr>
<td>2. A schematic sketch of the capacitance dilatometer cell</td>
<td>19</td>
</tr>
<tr>
<td>3. A schematic sketch of the experimental apparatus</td>
<td>21</td>
</tr>
<tr>
<td>4. Preparation of dilatometer samples from the 2 1/4 Cr-1 Mo steel weldment</td>
<td>26</td>
</tr>
<tr>
<td>5. Plots of the dilatometric data of the base metal</td>
<td>27</td>
</tr>
<tr>
<td>6. Capacitance-Time plots for the base metal sample</td>
<td>29</td>
</tr>
<tr>
<td>7. Capacitance-Time plots for the weld metal sample</td>
<td>36</td>
</tr>
<tr>
<td>8. Carbide distribution map of Baker and Nutting (22) with the positions of the samples marked on it</td>
<td>43</td>
</tr>
<tr>
<td>9. Capacitance-Time plots for the sample XT1 at 823 K</td>
<td>45</td>
</tr>
<tr>
<td>10. Capacitance-Time plots for the sample XT2 at 823 K</td>
<td>46</td>
</tr>
</tbody>
</table>
11. Capacitance-Time plots for the sample
   XT3 at 823 K .................................. 47
12. Capacitance-Time plots for the sample
   XT4 at 823 K .................................. 48
13. Microphotographs of two different
    regions from the weld metal after long
    term hydrogen attack .......................... 52
14. Microphotographs of regions from the
    base metal after long term hydrogen
    attack ......................................... 53
15. Arrhenius plot for a constant hydrogen
    pressure of 20.3 MPa for the base metal
    and the weld metal ........................... 64
16. K(T) for various carbides in 2 1/4 Cr-1 Mo
    steel at different temperatures (Ref. 36) ... 66
17. Methane pressures in equilibrium with
    M3C carbide in a commercially quenched and
    tempered 2 1/4 Cr-1 Mo steel (690 C, 20hrs) .. 69
18. Arrhenius plot at a constant driving force
    of 400 MPa for the base metal ............... 71
19. Arrhenius plot at a constant driving force
    of 400 MPa for the weld metal ............... 72
20. Nelson Curves for the base metal and
    weld metal compared with the API curve ...... 74
21. Variation of carbon activity and HA
    strain rate with the tempering parameter .... 78
22. HA strain rates of different tempered structures plotted against the driving force 80
23. Effect of jacking on the grain boundary diffusional growth rate of the bubble .... 100
24. Interactive growth of bubbles by power-law creep ....................... 111
25. The steady-state stress distribution between the bubbles growing by grain boundary diffusion ....................... 116
26. Variation of the stress at the half-bubble spacing distance with half-bubble spacing, for grain boundary diffusion controlled growth of bubbles ....................... 119
27. Variation of the stress at the half-bubble spacing distance, with half-bubble spacing for surface diffusion controlled growth of bubbles ....................... 123
28. Methane pressures in equilibrium with Fe3C as a function of hydrogen partial pressure for different temperatures in the range 300-600°C .......... 129
29. Comparison of model predictions with the data of McKimpson ............... 134
30. Comparison of model predictions with the data of McKimpson in the high pressure regime ............... 135
31. Comparison of model predictions with the data of McKimpson for the hydrogen pressure dependence at 385 C................. 136
32. Bubble growth mechanism map for carbon steel with parameters as shown................. 137
33. Comparison of model predictions with Panda's data in the low pressure regime..... 140
34. Comparison of model predictions with Panda's data in the intermediate pressure regime................................. 141
35. Bubble growth mechanism map for Al-killed carbon steel with parameters as shown..... 142
36. Comparison of model predictions with Panda's results in the surface diffusion control regime................................. 145
37. Comparison of model predictions with Panda's results in the power-law creep regime....... 148
38. Comparison of model predictions with results of the present work on the base metal of 2 1/4 Cr-1 Mo steel weldment.............. 151
39. Bubble growth mechanism map for the base metal of 2 1/4 Cr-1 Mo steel weldment.. 152
40. Comparison of model predictions with results of the present work on the weld metal of 2 1/4 Cr-1 Mo steel weldment.............. 154
41. Bubble growth mechanism map for

-x-
2 1/4 Cr-1 Mo steel of bubble radius and density the same as that of the weld metal of the present work.......................... 156

42. Comparison of model predictions with results of the studies on the tempering effects..... 158

42. Comparison of model predictions with results of the studies on the tempering effects..... 159

43. Comparison of model predictions with the data of Yu (Ref. 9) on 2 1/4 Cr-1 Mo Q&T steel... 160

44. Nelson Curves calculated using the model for carbon and 2 1/4 Cr-1 Mo steels.......... 164
INTRODUCTION

Carbon and low alloy steels exposed to hydrogen at high pressures and temperatures, suffer a loss in mechanical properties after a long incubation time, during which no changes in mechanical properties are noticed. This phenomenon called Hydrogen Attack (HA) was discovered in Germany in 1930, in steel vessels used for the ammonia production by the Haber process. The surfaces of the vessels were found to be cracked and decarburized. The Germans also found in the thirties that the addition of carbide forming alloying elements increased the resistance of the steel to hydrogen attack. Since then many alloy steels have been developed for HA resistance, and 2 1/4 Cr-1 Mo steel is the most widely used since it is the least expensive alloy with good HA resistance.

The phenomenon of HA is now known to be caused by the formation of methane bubbles, which grow with time and eventually, link up to form fissures. The
incubation period is characterized by the growth of isolated bubbles, and hence the tensile and impact properties are unaffected. However the formation and growth of the isolated bubbles might affect the creep properties of the steel. The length of the incubation period was used as a means of studying the kinetics of HA by early investigators (2,3). Later, the importance of the structural changes occurring during the incubation period was pointed out by Shewmon (4). He suggested that if HA is to be avoided, the factors leading to fissuring must be influenced, and thus the kinetics of processes occurring during the incubation period need to be studied, rather than just the incubation time. The growth of methane bubbles during the incubation period results in swelling of the steel suffering HA. Thus by studying the kinetics of swelling rate of a steel suffering HA, its HA behavior during the incubation period can be characterized.

Several investigations (5,6,7,8,9) have been conducted using a sensitive dilatometer to measure the swelling rates of steels during the incubation stage of HA. The experimental data thus generated have helped us in understanding the mechanisms that control HA in steels.

From the engineering viewpoint, the hydrogen attack behavior of 2 1/4 Cr-1 Mo steel is of current interest
due to the following reasons. As mentioned before it is the leanest alloy with good HA resistance. From the experience of the industry, it is known to be resistant to hydrogen attack at temperatures up to about 450°C, as shown by the industrially developed Nelson Curves (57) of API. This has led the industry to identify 2 1/4 Cr-1 Mo steel as a potential structural material for future applications in coal conversion plants and in nuclear fission reactors. But the operating temperatures of the future applications are in the range 500°C to 600°C. In the absence of industrial experience in this range, there is considerable interest in the study of the hydrogen attack behavior of 2 1/4 Cr-1 Mo steels in this temperature range.

Li and co-workers (12) were the first to show that 2 1/4 Cr-1 Mo steel suffers a marked reduction in creep ductility when exposed to the relatively mild hydrogen conditions of 2 ksi (16.9 MPa) hydrogen for a day at 550°C. Similar results were obtained by Erwin (13) who showed that after a long term exposure (>3x10⁴ hrs) at 460°C and 2 ksi (16.9 MPa) hydrogen, a 2 1/4 Cr-1 Mo steel suffers a substantial reduction in ductility in a hot tensile test. Erwin (64) also reported appreciable bubble growth after hydrogen attack of 2 1/4 Cr-1 Mo
steel at 455 C and 20.3 MPa hydrogen for about five years. Thus although the methane bubbles do not link up to form fissures, the toughness of 2 1/4 Cr-1 Mo steel is impaired by exposure to the limiting conditions defined by the Nelson Curve (57) for this alloy. This has necessitated the study of the kinetics of HA of the 2 1/4 Cr-1 Mo steel, to identify the mechanisms of bubble growth in this steel.

The kinetics of HA of 2 1/4 Cr-1 Mo steel has been studied by Yu (9) at 20.3 MPa hydrogen in the temperature range 550 C to 580 C. From the activation energy of HA strain rates, he concluded that the bubbles grew under a grain boundary diffusion controlled mechanism. Extrapolating his results to lower temperatures (350 C -400 C ), and comparing them with the results of McKimpson on carbon steels at 17.3 MPa hydrogen and 350 C to 400 C, the HA rates of the 2 1/4 Cr-1 Mo steel are found to be 3 to 4 orders of magnitude lower than those of the carbon steel, for a given hydrogen pressure. The results of Sundararajan (7) on carbon and low alloy steels at 21 MPa hydrogen also suggest such a huge difference between the HA rates of carbon and 2 1/4 Cr-1 Mo steels. One obvious reason for the difference is the difference in carbon activities of the two steels. But
the carbon activity of a commercially quenched and tempered 2 1/4 Cr-1 Mo steel of 0.1 Wt% C has been measured to be just one tenth that of a carbon steel at 550 C (14), and this corresponds to a drop in methane pressure by a factor of only three, due to fugacity corrections. Thus carbon activity alone cannot be responsible for the 3 to 4 orders of magnitude difference in HA rates. Additional factors must account for the observed differences. Restraint on the bubble growth caused by the high matrix creep strength of the 2 1/4 Cr-1 Mo steel is thought to be one reason for the very low HA rates (10,15), but its nature and role in HA are not understood. A much lower bubble density caused by lower methane pressures could be another effect that would explain the difference.

The effect of industrial operations like welding and tempering on the hydrogen attack behavior of 2 1/4 Cr-1 Mo steel, has been the other major concern of the industry. The work by the Japanese Pressure Vessel Research Council (16) on the effects of welding on the HA behavior of 2 1/4 Cr-1 Mo steel has shown that there is a significant increase in the HA rates of simulated heat affected zone (HAZ) samples compared to those of the base metal. Others (17,18) have shown that welding or improper tempering accelerates the onset of
HA of this steel. Thus from the engineering standpoint, it is necessary to quantify the effects of welding and improper tempering on the HA rates of this steel. There has been no work done so far, to study the effects of welding and tempering on the kinetics of HA of 2 1/4 Cr-1 Mo steel.

In the present work, a commercial quenched and tempered 2 1/4 Cr-1 Mo steel weldment representative of practice of about 10 years ago, was used. It was run in parallel with a modern steel weldment(26). The swelling rates of the base metal and the weld metal of the weldment were studied using a sensitive capacitance dilatometer, in the temperature range of 460 C to 590 C. Further, samples from the base metal were austenitized, quenched, and tempered at different temperatures for different times, and the strain rates of the samples were measured at 550 C as a function of hydrogen pressure and extent of tempering.

Since the carbon activity of the steel determines directly the methane pressure driving the bubble growth, an equilibration technique was developed to measure the carbon activity of low alloy steels at 550 C. The variation of carbon activity with tempering was studied using the technique and the results compared with HA behavior.
The results of the experiments are presented and
discussed in the first section of this dissertation. In
the second section, the mechanisms of growth of
internally pressurized bubbles are analyzed in detail,
and a model for HA kinetics is presented to explain all
the dilatometric results obtained by previous
investigators and those obtained in the present work.
SECTION I

EFFECTS OF WELDING AND TEMPERING ON THE

HYDROGEN ATTACK KINETICS OF 2 1/4 Cr-1 Mo QT STEEL
BACKGROUND

The current knowledge of hydrogen attack can be discussed in terms of the basic understanding of the mechanisms of HA and the amount of experimental work that has been conducted to improve our understanding.

BASIC UNDERSTANDING

When a steel is exposed to hydrogen at high pressures (>2MPa) and temperatures (300 C-600 C), hydrogen diffuses into the steel and reacts with the carbides to form methane. Since methane has a low diffusivity in steel, it stays within the steel at internal discontinuities, such as pre-existing voids at interfaces and grain boundaries, forming methane bubbles. The nucleation of the methane bubbles is not yet understood. But Lopez and Shewmon (19) have reported TEM-replica observations of pre-existing voids in quenched and tempered steels. They have also shown that such voids get filled with methane during HA, thus
forming bubbles of methane. Once a bubble forms within a steel, the various mechanisms by which the bubble can grow have been identified. But the mechanism that controls the rate of bubble growth varies from one steel to another and from one set of HA conditions to another. Such variations in the controlling mechanisms of the bubble growth have not been well understood.

The various mechanistic steps required for bubble growth have been summarized by Sundararajan and Shewmon (10) in the form of a schematic line diagram, reproduced as Figure 1. The figure shows the sequence by which the mechanistic steps should take place for the bubble growth. Of the steps given in figure 1, some can be ruled out as too fast to be rate controlling. Both carbon and hydrogen are known to diffuse at very high rates above 300 C, and thus cannot control the rate of bubble growth. During the initial stages of HA, the total volume of bubbles and the volumetric growth rate of the bubbles, are so small that equilibrium methane pressures must be developed within the bubbles. Further recent experiments by Natan and Johnson (20) have shown that near equilibrium methane pressures exist in carbon steels for relatively long times after equilibrium is reached, and this period is within the normal operating times of the dilatometer
FIG 1: Sequence of mechanistic steps for bubble growth during hydrogen attack (Ref.10)
used to study HA kinetics. Thus methane formation can also be ruled out as too fast to be rate controlling during the incubation stage.

Once equilibrium methane pressures are known to exist within the bubbles, the bubble growth depends on the rate at which atoms can be moved away from the bubble surface. From the literature on creep cavity growth (11), it is known that atoms are removed from the bubble surface and ultimately deposited on the grain boundaries. This requires the diffusion of atoms along the bubble surface and then along the grain boundary. Thus both surface diffusion and grain boundary diffusion processes are necessary for the bubbles to grow. Since the two processes have to take place in series, the slower of the two will control the bubble growth rate. However the bubbles can also grow by directly expanding the matrix around it, by moving dislocations, i.e., by power law creep. Yacaman et al (21) have conducted transmission electron microscopic (TEM) studies to show that in a 1020 steel, a high density of dislocations form close to methane bubbles, confirming the role of power law creep in bubble growth. Since creep (power law) growth is a process independent of the diffusional growth processes, the faster of the two processes, as seen
from Figure 1, will control the overall bubble growth rate. Further, it is known that only a fraction of the grain boundaries are cavitated during HA, and hence the growth of bubbles may have to be accommodated by creep processes in the uncavitated grains. This process of accommodation can also be a rate limiting step, if it is slower than the bubble growth processes.

EXPERIMENTAL WORK

The objective of the dilatometric studies has been, and is, to establish the rate limiting step for the different steels of interest under various conditions of HA. Since bubble growth occurs by absorption of vacancies, and since the equilibrium vacancy concentration is always maintained elsewhere in the material, the bubble growth translates directly into external volume change of the steel. The swelling rate of the steel will thus be directly dependent on the rate limiting step for bubble growth. Since the swelling rates amount to very low strain rates (10^{-8} to 10^{-7} per hour) during the incubation stage of HA, a highly sensitive dilatometer is required to study the kinetics of HA. Such a dilatometer has been designed, built, and used successfully (6,7,8,9)
to study HA kinetics of carbon and low alloy steels. The capacitance dilatometer is now a well established tool to study the HA of steels.

Since the activity of carbon determines directly the equilibrium methane pressure that develops within the bubble, the addition of alloying elements that form stable carbides has been the principal technique of controlling HA. Of the several steels thus developed, 2 1/4 Cr-1 Mo steel is the leanest alloy with good HA resistance. Thus the properties of this steel have been very widely studied. However the only quantitative study of its HA resistance has been the dilatometric work of Yu (9). He studied a 2 1/4 Cr-1 Mo steel in the quenched and tempered condition, and another in the normalized and tempered condition. He found negligible or no expansion at 500 C and 20.3 MPa of hydrogen, but measurable strain rates ( > 10^-8 per hour ) at 550 C and 20.3 MPa of hydrogen. This is contradictory to previous studies (6,7,8) on plain carbon steels, in that the strain rates of carbon steels decreased continuously with temperature instead of a sudden drop to zero. Thus further studies are necessary to understand the mechanisms controlling HA of the 2 1/4 Cr-1 Mo steel.
Further, tempering a quenched 2 1/4 Cr-1 Mo steel to differing extents will mean different methane pressures and hence differing HA behavior. The effect of tempering of a quenched/normalized 2 1/4 Cr-1 Mo steel, on its microstructure has been studied by Baker and Nutting (22). According to their work, tempering a normalized 2 1/4 Cr-1 Mo steel at 700 C for 50 hours should remove all $M_3C$ carbides in the steel. Yu (23) has also found that a normalized 2 1/4 Cr-1 Mo steel loses $M_3C$ carbides rapidly on tempering. Such a loss of $M_3C$ carbides will significantly drop the carbon activity of the steel. Thus excessive tempering may be expected to result in the elimination of HA of this steel.

Or, the HA rate of 2 1/4 Cr-1 Mo steels may be limited by the creep strength of their matrix. If so, excessive tempering will cause carbide coarsening and depletion of solid solution hardening elements like Mo, and thus decrease the creep strength of the matrix, which in turn may result in enhanced HA rates. Therefore, there are counteracting effects of tempering on the HA behavior of 2 1/4 Cr-1 Mo steels. The study of such effects will be very interesting and useful. In order to separate out the effects of carbon activity and creep strength of the matrix, the determination of
the variation of carbon activity with tempering is necessary. Hence the effects of tempering a quenched 2 1/4 Cr-1 Mo steel on its HA behavior and on its carbon activity were studied in the present work.

A second major engineering operation that is known to affect the HA behavior of steels is welding. The deleterious effects of welding and cold work on the HA of carbon steels are well documented (24). However, there has been no quantitative study of the HA kinetics of welds of the industrially important 2 1/4 Cr-1 Mo steel. To determine the effects of welding, a dilatometric study comparing the base metal with the weld metal of a quenched and tempered 2 1/4 Cr-1 Mo steel weldment was conducted. The results of all the dilatometric work and carbon activity measurements are reported in this section of the dissertation.
EXPERIMENTAL STUDIES

The experimental studies conducted in the present work consisted of dilatometric work to follow HA kinetics, metallography to study the shape and distribution of bubbles, and carbon activity measurements to determine the effect of tempering on HA behavior.

DILATOMETRY

Equipment:

To study the kinetics of HA during the incubation stage, a highly sensitive dilatometer is required since the swelling rates, especially those of low alloy steels, are very low. For a 2 1/4 Cr-1 Mo steel in the commercial quenched and tempered condition (690 C; 10-20 hours), linear strain rates caused by swelling of the order of 10-8 to 10-7 per hour have to be measured (7,9). The best known technique for this purpose is the capacitance dilatometer.
A schematic sketch of the capacitance dilatometer used in this study is shown in Figure 2. The specimen to be studied was machined to a dumb-bell-shaped sample about an inch in length and 3/4 inch in diameter. It was then enclosed in a capacitance dilatometer cell. Within the dilatometer cell, as seen from Figure 2, a capacitance is formed between the top surface of the dumb-bell-shaped sample and a reference electrode. Both the sample and the reference electrode on top of the sample, were electrically insulated from the cage of the dilatometer cell by alumina insulators. The cage and the reference electrode were made of decarburized steel to prevent them from being attacked by hydrogen. The sample is fixed to the bottom of the cage, and the reference electrode to the top of the cage. Thus as the sample swells during HA, the gap between the two electrodes decreases, and an increase in capacitance results. By measuring the rate of increase in capacitance with time, the linear swelling rates of HA of the sample can be determined.

Since such a dilatometer is inherently sensitive, it was necessary to polish the top and bottom surfaces of the sample to a 600 grit finish, and maintain the variations in the length around the circumference of the sample to within +/- 0.0002". The specimen length
FIG 2: A schematic sketch of the capacitance dilatometer cell
was measured using a micrometer with a least count of 0.0001". The alumina insulator between the sample and the cage was also polished to a 600 grit finish with less than 0.0002" of variations in its thickness. Finally the top surface of the sample and the reference electrode surface were polished to 0.05 micron finish using alumina powder.

To control the conditions of HA of the sample, the entire assembly of the dilatometer cell with the mounted sample, was enclosed in a pressure vessel made of 316 stainless steel as shown in Figure 3. The pressure vessel (HIP Bolted Closure Reactor Cat. No. BC-1) had a port for pressurizing the vessel with hydrogen up to 27 MPa (4000 psi), using a pressure booster. Three high pressure seals were used in the top cover of the vessel. Two of the seals (CONAX EG-093-B) were used for electrical leads from the sample and reference electrode forming the capacitance. The third seal (CONAX TG-20-B-2-T) was used to carry thermocouple leads to measure the temperature of the sample. The pressure vessel assembly was then contained within a furnace built using 1000 C Lindberg electric heating units (Model 50311 Type 86-SP). Using a Barber-Colman temperature controller, the temperature of the sample could be maintained within +/- 0.5 C of the required setting.
FIG 3: A schematic sketch of the experimental apparatus
The capacitance across the sample and the reference electrode was measured using a capacitance bridge (General Radio: Type 1615-A) and an audio oscillator (General Radio: Type 1311-A). A strip chart recorder (Heath Schlumberger: Model SR-204) was used along with a lock-in amplifier (ORTEC Brookdeal - 9504) to record the variation of capacitance with time. The variation in capacitance during HA of a low alloy steel is typically of the order of 10^-4 pF/hr. This variation is so small that temperature fluctuations in the sample of +/- 0.5 C resulted in significant variations in the capacitance. The temperature effects are compensated to some extent by having the cage made out of the same material as the sample, i.e., by making the cage out of decarburized steel. In addition, all the capacitance values measured were corrected for temperature effects in the following manner. The change in capacitance per degree centigrade was measured, and noting the temperature of the sample (thermocouple in Fig. 3), the capacitance value was corrected to the set temperature. For this reason the chart recorder could not be used for strain rates less than about 10^-7 per hour. Instead the capacitance was measured at regular intervals of time and corrected for temperature effects as described above.
To convert the rates of capacitance increase with time to linear strain rates of the sample, the dilatometer had to be calibrated. The procedures of dilatometer calibration and data conversion are explained in Appendix I.

**Material:**

The material studied was a welded plate of a quenched and tempered 2 1/4 Cr-1 Mo steel (A542 C13), received from the Westinghouse Research Laboratories. The six inch thick steel plate was austenitized at 940 C (1724 F) for 3 hours, quenched, tempered at 680 C (1256 F) for 6 hours, and cooled in air. It was then welded using a multi-pass shielded metal arc welding (SMAW) technique, and given a post-weld heat treatment at 680 C (1256 F) for 15 hours followed by air cooling. This was the as-received condition of the 2 1/4 Cr-1 Mo steel weldment. The steel composition and the above-mentioned heat treatment and welding procedures are representative of practice about ten years ago. The compositions of the base metal and the weld metal were determined at Westinghouse Research Laboratories and are given in Table 1. The average hardness of the base metal was 230 VHN and that of the weld metal was 192 VHN. The hardness measurements were
made using a 1 Kg load. Portions of the base metal and the weld metal were cut from the weldment, as shown in Figure 4. Capacitance dilatometer samples of the dimensions given in Figure 4, were machined out of the cut portions of the base metal and the weld metal. The sample surfaces were polished to a 0.05 micron finish, as described earlier.

Results:

**Base Metal**: On initial heating of the base metal sample to 500°C, with hydrogen at a pressure of 20.3 MPa, the capacitance increased with time rapidly. But the rate of increase in capacitance dropped with time, as shown in Figure 5. The figure also shows a plot of the calculated linear strain rate versus time. The standard error of the slope of the capacitance-time plot was obtained using a standard computer program for linear regression (25).

On changing the temperature to 550°C, keeping the hydrogen pressure at 20.3 MPa, the capacitance-time plot showed an initial transient, but a steady-state was reached in nearly 50 hours. The sample was then studied at various settings of temperature and hydrogen pressure, and it was found that a steady state was reached at all the settings within a relatively short
TABLE 1: Chemical compositions of the base metal and the weld metal

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>BASE METAL</th>
<th>WELD METAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.13</td>
<td>0.055</td>
</tr>
<tr>
<td>Mn</td>
<td>0.51</td>
<td>0.69</td>
</tr>
<tr>
<td>P</td>
<td>0.006</td>
<td>0.01</td>
</tr>
<tr>
<td>S</td>
<td>0.008</td>
<td>0.012</td>
</tr>
<tr>
<td>Si</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>Cr</td>
<td>2.32</td>
<td>2.42</td>
</tr>
<tr>
<td>Mo</td>
<td>0.98</td>
<td>1.01</td>
</tr>
<tr>
<td>As</td>
<td>0.031</td>
<td>0.022</td>
</tr>
<tr>
<td>Sb</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Sn</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>Al</td>
<td>0.019</td>
<td>0.014</td>
</tr>
</tbody>
</table>
FIG 4: Preparation of dilatometric samples from the 2 1/4 Cr-1 Mo steel weldment
FIG 5: Plots of the dilatometric data of the base metal sample (A) Capacitance-Time (B) Strain rate-Time

$\frac{dc}{dt} = 0.16 \pm 0.22 \times 10^{-4}$ pF/hr
time. Figure 6 shows the plots of capacitance-time measurements for the various temperatures and hydrogen pressures studied with the base metal sample. The results of the measured and converted data are summarized in Table 2.

**Weld Metal**: The sample taken from the weld metal was studied in a similar manner. The strain rate at 500°C and 20.3 MPa of hydrogen was nearly an order of magnitude higher than that of the base metal. Hence measurements were made at lower temperatures of 480°C and 460°C. Appreciable strain rates were measured even at 460°C and 20.3 MPa of hydrogen. On increasing the temperature, the strain rate increased at a decreasing rate, and at 570°C, the strain rate was actually lower than that measured at 540°C. On decreasing the temperature back to 500°C, keeping the hydrogen pressure constant at 20.3 MPa, the strain rate was found to be almost the same as that obtained initially. Thus the strain rate measured at a temperature and hydrogen pressure was found to be fairly independent of the history, as was observed by previous investigators (6,7,8,9). The hydrogen pressure dependence measured for the weld metal at 500°C was greater than that measured for the base metal (at 580°C). Capacitance-time plots for all the
FIG 6: Capacitance-Time plots for the base metal sample (A) 823 K, 20.3 MPa (B) 838 K, 20.3 MPa

\[
\frac{dc}{dt} = 0.428 \pm 0.005 \times 10^{-4} \text{ pF/hr}
\]

\[
\frac{dc}{dt} = 1.153 \pm 0.049 \times 10^{-4} \text{ pF/hr}
\]
FIG 6 (Cont'd): (C) 853 K, 20.3 MPa  (D) 863 K, 20.3 MPa

\[
\frac{dc}{dt} = 2.24 \pm 0.067 \times 10^{-4} \text{pF/hr}
\]

\[
\frac{dc}{dt} = 4.26 \pm 0.07 \times 10^{-4} \text{pF/hr}
\]
FIG 6 (Cont'd):  (E) 853 K, 16.9 MPa  (F) 853 K, 13.5 MPa

\[
\frac{dc}{dt} = 1.46 \pm 0.08 \times 10^{-4} \text{ pF/hr}
\]

\[
\frac{dc}{dt} = 0.89 \pm 0.08 \times 10^{-4} \text{ pF/hr}
\]
FIG 6 (Cont'd):  (G) 853 K, 20.3 MPa  (H) 773K, 20.3 MPa

\[
\frac{dc}{dt} = 3.27 \pm 0.08 \times 10^{-4} \text{pF/hr}
\]

\[
\frac{dc}{dt} = 0.21 \pm 0.01 \times 10^{-4} \text{pF/hr}
\]
FIG 6 (Cont'd): (I) 823 K, 20.3 MPa

\[
\frac{dc}{dt} = 1.22 \pm 0.03 \times 10^{-4} \text{ pF/hr}
\]

(J) 838 K, 20.3 MPa

\[
\frac{dc}{dt} = 2.35 \pm 0.04 \times 10^{-4} \text{ pF/hr}
\]
<table>
<thead>
<tr>
<th>SEQUENCE</th>
<th>TEMPERATURE (K)</th>
<th>HYDROGEN PRESSURE (MPa)</th>
<th>( \frac{dc}{dt} \times 10^4 \text{ pF/h} )</th>
<th>( \varepsilon \times 10^8 \text{ h}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>773</td>
<td>20.3</td>
<td>0.16 ± 0.22</td>
<td>1.44 ± 1.94</td>
</tr>
<tr>
<td>2</td>
<td>823</td>
<td>20.3</td>
<td>0.43 ± 0.09</td>
<td>3.79 ± 0.75</td>
</tr>
<tr>
<td>3</td>
<td>838</td>
<td>20.3</td>
<td>1.15 ± 0.05</td>
<td>10.21 ± 0.43</td>
</tr>
<tr>
<td>4</td>
<td>853</td>
<td>20.3</td>
<td>2.24 ± 0.09</td>
<td>19.84 ± 0.77</td>
</tr>
<tr>
<td>5</td>
<td>863</td>
<td>20.3</td>
<td>4.26 ± 0.07</td>
<td>37.77 ± 0.59</td>
</tr>
<tr>
<td>6</td>
<td>853</td>
<td>16.9</td>
<td>1.46 ± 0.08</td>
<td>12.91 ± 0.73</td>
</tr>
<tr>
<td>7</td>
<td>853</td>
<td>13.5</td>
<td>0.89 ± 0.03</td>
<td>7.85 ± 0.70</td>
</tr>
<tr>
<td>8</td>
<td>853</td>
<td>20.3</td>
<td>3.27 ± 0.08</td>
<td>29.00 ± 0.68</td>
</tr>
<tr>
<td>9</td>
<td>773</td>
<td>20.3</td>
<td>0.21 ± 0.01</td>
<td>1.87 ± 0.07</td>
</tr>
<tr>
<td>10</td>
<td>823</td>
<td>20.3</td>
<td>1.22 ± 0.03</td>
<td>10.87 ± 0.24</td>
</tr>
<tr>
<td>11</td>
<td>838</td>
<td>20.3</td>
<td>2.35 ± 0.04</td>
<td>20.80 ± 0.36</td>
</tr>
</tbody>
</table>

**TABLE 2:** Hydrogen Attack strain rates of the base metal
temperatures and hydrogen pressures studied are given in Figure 7. The measured and the converted dilatometric data on the weld metal are summarized in Table 3.

Tempering Effects: Since tempering to different extents results in different carbide distributions (22), the effect of tempering on the HA behavior was studied as follows. Samples were machined from portions of the base metal, and then austenitized at 950°C for 5 hours to dissolve the carbides. The austenitizing treatment was given after enclosing all the samples in a single evacuated and sealed Vycor tube. The encapsulation was done by evacuating the Vycor tube with a mechanical forepump, backfilling with hydrogen (0.25 atm), and then sealing it. The enclosed samples were kept in a muffle furnace at 950°C for 5 hours, and then cooled in air at about 50°C per minute, to simulate industrial quenching rates of thick steel plates. The samples were then taken out of the tube, and re-encapsulated individually in the same manner. The enclosed samples were then tempered at different temperatures for different times, as summarized in Table 4.
FIG 7: Capacitance-Time plots for the weld metal sample (A) 773 K, 20.3 MPa (B) 753 K, 20.3 MPa

\[ \frac{dc}{dt} = 1 \pm 0.07 \times 10^{-4} \text{ pF/hr} \]

\[ \frac{dc}{dt} = 0.25 \pm 0.06 \times 10^{-4} \text{ pF/hr} \]
FIG 7 (Cont'd): (C) 733 K, 20.3 MPa  
\[
\frac{dc}{dt} = 0.44 \pm 0.09 \times 10^{-4} \text{ pF/hr}
\]

(D) 793 K, 20.3 MPa  
\[
\frac{dc}{dt} = 2.29 \pm 0.12 \times 10^{-4} \text{ pF/hr}
\]
FIG 7 (Cont'd): (E) 773 K, 16.9 MPa  \( \frac{dc}{dt} = 0.31 \pm 0.06 \times 10^{-4} \text{ pF/hr} \)  
(F) 773 K, 23.7 MPa  \( \frac{dc}{dt} = 1.322 \pm 0.31 \times 10^{-4} \text{ pF/hr} \)
FIG 7 (Cont'd): (G) 813 K, 20.3 MPa

\[ \frac{dc}{dt} = 3.07 \pm 0.35 \times 10^{-4} \text{ pF/hr} \]
FIG 7 (Cont'd):  (H) 843 K, 20.3 MPa  (I) 773 K, 20.3 MPa

\[
\frac{dc}{dt} = 1.17 \pm 0.08 \times 10^{-4} \text{ pF/hr}
\]

\[
\frac{dc}{dt} = 1.0 \pm 0.12 \times 10^{-4} \text{ pF/hr}
\]
TABLE 3: Hydrogen Attack strain rates of the weld metal

<table>
<thead>
<tr>
<th>SEQUENCE</th>
<th>TEMPERATURE K</th>
<th>HYDROGEN PRESSURE MPa</th>
<th>$\frac{dc}{d\varepsilon} \times 10^4$ pF/h</th>
<th>$\dot{\epsilon} \times 10^8$ h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>773</td>
<td>20.3</td>
<td>1.00 ± 0.07</td>
<td>1.56 ± 0.11</td>
</tr>
<tr>
<td>2</td>
<td>753</td>
<td>20.3</td>
<td>0.25 ± 0.06</td>
<td>0.59 ± 0.09</td>
</tr>
<tr>
<td>3</td>
<td>733</td>
<td>20.3</td>
<td>0.44 ± 0.09</td>
<td>0.69 ± 0.15</td>
</tr>
<tr>
<td>4</td>
<td>793</td>
<td>20.3</td>
<td>2.29 ± 0.12</td>
<td>3.57 ± 0.18</td>
</tr>
<tr>
<td>5</td>
<td>773</td>
<td>16.9</td>
<td>0.31 ± 0.06</td>
<td>0.48 ± 0.09</td>
</tr>
<tr>
<td>6</td>
<td>773</td>
<td>23.7</td>
<td>1.32 ± 0.31</td>
<td>2.06 ± 0.48</td>
</tr>
<tr>
<td>7</td>
<td>813</td>
<td>20.3</td>
<td>3.07 ± 0.35</td>
<td>4.79 ± 0.54</td>
</tr>
<tr>
<td>8</td>
<td>843</td>
<td>20.3</td>
<td>1.34 ± 0.08</td>
<td>2.09 ± 0.13</td>
</tr>
<tr>
<td>9</td>
<td>773</td>
<td>20.3</td>
<td>1.00 ± 0.12</td>
<td>1.56 ± 0.18</td>
</tr>
</tbody>
</table>
TABLE 4: Heat Treatments of samples used for the study of tempering effects on HA behavior and carbon activity

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>TEMPERATURE (C)</th>
<th>TIME (HRS)</th>
<th>VHN</th>
</tr>
</thead>
<tbody>
<tr>
<td>XQ</td>
<td>--</td>
<td>--</td>
<td>410</td>
</tr>
<tr>
<td>XT1</td>
<td>600</td>
<td>5</td>
<td>325</td>
</tr>
<tr>
<td>XT2</td>
<td>650</td>
<td>1.5</td>
<td>268</td>
</tr>
<tr>
<td>XT3</td>
<td>700</td>
<td>50</td>
<td>218</td>
</tr>
<tr>
<td>XT4</td>
<td>700</td>
<td>500</td>
<td>154</td>
</tr>
<tr>
<td>BM\textsuperscript{a}</td>
<td>680</td>
<td>21</td>
<td>230</td>
</tr>
</tbody>
</table>

\textsuperscript{a} - BM is the base metal of the 2 1/4 Cr-1Mo steel weldment
FIG 8: Carbide distribution map of Baker and Nutting(22), with the positions of the samples marked on it
The temperatures and times of tempering were chosen such that the tempered structures would contain different carbide distributions ranging from $M_{3C}$ carbides to $M_{23C_6}$ carbides, as would be expected from the work of Baker and Nutting (22). The carbide distribution map developed by Baker and Nutting is reproduced as Figure 8. The conditions of the samples of the present study are marked on the map, depending on the temperature and time of tempering of each of the samples. It is seen that the resulting structures of the samples can be expected to vary widely. Table 4 also gives the as-tempered hardness of the various samples. As can be expected, the hardness decreases monotonically with tempering. There is a marked decrease in hardness on tempering at 700°C for 500 hours. Taking hardness as a measure of the matrix creep strength of the tempered structure, the excessively tempered structure would be expected to result in enhanced HA rates, if HA of this structure is controlled by matrix creep.

To study and compare the HA behavior of the tempered structures, a test temperature had to be chosen such that it was not high enough to significantly change the tempered structure during the test, but not low enough to affect the accuracy of measurement of the strain.
FIG 9: Capacitance-Time plots for the sample XT1 at 823 K
(A) 20.3 MPa  (B) 16.9 MPa  (C) 13.5 MPa

\[ \frac{dc}{dt} = 4.74 \pm 0.16 \times 10^{-4} \text{pF/hr} \]

\[ \frac{dc}{dt} = 2.93 \pm 0.32 \times 10^{-4} \text{pF/hr} \]

\[ \frac{dc}{dt} = 1.93 \pm 0.17 \times 10^{-4} \text{pF/hr} \]
FIG 10: Capacitance plots for the sample XT2 at 823 K
(A) 20.3 MPa  (B) 16.9 MPa  (C) 10.2 MPa
FIG 11: Capacitance-Time plots for the sample XT3
(A) 20.3 MPa  (B) 23.7 MPa  (C) 16.9 MPa
FIG 12: Capacitance-Time plots for the sample XT4
(A) 20.3 MPa  (B) 23.7 MPa  (C) 16.9 MPa
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>HYDROGEN PRESSURE MPa</th>
<th>$\frac{dc}{dt} \times 10^4$ pF/h</th>
<th>$\dot{\varepsilon} \times 10^8$ h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>XT1</td>
<td>20.3</td>
<td>4.74 ± 0.16</td>
<td>43.7 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
<td>2.93 ± 0.32</td>
<td>27.0 ± 2.9</td>
</tr>
<tr>
<td></td>
<td>13.5</td>
<td>1.93 ± 0.17</td>
<td>17.8 ± 1.5</td>
</tr>
<tr>
<td>XT2</td>
<td>20.3</td>
<td>2.16 ± 0.09</td>
<td>20.1 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
<td>1.55 ± 0.09</td>
<td>14.4 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>0.90 ± 0.09</td>
<td>8.4 ± 0.9</td>
</tr>
<tr>
<td>XT3</td>
<td>20.3</td>
<td>0.63 ± 0.05</td>
<td>5.8 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>23.7</td>
<td>0.97 ± 0.06</td>
<td>9.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
<td>0.43 ± 0.04</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>XT4</td>
<td>20.3</td>
<td>0.54 ± 0.15</td>
<td>5.0 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>23.7</td>
<td>0.65 ± 0.07</td>
<td>6.0 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
<td>0.41 ± 0.01</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>XQ</td>
<td>20.3</td>
<td>33.6</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
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<td>333</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>21.8</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>5.1</td>
<td>11.5</td>
<td>107</td>
</tr>
</tbody>
</table>
rates. A temperature of 550 °C was chosen for the above reasons. This temperature also falls in the range of industrial interest of HA of 2 1/4 Cr-1 Mo steels. The samples were studied at different hydrogen pressures. Plots of the measured capacitances versus time for the samples XT1, XT2, XT3 and XT4 are shown in Figures 9 through 12. In addition to these four samples, a sample was tested in the as-quenched structure. Strain rates over 10^-6 per hour were measured for this sample, and hence the chart recorder was used. The results of the experiments are summarized in Table 5.

METALLOGRAPHY

In order to study the shape and distribution of methane bubbles formed during hydrogen attack, scanning electron microscopy was used. The bubbles formed during short time hydrogen attack were too small to be resolved under the SEM. However, using a TEM replica technique, Lopez (26) has shown that the change in the density of bubbles as HA proceeds, is negligible in 2 1/4 Cr-1 Mo steels. Hence the bubble distribution after a long time hydrogen attack exposure will be the same as the short time distribution. Long term exposures were made at 550 °C and 20.3 MPa of hydrogen
for about 2250 hours. The samples were then mechanically polished, etched with 5% Nital, and observed under a JEOL 35 scanning electron microscope.

The bubbles in the base metal and the weld metal were both nearly spherical in shape. The bubbles in the base metal were preferentially located at the grain boundaries. But the bubbles in the weld metal were found to exhibit no preference for the grain boundaries, and were found both within the grains and at the grain boundaries. Figure 13 shows SEM micrographs of the regions found in the base metal, and Figure 14 shows the bubble shape and distribution in the weld metal after hydrogen attack. The black spots seen in the Figures 13 and 14 are believed to be bubbles, since EDAX analysis of the spots showed no difference in composition from that in the matrix. It is clear from the pictures that no preference for the grain boundaries exists in the weld metal, while almost all the bubbles in the base metal are at grain boundaries. The half-bubble spacing at the grain boundaries for the base metal is seen to be about 5 microns. The half-bubble spacing of the bubbles distributed through the bulk of the weld metal is also about 5 microns. These values correspond to bubble densities of $10^{-3}$ per square micron for the weld metal,
FIG 13: Microphotographs of two different regions from the weld metal after long-term hydrogen attack
FIG 14: Microphotographs of regions from the base metal after long-term hydrogen attack
and 2x10^{-3} per square micron for the base metal. Thus a higher density of bubbles was found in the weld metal compared to the base metal.

Transmission electron microscopy using a two-stage replica technique was conducted on the base metal and the weld metal by Lopez (27), to determine the average bubble radius and the density of bubbles. He studied the samples after hydrogen attack at 550 C and 20.3 MPa of hydrogen for 880 hours. He determined the average bubble radii to be 0.049 microns and 0.076 microns, for the base metal and the weld metal respectively. The bubble densities were found to be about 6x10^{-3} and 7x10^{-3} per square micron, for the base metal and the weld metal respectively.

CARBON ACTIVITY MEASUREMENTS

The carbon activity of 2 1/4 Cr-1 Mo steel was measured by Natesan et al (14) at 550 C using an equilibration technique. But they did not measure the variation of the carbon activity with the extent of tempering. From the work of Baker and Nutting (22), it is known that the carbide distribution in a quenched and tempered 2 1/4 Cr-1 Mo steel varies with the extent of tempering and hence the carbon activity should also be clearly affected by tempering.
The technique used to measure the carbon activity was similar to that used by Natesan et al (14,28). It involved equilibration of a pure nickel foil with the 2 1/4 Cr-1 Mo steel, in an evacuated and sealed Vycor tube, at the temperature of interest (550 C). The carbon content of the equilibrated nickel foil was then measured, and knowing the graphite solubility in nickel at that temperature (550 C), the carbon activity with respect to the graphite standard state was calculated as follows. Applying Henry's law to the solubility of graphite in nickel, the carbon activity with respect to graphite is given by:

\[
\text{CARBON ACTIVITY} = \frac{\text{CARBON CONTENT}}{\text{CARBON SOLUBILITY}} \quad \ldots (1)
\]

All the measurements were made at 550 C, since the objective was to correlate the carbon activity data with the HA strain rate measurements.

The specimens studied were the HA dilatometry samples XT1, XT2, XT3, XT4 and the base metal of the 2 1/4 Cr-1 Mo steel weldment in the as-received condition. Each of the samples weighed about 25 grams, while the nickel foil weighed one gram. Thus carbon starvation was eliminated. The nickel foil was prepared by rolling a rod of commercial purity (Ni-200) nickel in a cold rolling mill, using several passes without
intermediate annealing. The foil was reduced to a final thickness of about 100 microns. It was then decarburized at a temperature of 950 °C, by annealing in flowing hydrogen bubbled through water. After 10 hours of decarburization, the carbon content of the nickel foil was reduced to less than 0.0008 Wt% C.

The equilibration time was calculated as follows. Berry (29) has summarized the diffusivity data of carbon in nickel, and only two investigations have been conducted below 600 °C. From the work of Massaro and Petersen (30) and Diamond and Wert (31), an average value for the carbon diffusivity in nickel at 550 °C is found to be about 5x10^-11 cm^2/sec. The relaxation time $\tau$ for diffusion out of a slab of thickness $h$ is given by (32),

$$\tau = \frac{h^2}{\pi^2 D} \quad \ldots \quad (2)$$

Using this expression, the relaxation time, for diffusion of carbon out of a 100 micron thick nickel foil is found to be about 56 hours. For 99% equilibration ($6\tau$) 14 days of annealing is required. To be on the safe side, 16 days at 550 °C was used for equilibration.

The evacuation and sealing was done using a mechanical forepump. During evacuation, the Vycor tube
was kept heated using a hand torch while evacuating. The heating removed the moisture absorbed in the Vycor tube. Using hydrogen instead of vacuum resulted in a dull surface finish on the nickel foil, and the carbon contents were inconsistent. If the Vycor tube was not heated while evacuating, once again inconsistent results were obtained. This is understandable, since Grabke (33) has shown that moisture has a significant effect on the carbon activity of methane-hydrogen gas mixtures, and a similar effect is expected in a CO/CO2 gas mixture, which is the carbon transfer medium in the equilibration procedure used in the present work.

The procedure finally found suitable was, to evacuate and seal the Vycor tube, while the tube is kept heated by a hand torch. During annealing, the specimen and the foil were kept next to each other (lying side by side), and the Vycor tube was kept in a muffle furnace controlled at 550 °C ± 1 °C for sixteen days, and then cooled in air.

The carbon content of the nickel foils were measured at Armco Research Laboratories, using a Leco Carbon Analyzer. The carbon contents were averaged over 2 to 3 measurements and reported correct to ± 0.0008 Wt%. The carbon activity with respect to the graphite
standard state was calculated by applying Henry's law to Hansen's data (35) for the graphite solubility in nickel at 550 C. Dyson (34) has fitted an equation to the solubility data of Hansen, and the carbon atom fraction solubility, Nc is given by:

\[
N_c = 0.5 \exp \left( \frac{-39600 \text{ J/mol}}{RT} \right) \]  \[\cdots (3)\]

where R is the gas constant in Joules per mole K. From Equation 3, the graphite solubility in nickel at 550 C is obtained as 0.031 Wt%. As a check, nickel foils were equilibrated with a pure iron-carbon alloy, and carbon contents of 0.029 to 0.032 Wt% were obtained. However, significant iron transfer was observed during these anneals for reasons given elsewhere (63). The variation in carbon content is attributed to this effect, but the average carbon content agrees well with the value obtained from Equation 4. Using this value the carbon activities were calculated. The measured carbon contents and the calculated carbon activity values for the five samples studied are given in Table 6. The standard errors in the carbon content and carbon activity values given in the table correspond to the standard error in the measurement of the carbon content. The results compare very well with the carbon activity values reported by Natesan et al (14). They measured the variation of carbon activity with the
TABLE 6: Measured carbon contents of the nickel foils equilibrated with the different 2 1/4 Cr-1 Mo steel samples and the calculated carbon activity values with respect to graphite standard state

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Wt. % C (+ 0.0008)</th>
<th>CARBON ACTIVITY (+ 0.026)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XT1</td>
<td>0.0108</td>
<td>0.348</td>
</tr>
<tr>
<td>XT2</td>
<td>0.0072</td>
<td>0.232</td>
</tr>
<tr>
<td>XT3</td>
<td>0.0022</td>
<td>0.071</td>
</tr>
<tr>
<td>XT4</td>
<td>0.0020</td>
<td>0.065</td>
</tr>
<tr>
<td>BM</td>
<td>0.0038</td>
<td>0.123</td>
</tr>
</tbody>
</table>
carbon content of a commercially quenched and tempered 2 1/4 Cr-1 Mo steel, and found that it varied linearly with the carbon content of the steel. They report a value of 0.1 for a 0.1 Wt% C steel, and it decreases to 0.05 for a 0.05 Wt% C steel. The base metal of the present work had a carbon content of 0.13 Wt% and the measured carbon activity is 0.123 +/- 0.026. Thus within experimental error, the results agree well with previous results.
ANALYSIS OF EXPERIMENTAL RESULTS AND DISCUSSION

The kinetics of HA of a steel is usually studied by measuring the strain rates at different temperatures, at a constant hydrogen pressure (6,7,8,9). The strain rates thus obtained are plotted on a semi-logarithmic graph as ln(ε-1/T), to obtain an 'apparent' activation energy. This 'apparent' activation energy, Q, is made up of the activation energies of two processes, the methane formation reaction and the rate limiting step of the bubble growth. That part of Q caused by the variation in the equilibrium methane pressure is positive, and that caused by the bubble growth is negative. Thus the 'apparent' activation energy is always less than the true activation energy of the rate limiting step of the bubble growth. Hence the true activation energy of the rate limiting step is obtained from a knowledge of the variation of the equilibrium constant of the methane formation reaction with temperature.

An additional means of identifying the rate limiting step is by studying the effect of hydrogen pressure on
the swelling rate of the steel at a constant temperature. The slope of the \( \ln \varepsilon - \ln P_{H_2} \) plot gives once again an 'apparent' pressure exponent for the following reasons. Methane is not an ideal gas and it deviates markedly from ideality beyond pressures of 80 MPa. In the range of interest of HA, the fugacity of methane has to be converted to partial pressure using a suitable equation of state. Thus the methane pressure does not increase as the square of the hydrogen partial pressure and the non-ideality of methane results in an 'apparent' pressure dependence. With a knowledge of the equation of state, the methane pressure dependence can be calculated from the hydrogen pressure dependence.

From the activation energy and the methane pressure dependence, the rate limiting mechanistic step can be identified, knowing the activation energies for the bulk, grain boundary and surface self diffusion of iron, and the stress dependence for each of the possible controlling mechanisms.

The dilatometric results are fit to an equation of the type,

\[
\varepsilon = A P_{H_2}^n \exp\left(-\frac{Q}{RT}\right) \quad \ldots \quad (4)
\]
where $A$ is a constant, $Q$ is the 'apparent' activation energy, $n$ is the hydrogen pressure dependence, and $P_{H_2}$ is the hydrogen partial pressure. Using such an equation, a safe temperature-hydrogen pressure (Nelson) curve can be drawn, by setting a total strain of about $10^{-3}$ as the mark of the end of the incubation time (6), and choosing a safe operating time such as 20,000 hours.

Analysis of the dilatometric results of the present work was done in a slightly different manner, and the controlling mechanisms were identified for the weld metal and base metal of the 2 1/4 Cr-1 Mo steel weldment. The effect of tempering on the controlling mechanism was also analyzed.

BASE METAL AND WELD METAL

A plot of the results obtained for the base metal and the weld metal, at different temperatures and a constant hydrogen pressure of 20.3 MPa, is shown in Figure 15. It is seen that while the data of the base metal would fall along a straight line, those of the weld metal do not. Thus an apparent activation energy could not be obtained for the weld metal.
FIG 15: Arrhenius plot for a constant hydrogen pressure of 20.3 MPa for the base metal and the weld metal
To examine this problem, a slightly different approach was used. Clearly, an Arrhenius plot for a constant methane pressure would directly give the activation energy of the controlling mechanism. Since experimental data were obtained at a constant hydrogen pressure, the data had to be converted, or normalized, to a constant methane pressure. This required the knowledge of the methane pressure dependence of the strain rates. The methane pressure dependence can be obtained using the hydrogen pressure dependence, but this requires the conversion of hydrogen pressures to methane pressures.

The conversion of hydrogen pressure to methane pressure involves two steps. Since methane is not an ideal gas, the thermodynamics of the methane formation reaction determines only the fugacity of methane, whereas it is the methane pressure that drives the bubble growth. Thus the methane fugacity is calculated first and then converted to methane pressure using a suitable equation of state.

The thermodynamics of methane formation from various carbides in steels have been worked out by Geiger and Angeles (36). They have reported values for the temperature dependent constant, K(T) in the expression:

$$f_{CH_4} = K(T) P_{H_2}^2$$ ... (5)
FIG 16: $K(T)$ for various carbides in 2 1/4 Cr-1 Mo steel at different temperatures (Ref. 36)
where \( f_{CH_4} \) is the equilibrium methane fugacity, and \( P_{H_2} \) is the hydrogen partial pressure. Plots of the variation of \( K(T) \) with temperature for the cases of \( Fe_3C \), tempered \( M_3C \) in a quenched and tempered 2 1/4 Cr-1 Mo steel, \( Cr_23C_6 \) and \( Cr_7C_3 \) carbides are shown in Figure 16. The \( K(T) \) values given are for a standard state of 1 MPa for the gases. It can be seen that methane pressures in equilibrium with \( Cr_23C_6 \) and \( Cr_7C_3 \) carbides are too low to cause the strain rates observed in the present work. Hence the values of \( K(T) \) given by Geiger and Angeles for \( M_3C \) carbides in a commercial quenched and tempered 2 1/4 Cr-1 Mo steel were used for the analysis of the data of the base metal and the weld metal.

An Arrhenius fit of the \( K(T) \) values given by Geiger and Angeles results in the following expression:

\[
\frac{r_{\text{u}}}{D} = \frac{n_u}{n_i} A U k \exp \left( \frac{100800 \text{ J/mol}}{RT} \right) P_{H_2}^2 \quad \ldots (6)
\]

Both \( P_{H_2} \) and \( f_{CH_4} \) are expressed in MPa in Equation 6. Using this expression, the fugacity of methane was calculated for the various pressures of hydrogen and temperatures studied experimentally.

To convert the methane fugacity to methane pressure, an equation of state for methane is required. Odette and Vagarali (37) have analyzed the equation of state
of methane and arrived at an expression relating the fugacity of methane, \( f_{\text{CH}_4} \), to its partial pressure, \( P_{\text{CH}_4} \), through a temperature dependent constant, \( C(T) \) as given below.

\[
f_{\text{CH}_4} = P_{\text{CH}_4} \exp \left( C(T) P_{\text{CH}_4} \right)
\]

where,

\[
C(T) = \frac{1.19}{T} + 3.09 \times 10^{-3} \quad \text{for} \quad 10^3 < f_{\text{CH}_4} < 10^4 \text{MPa}
\]

\[
= 0.005 \quad \text{for} \quad 10^3 < f_{\text{CH}_4}
\]

A plot of methane partial pressure versus hydrogen partial pressure for different temperatures obtained using Equations 6 and 7, is shown in Figure 17.

Knowing the methane pressures for the hydrogen pressures studied experimentally, the variation of the strain rate with methane pressure can be determined. However, the driving force for the bubble growth must work against a sintering force due to surface tension. The sintering force is given by \( 2\gamma/r_b \), where \( \gamma \) is the surface tension, and \( r_b \) is the bubble radius. A value of 1 J/m\(^2\) was used for \( \gamma \). This is half that reported for pure iron (62), thus accounting for probable reductions in \( \gamma \) caused by segregation effects. The average radius of the bubbles was determined by Lopez (27), by a TEM replica technique. The base metal after hydrogen attack at 550 C and 20.3 MPa of hydrogen
FIG 17: Methane pressures in equilibrium with M₃C carbide in a commercially quenched and tempered 2 1/4 Cr-1 Mo steel (690 C.20 hrs)
for 880 hours, had an average bubble radius of 0.05 microns. The weld metal after HA had an average bubble radius of 0.076 microns.

From the values of \( \ln \dot{\varepsilon} \) and the calculated \( \ln \left( \frac{P_{CH_4}}{2 \gamma/r_b} \right) \), the stress exponents were calculated using a standard computer program (25) for linear regression. Stress exponents of 1.76 +/- 0.4 (standard error) for the base metal and 6.6 +/- 1.5 for the weld metal were obtained.

From these values of stress exponents, all the data were normalized to a constant driving force at different temperatures. A value of 400 MPa was arbitrarily chosen for the driving force, but it should be noted that the choice of the driving force does not affect the slope of the Arrhenius plot. The Arrhenius plots of the normalized data for the base metal and the weld metal are shown in Figures 18 and 19. It is seen from the figures that the normalized data fall reasonably well along a straight line, for both the base metal and the weld metal. From the slopes, activation energies of 256 +/- 4.5 KJ/mole and 313 +/- 36 KJ/mole were obtained, where the +/- numbers correspond to the standard error of the linear regression fit. The data are then described by the following equations.

\[
\dot{\varepsilon} = 9 \times 10^4 \left( \frac{P_{CH_4}}{2 \gamma/r_b} \right)^{1.76} \exp\left(\frac{-256 \text{KJ/mol}}{RT}\right)
\]  

.. (8)
FIG 18: Arrhenius plot at a constant driving force of 400 MPa for the base metal

\[ Q = 256 \pm 5 \text{ kJ/mole} \]
FIG 19: Arrhenius plot at a constant driving force of 400 MPa for the weld metal.
\[ \varepsilon = 4.6 \times 10^{-4} (P_{CH_4} - 2\gamma/r_b)^{6.6} \exp(-\frac{313 KJ/mol}{RT}) \]  \hspace{1cm} (9)

From these equations, Nelson Curves were drawn as follows. For a lifetime of 20,000 hours and a critical strain for failure of 10^{-3}, a strain rate of 5 \times 10^{-8} per hour will define the safe limit for hydrogen attack. Using the Equations 8 and 9, the corresponding methane pressure at each temperature for a strain rate of 5 \times 10^{-8} per hour, was determined. The methane pressure values were then converted to hydrogen pressures using Equations 6 and 7. The hydrogen pressure-temperature settings for safe operation were thus obtained to plot the Nelson Curves shown in Figure 20. Figure 20 also shows the Nelson Curve calculated using the dilatometric results of Lopez (26) on a weld representative of modern steel making and welding techniques. The two curves together indicate the scatter in the HA behavior of welds of different practices.

From the metallographic observations, and the calculated activation energies and stress dependences, the mechanisms controlling bubble growth in the base metal and in the weld metal, can be arrived at as follows. The bulk diffusion coefficient of \(\alpha\)-iron below its Curie temperature, has been measured by Hettitch et al (38). From their data, the activation
FIG 20: Nelson Curves for the base metal and weld metal compared with the API curve.
energy for bulk self-diffusion is calculated to be 320 KJ/mole. The stress dependence of power law creep strain rate of α-iron has been empirically determined to be 6.9 by Mukherjee et al (39) for stresses of 2 to 10 MPa in the temperature range of 605 C-753 C. The activation energy and stress dependence for hydrogen attack of the weld metal are 313 KJ/mole and 6.6. Comparing these with the activation energy for bulk diffusion and the stress dependence for power law creep, it is clear that the weld metal swells by power law creep of the matrix surrounding the bubbles. This conclusion is also supported by the fact that the bubbles in the weld metal were found to be distributed throughout the bulk, with no preference for the grain boundaries. The bubbles were also found to be spherical in shape.

The controlling mechanism for bubble growth in the base metal is not obvious. The bubbles were found to be nearly spherical in shape and hence surface diffusion controlled growth could be ruled out. The activation energy for grain boundary self-diffusion of α-iron below its Curie temperature, was recalculated by Panda (8) using the bulk diffusivity data of Hettitch et al (38), and it was found to be 207 KJ/mole. The stress dependence for the diffusional growth limited by
grain boundary diffusion is unity. The activation energy for hydrogen attack is 256 KJ/mole and the stress dependence is 1.76. Thus the values are between those of grain boundary diffusional growth and power law creep growth. The bubbles most probably grow by grain boundary diffusion assisted or inhibited somewhat by power law creep of the matrix, but the exact mechanism is not clear. As will be seen presently, the analysis of the results of experimental studies on the effects of tempering, provide more information on the mechanism(s) of bubble growth in 2 1/4 Cr-1 Mo quenched and tempered steels.

TEMPERING EFFECTS

All the data generated to study the effect of tempering on the hydrogen attack kinetics were at 550 C, for the reasons mentioned earlier. To quantify the extent of tempering, a tempering parameter was used and is as defined below.

\[
\text{TEMPERING PARAMETER} = T(20+\log t) \ldots (10)
\]

where \( T \) is the temperature in Kelvin and \( t \) is the time in hours. Plots of strain rate versus the tempering parameter for 16.9 MPa and 20.3 MPa of hydrogen are shown in Figure 21. The variation of carbon activity
with tempering is also plotted on the same graph for comparison. Figure 21 suggests that the carbon activity accounts for most of the effect of tempering, since both the HA strain rate and the carbon activity decrease monotonically with tempering.

A more quantitative analysis was done to examine other possible effects caused by tempering. The analysis was similar to that performed for the base metal and the weld metal. The methane pressure was calculated using the Equations 6 and 7, except that an additional factor was used to account for the variation in carbon activity. The carbon activity factor was simply the ratio of the carbon activity of the particular sample with respect to that of the base metal. The base metal was taken to obey Equation 6 (given by Geiger and Angeles) for a commercial quenched and tempered 2 1/4 Cr-1 Mo steel. For each hydrogen pressure and temperature used, the corresponding equilibrium methane pressure was calculated. The data of the base metal were also included in the tempering experiments since its tempering parameter was known. Taking the average bubble radius to be the same as that of the base metal, viz., 0.05 microns, the driving force, \((P_{CH_4} - 2\gamma/r_b)\) was calculated for each temperature-hydrogen pressure
FIG 21: Variation of carbon activity and HA strain rate with the tempering parameter
setting of each sample. The calculated driving force values were plotted against the corresponding linear strain rates measured, on a ln-ln scale. The data of all the samples were plotted on a single graph and are shown in Figure 22. It can be seen that all the normalized data, except for one data point, fall along a single curve. The curve has a slope of unity at low driving forces, and increases to >4 at higher driving forces.

Figure 22 demonstrates that the samples tempered to different extents behave in a manner consistent with each other, and that their strain rates differ only due to the differences in the driving force, which in turn is caused by the variations in the carbon activity. It is also inferred that the bubble growth is predominantly diffusion controlled for driving forces less than about 300 MPa at 550 °C, since the slope of the $\ln \varepsilon - \ln \left( P_{CH_4} - 2\gamma / r_b \right)$ plot is unity. A driving force of 300 MPa at 550 °C corresponds to a hydrogen pressure of about 20 MPa on a commercially quenched and tempered steel. For less tempered steels, the slope is greater than unity, indicating possible power law creep growth of bubbles even for 16 MPa of hydrogen.
FIG 22: HA strain rates of different tempered structures plotted against the driving force.
Excessive tempering beyond the commercial practice does not eliminate hydrogen attack, although slightly higher hydrogen pressures could be tolerated due to a lowering of the carbon activity. However, there is a negligible difference in the carbon activity between a steel tempered for 50 hours at 700 °C and one tempered for 500 hours at 700 °C. This suggests that sufficient M_3C carbides exist to control the carbon activity, in a quenched 2 1/4 Cr-1 Mo steel even after tempering for 500 hours at 700 °C. Further, since the bubbles in an excessively tempered steel grow by diffusion controlled growth, the loss of creep strength of the matrix caused by excessive tempering does not affect the HA behavior, for hydrogen pressures less than about 20 MPa at 550 °C.
CONCLUSIONS

1) The base metal of the quenched and tempered 2 1/4 Cr-1 Mo steel weldment, exhibited an activation energy for bubble growth of $256 +/- 5$ KJ/mole and a stress exponent of $1.76 +/- 0.4$. The bubbles were nearly spherical in shape and formed preferentially at the grain boundaries.

2) The weld metal exhibited an activation energy of $313 +/- 36$ KJ/mole and a stress exponent of $6.6 +/- 1.5$. The bubbles were spherical in shape, and distributed homogeneously throughout the material with no preference for the grain boundaries. The bubble growth was limited by power law creep of the matrix.

3) The base metal hydrogen attack strain rate was expressed by the equation:

$$\varepsilon = 9 \times 10^4 (P_{CH_4} - 2\gamma/r_b)^{1.76} \exp\left(-\frac{256 \text{KJ/mol}}{RT}\right)$$
and the weld metal hydrogen attack strain rates followed the equation:

\[ \dot{\varepsilon} = 4.6 \times 10^{-4} (P_{CH_4} - 2\gamma/r_b)^{6.6} \exp \left( \frac{-313 \text{kJ/mol}}{RT} \right) \]

Nelson Curves for both the base metal and the weld metal were drawn using the above expressions. The safe operating temperature limit of the weld metal was about 100°C lower than that of the base metal.

4) The effect of tempering was to decrease both the hydrogen attack strain rate and the carbon activity monotonically. Excessive tempering (500 hours at 700°C) did not decrease the carbon activity (graphite standard state) below 0.05. Presumably, sufficient M_3C carbides remain to control the carbon activity, even after tempering at 700°C for 500 hours.

5) A plot of ln \(\dot{\varepsilon} - \ln (P_{CH_4} - 2\gamma/r_b)\), of all the samples studied for tempering effects, showed that all the samples tempered to different extents, behaved in a manner consistent with each other. The differences in the hydrogen attack strain rates between the samples, are largely due to the differences in the carbon activity, which give rise to differing methane pressures for the same hydrogen pressure. However, for
the samples tempered to an extent less than the commercial practice, the bubble growth was enhanced caused by power law creep effects.

6) The bubbles in steels tempered to extents greater than the commercial practice grow under diffusion control for hydrogen pressures less than about 20 MPa at 550 C.
SECTION II

MECHANISMS OF HYDROGEN ATTACK
LIMITATIONS OF EXISTING MODELS

The dilatometric studies on the kinetics of hydrogen attack (HA) have resulted in the development of models for the growth of internally pressurized methane bubbles in steels. This is due to the fact that the dilatometric studies provide the best means of evaluating models of hydrogen attack. As will be seen later, since the growth of internally pressurized bubbles is quite similar to external stress driven growth of creep cavities, the dilatometric studies also provide us with an excellent means of checking models for creep cavitation. The advantage of HA study over the conventional creep experiment is that all the measured strain rate is entirely due to bubble growth, in HA experiments.

The dilatometric results of Mcimpson (6) on carbon steel were used by Sundararajan ad Shewmon (10) to present a comprehensive model for the HA of steels. To calculate the bubble growth rate by grain boundary and surface diffusion processes, they used the equations derived by Chuang et al (11) for the growth
of creep cavities under an externally applied stress. The treatment given here improves upon (or differs from) their treatment in three important respects.

First, the applicability of the creep equations (11) directly to HA is not obvious; And they did not justify the use of the equations derived for external stress driven cavity growth, to model the growth of internally pressurized bubbles. Secondly, for the surface diffusion controlled growth of bubbles, they used the expression for the crack extension rate to predict the external swelling rate, tacitly assuming that the bubble width did not change with time. It will be shown in the present analysis, that if the change in bubble width is taken into account, the methane pressure dependence of the external swelling rate will be 2 instead of 3 as predicted by previous investigators (8,10) for surface diffusion controlled growth; And for 'mixed grain boundary diffusion-surface diffusion' controlled growth, the methane pressure dependence is predicted to be unity instead of 1.5. Hence their model would predict erroneous methane pressure dependences for the experimentally measured HA strain rates. Finally, for their model predictions to agree
with the experimentally measured HA strain rates, the bubble spacing (a model parameter) had to be changed as the hydrogen pressure-temperature conditions were changed. This would mean that repeated cycling of the conditions, would give consistent strain rates as was observed by McKimpson, only if the bubble density increased and/or decreased as the conditions were changed.

Odette and Vagarali (40) proposed a carbide inhibited diffusional growth model to explain McKimpson's dilatometric data. They suggested that atom plating on the grain boundaries was inhibited by the grain boundary carbides, as was suggested by Harris (41) for creep cavity growth. But recent work by Dyson et al (42) has shown that grain boundary carbides do not prevent atom plating. Hasegawa and Nomura (59) studied the effect of cementite distribution on HA of low carbon steels, and found that the susceptibility of the steel to HA was higher when the carbides were precipitated continuously along the grain boundary than when they were homogeneously dispersed in the matrix. This observation is clearly in contrast with the carbide inhibition model. Further, the extension of the carbide inhibition model to explain the results of Yu (9) on 2 1/4 Cr - 1 Mo steel was not
satisfactory (15), and Odette et al (15) proposed an accommodation creep controlled growth model to explain the results.

Since many of the grain boundaries have no bubbles on them, it is important to know the degree to which the bubble free boundaries inhibit the diffusional growth of bubbles on other boundaries. Dyson (43) has analyzed the effect of volume fraction of grains cavitated on the extent of constraint due to the 'cage' of uncavitated grains. From his work, a volume fraction of grains cavitated of unity amounts to negligible constraint. It is shown in the present work that for a fraction of grain boundaries cavitated of 0.15, which Odette and Vagarali used in their model, the volume fraction of grains cavitated is unity. An accommodation controlled growth model is thus not applicable to cases where the fraction of grain boundaries cavitated is 0.15 or higher.

In the present work, the growth of internally pressurized bubbles is analyzed, following the treatment by Chuang et al (11) of externally applied stress assisted growth of creep cavities. Equations are rederived for the growth rate of bubbles under equilibrium and non-equilibrium conditions. The
rederivation of the equations results in expressions for the steady-state stress distribution between growing bubbles. These expressions are used to explain bubble nucleation during hydrogen attack of carbon steels.

The resulting model was found to explain all the dilatometric data generated for both carbon and low alloy steels. The model predictions are used to construct mechanistic regime maps, which give the controlling mechanism at various temperatures and hydrogen pressures. Nelson Curves for both carbon and low alloy steels are also constructed using the model.
GROWTH OF INTERNALLY PRESSURIZED BUBBLES

DIFFUSIVE GROWTH

Spherical Equilibrium Shape

The hydrostatic stress field around an internally pressurized spherical bubble is zero everywhere \((44)\). Thus the vacancy chemical potential in the matrix surrounding the bubble, is unaffected by the mechanical stresses generated by the methane pressure in the bubble. But if a vacancy is transferred from the matrix to the bubble surface, the bubble expands by one atomic volume, and in doing this work, it decreases the free energy of the system. Thus the vacancy chemical potential at the bubble surface is less than that in the matrix, by an amount given by the Helmholtz free energy change per vacancy added to the bubble. If \(P_{\text{CH}_4}\) is the equilibrium methane pressure in the bubble, \(\gamma\) the surface free energy, and \(r_b\) the bubble radius, then the excess (over the stress free state) vacancy
chemical potential at the bubble surface is given by the equation.

\[ \Delta \mu |_{r=r_b} = \left( \frac{\partial F}{\partial n} \right)_{T,V} \]

\[ = - (P_{CH_4} - 2\gamma/r_b)\Omega \quad \ldots \quad (11) \]

where \( r \) is the radial distance from the bubble center, \( \Omega \) is the atomic volume (roughly the same as vacancy volume), and \( \left( \frac{\partial F}{\partial n} \right)_{T,V} \) is the Helmholtz free energy change per vacancy added at constant temperature and volume. Thus the initial distribution of excess vacancy chemical potential around the bubble is a step function, with a value of \(- (P_{CH_4} - 2\gamma/r_b)\Omega \) at the bubble surface and zero everywhere else.

The steep gradient at the bubble surface will be soon smoothed out by diffusion of vacancies from the matrix to the bubble surface. If the matrix is free of vacancy sources, then the bubble growth is limited by the amount of vacancies initially present in the matrix. The bubble would practically stop growing after a short transient growth period.

On the other hand, if the bubble is at a grain boundary, then the grain boundary acts as a source of vacancies, as is known to happen in diffusional creep. In this case, the vacancies are emitted by the grain
boundary edge dislocations as fast as they are consumed by, or transported to, the bubble surface. Thus the bubble growth is limited by diffusion of vacancies along the grain boundary. The diffusion of vacancies along the boundary is governed by the differential equation,

\[ J = -\frac{\Db}{\Omega kT} \nabla (\Delta \mu) \quad \ldots \quad (12) \]

where \( J \) is the vacancy flux per unit area per second, \( \Db \) is the grain boundary self-diffusion coefficient, \( k \) is Boltzmann's constant, and \( T \) is the temperature. Following the treatment by Raj and Ashby (45), a steady-state would be reached when the rate of vacancy emission is uniform throughout the grain boundary between the bubbles. If \( \beta \) is the vacancy emission rate per unit volume of the grain boundary, then the steady-state distribution of the excess vacancy chemical potential, along the grain boundary around the bubble, should obey the equation,

\[ \nabla J = \beta \quad \ldots \quad (13) \]

OR \[ \nabla^2 (\Delta \mu) = -\frac{\beta kT \Omega}{\Db} \quad \ldots \quad (14) \]

Following the treatment by Shewmon (4), consider a uniform array of bubbles along the grain boundaries, with a half bubble spacing of \( \lambda \). The symmetry of such an array results in the boundary condition,

\[ \frac{\partial (\Delta \mu)}{\partial r} \bigg|_{r=\lambda} = 0 \quad \ldots \quad (15) \]
The excess vacancy chemical potential at the bubble surface is always maintained at $-(P_{CH_4} - 2\gamma/r_b)\Omega$ and this results in another boundary condition given by,

$$\Delta \mu \bigg|_{r=r_b} = -(P_{CH_4} - 2\gamma/r_b)\Omega \quad \ldots \quad (16)$$

The solution to the differential Equation 14, subject to the boundary conditions 15 and 16, is

$$\Delta \mu(r) = \frac{\beta kT\Omega}{4DB} (r^2 - r_b^2) - \frac{\beta kT\Omega}{2DB} \chi^2 \ln \frac{r_b}{r} - (P_{CH_4} - 2\gamma/r_b)\Omega \quad \ldots \quad (17)$$

Equation 17 describes the variation of the excess vacancy chemical potential with radial distance from the bubble center, along the grain boundary at steady-state. The only unknown in the equation is $\beta$, the vacancy emission rate. To evaluate the vacancy emission rate, a third boundary condition is required. In the case of creep cavity growth, the third boundary condition is obtained by equating the integral of the steady-state normal stress over the boundary regions around the bubbles, to the total external force applied on the grain boundary regions around the bubbles, i.e., external stress $\sigma_m$ over an area $\pi \lambda^2$. In the case of internally pressurized bubbles, there is no stress applied directly on the grain boundary regions around
the bubbles. The only mechanical force on the grain boundary that can cause vacancy emission from the boundary, is the normal (to the grain boundary) force due to the methane pressure less the sintering force, acting over an area of $\pi r_b^2$. This mechanical force of $(P_{CH_4} - 2\gamma/r_b)x\pi r_b^2$ is negligible compared to an externally applied force of $c_\infty x\pi \lambda^2$, simply because $r_b$ is usually ten times smaller than $\lambda$. Hence it seems that merely replacing the external stress by $P_{CH_4}$ will grossly overestimate the bubble growth rate. Thus modelling the growth of internally pressurized bubbles, by replacing the 'externally applied stress' in creep equations by the methane pressure, will be erroneous.

For the case of internally pressurized bubble growth, the third boundary condition is obtained as follows. The grain boundary edge dislocations can climb under an osmotic force, thus tending to smooth out the excess vacancy chemical potential distribution that is to be maintained for steady-state growth. Hence it is necessary to develop and maintain a normal stress field $p(r)$, along the grain boundary such that the stress field obeys the equation,

$$p(r) = \Delta \mu(r) / \Omega$$

... (18)
Since the equilibrium vacancy chemical potential at a dislocation under a normal stress $\sigma$, is $\sigma \Omega$ (44), the stress distribution given by Equation 18 will maintain the excess vacancy chemical potential distribution given by Equation 17. Physically, the steady-state stress field is achieved by the redistribution of grain boundary dislocations as they climb during the transient period, resulting in a pile-up stress field along the grain boundary. Alternatively, the stress field can be thought of as the back stress arising from the wedge of atoms driven into the boundary by the bubble, as described by Shewmon (4).

Thus by thermodynamically maintaining an excess vacancy chemical potential of $-(P_{\text{CH}_4} - 2\gamma/r_b)\Omega$ at the bubble surface, the internally pressurized bubbles force a stress distribution to develop along the grain boundary between them by merely redistributing the grain boundary edge dislocations. This results in a steady-state growth of bubbles, by vacancy emission from the grain boundaries. Since the stress distribution was achieved by merely redistributing or generating the grain boundary edge dislocations, the integral of the stress distribution caused by the thermodynamic forces must be zero. This thermodynamic driving force is assisted by the normal
stress\left(P_{CH_4} - 2Y/r_b\right)\pi r_b^2\right) acting on the grain boundary due to the mechanical stress generated by the bubble. Hence, the integral of the steady-state distribution between the bubbles must satisfy the condition,

\[ \int_{r_b}^{\lambda} p(r)2\pi rdr = (P_{CH_4} - 2Y/r_b)\pi r_b^2 \quad \cdots (19) \]

It should be noted here that an internally pressurized bubble can grow under thermodynamic forces, even if there is no assistance from the mechanical stresses. However, it is not possible to develop the thermodynamic force without generating mechanical stresses simultaneously. When an externally applied stress, \(\sigma_\infty\) (normal to the grain boundary) is also present, Equation 19 becomes,

\[ \int_{r_b}^{\lambda} p(r)2\pi rdr = (P_{CH_4} - 2Y/r_b)\pi r_b^2 + \sigma_\infty \pi \lambda^2 \quad \cdots (20) \]

Combining Equations 18 and 20,

\[ \int_{r_b}^{\lambda} \Delta \nu(r)2\pi rdr = (P_{CH_4} - 2Y/r_b)\Omega \]

\[ + \sigma_\infty \pi \lambda^2 \quad \cdots (21) \]

Equation 21 is the third boundary condition that determines the value of \(\beta\), the vacancy emission rate. Using the Equation 17 for \(\Delta \nu(r)\) in Equation 21, the following expression is obtained for \(\beta\).

\[ \beta = \frac{-2DD}{kT} \frac{\sigma_\infty + P_{CH_4} - 2Y/r_b}{\lambda^2(3/4 + \ln(\Gamma_\infty \lambda)/\Gamma_b/\lambda^2(1-\Gamma_b/4\lambda^2))} \quad \cdots (22) \]
This result is interesting, since it shows that the effect of $P_{CH_4}$ generated within a small bubble, is exactly the same as the effect of an external stress applied over the entire boundary.

In order to compare the model predictions with the dilatometric data, it is necessary to determine the volumetric growth rate of the bubbles. This can be done as follows. The vacancy emission rate, $\delta_b$, is related to the rate of thickening at the grain boundary, $\delta_b\Omega$, by the equation,

$$\frac{\partial \delta}{\partial t} = \delta_b \Omega \quad \ldots \quad (23)$$

where $\delta_b$ is the thickness of the grain boundary. As pointed out by Beere and Speight (46) for creep cavity growth, the grains on either side of the grain boundary are jacked up by the deposition of atoms (or emission of vacancies) at the grain boundary, at the same rate as the rate of thickening at the grain boundary given by Equation 23. Thus the volumetric growth rate of the bubble, $\frac{dV}{dt}$, is given by the rate of thickening at the grain boundary times the area per bubble, $\pi \lambda^2$. Thus the volumetric growth rate of the bubble, $\frac{dV}{dt}$, is given by,

$$\frac{dV}{dt}_{\text{bubble}} = \delta_b \Omega (\pi \lambda^2) \quad \ldots \quad (24)$$

Equation 24 is compared with the equation used by Sundararajan et al (10) in Figure 23, in terms of the
radial growth rate of the bubble, \( \frac{dr_b}{dt} \). It is seen from the figure that the creep equation used by Sundararajan et al (10), approximates the above equation for low values of \( \frac{rb}{\lambda} \), but at higher values, there is a marked deviation.

Using the Equations 17 and 18, an expression is obtained for the steady-state stress field between the bubbles, and is given by:

\[
p(r) = -\frac{8kT}{4\pi \rho_b} (r^2 - r_b^2) - \frac{8kT}{2\rho_b} \left( \lambda^2 \ln \frac{r_b}{\lambda} \right)
- (p_{CH_4} - 2\gamma/r_b) \quad \text{... (25)}
\]

where \( \beta \), the vacancy emission rate is to be evaluated from equation 22.

**Non-Equilibrium Crack-Like**

Consider the case where surface diffusion is much slower than grain boundary diffusion, resulting in a crack-like bubble. Following the analysis for creep cavity growth by Chuang et al (11), the quasi-steady-state distribution of the excess vacancy chemical potential, and the grain boundary thickening rate, can be rederived as follows.

Following the arguments given for equilibrium shaped (spherical) bubbles, the excess chemical
FIG 23: Effect of jacking on the grain boundary diffusional growth rate of the bubble
potential of vacancies along the surface of a crack-like bubble is given by:

$$\Delta \mu(s) = -\{P_{CH_4} - \gamma_s (K_1 + K_2)\} \Omega$$ \hspace{1cm} (26)

where $K_1$ and $K_2$ are the principal curvatures, $P_{CH_4}$ is the equilibrium methane pressure in the bubble, $\gamma_s$ is the surface free energy of the crack surfaces, and $\Omega$ is the atomic volume. Note that by taking $K_1$ and $K_2$ to be $1/r_b$, Equation 26 becomes the same as Equation 11.

If $v$ is the rate of extension of the crack-like bubble ($\frac{dr_b}{dt}$), then the curvature and the surface flux rate at the crack tip, are given by Chuang and Rice (47) as:

$$K_{tip} = 2 \sin \left(\frac{\psi}{2}\right) \left(\frac{v}{B}\right)^{1/3}$$ \hspace{1cm} (27)

$$(J_s)_{tip} = -2 \sin \left(\frac{\psi}{2}\right) \left(\frac{B}{\Omega}\right) \left(\frac{v}{B}\right)^{2/3}$$ \hspace{1cm} (28)

where $\gamma_b$ is the grain boundary surface free energy, $D_s$ is the surface diffusion coefficient, $\gamma_s$ is the surface diffusion layer thickness, $k$ is the Boltzmann's constant, $T$ is the temperature, $J_s$ the surface flux of vacancies per unit length ($\gamma_s$ surface flux of atoms per unit length), and $B$ and $\psi$ are defined by the equations:

$$B = \frac{(D_s \delta_s \gamma_s) / kT}{2 \sin \left(\frac{\psi}{2}\right)}$$ \hspace{1cm} (29)

$$2 \sin \left(\frac{\psi}{2}\right) = \left(\frac{2\gamma_s - \gamma_b}{\gamma_s}\right)^{1/2} / \left(\gamma_s^{1/2}\right)$$ \hspace{1cm} (30)
Combining Equations 26 and 27, the excess vacancy chemical potential at the crack-tip is given by:

$$\Delta \mu |_{r=r_b} = -t^{PCH_4} - 2\gamma_s \sin(\psi/2) (v/B)^{1/3} \Omega \ldots \ldots (31)$$

Also since the flux of vacancies along the two crack surfaces at the crack tip must equal the grain boundary flux at the tip,

$$(J_s)_{\text{tip}} = 2(J_s)_{\text{tip}}$$

$$= -4\sin(\psi/2) (B/\Omega) (v/B)^{2/3} \ldots \ldots (32)$$

Now, the grain boundary flux is also given by:

$$(J_b)_{\text{tip}} = -\frac{Db\delta b}{\Omega KT} \left( \frac{\partial \Delta \mu (r)}{\partial \tau} \right) |_{r=r_b} \ldots \ldots (33)$$

where $J_b$ is the grain boundary flux per unit length, and the other parameters are as defined earlier.

Combining Equations 32 and 33, an expression is obtained for the excess vacancy chemical potential gradient at the crack-tip along the grain boundary as:

$$\frac{\partial \Delta \mu (r)}{\partial \tau} |_{r=r_b} = 4\gamma_s \Omega \sin(\psi/2) \left( \frac{Db\delta s}{DB\delta b} \right) (v/B)^{2/3} \ldots \ldots (34)$$

Consider a regular array of bubbles on the grain boundary, as in the case of equilibrium shaped bubbles. By symmetry the gradient of the excess vacancy chemical potential is zero at a distance $\lambda$ form the bubble center, where $\lambda$ is the half bubble spacing. Hence,
The Equations 31, 34 and 35 define the boundary conditions for the distribution of the excess vacancy chemical potential along the grain boundary between the bubbles. The differential equation to be solved using these boundary conditions is dictated by the conservation of mass. The differential equation is obtained by relating the grain boundary thickening rate to the divergence of flux at the grain boundary, as follows.

\[
\frac{\partial}{\partial t} (r J_b) = \frac{\partial \delta}{\partial t} \quad \ldots \quad (36)
\]

where \( \frac{\partial \delta}{\partial t} \) is the grain boundary thickening rate.

Combining Equations 33 and 36,

\[
\frac{Db\delta b}{kT} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Delta \mu(r)}{\partial r} \right) + \frac{\partial \delta}{\partial t} = 0 \quad \ldots \quad (37)
\]

The solution to the Equation 37, subject to the boundary conditions 31, 34 and 35 is

\[
\Delta \mu(r) = \left. \Delta \mu \right|_{r=r_b} + \left( r_b \left( \frac{\partial \Delta \mu(r)}{\partial r} \right) \right|_{r=r_b} / (1 - r_b^2/\lambda^2))
\]

\[
x \left( \ln(r_b/\lambda) - (r^2 - r_b^2)/2\lambda^2 \right) \quad \ldots \quad (38)
\]

Equation 38 gives the quasi-steady-state distribution of the excess vacancy chemical potential along the grain boundary. Differentiating Equation 38 and combining with Equation 37, the following expression is obtained for the grain boundary thickening rate.

\[
\frac{\partial \delta}{\partial t} = 2 \left( \frac{Db\delta b}{kT} \left( \frac{\partial \Delta \mu(r)}{\partial r} \right) \right|_{r=r_b} \left( \frac{r_b}{\lambda^2 \cdot r_b^2} \right) \quad \ldots \quad (39)
\]
All the parameters in Equations 38 and 39 are known or are model parameters, except for \( v \), the crack extension rate. The crack extension rate defines the gradient of the excess vacancy chemical potential at the bubble surface, as given by Equation 34. To determine and solve for the excess vacancy chemical potential distribution, another boundary condition is necessary. This is obtained in the same manner as was done in the case of the equilibrium shaped bubble growth. By the same arguments, the lowering of the excess vacancy chemical potential at the bubble surface, forces a steady-state stress distribution along the grain boundary around the bubbles, such that the following condition is satisfied.

\[
p(r) \approx \Delta \mu(r) / \Omega \quad \ldots \quad (40)
\]

The integral of the stress distribution over the entire grain boundary must be zero, since this stress distribution develops by a mere redistribution of grain boundary edge dislocations. However, as in the case of the spherical bubbles, the bubble growth is assisted by the normal stress developed due to the mechanical stresses generated by the methane pressure in the bubble, less the sintering force due to the surface tension of the bubble surfaces. For a crack-like bubble, the surfaces are relatively flat for most part.
of the bubble. As seen from Equation 26 the sintering force due to a flat surface ($K = K = 0$) is zero. So the sintering force will be largely due to the curvature at the crack tip. Approximating the bubble geometry to be one with a uniform curvature at the crack tip, with principal radii of curvature of $r_b$ and $r_t$, the sintering force is given by $((1/r_b)+(1/r_t))^2 r_b r_t$, neglecting $r_t$ compared to $r_b$. Thus the integral of the quasi-steady-state distribution of the stress along the grain boundary between the bubbles, must be as given by the equation:

$$\int_{r_b}^{\lambda} \frac{\lambda}{2 \pi r_b^2} PCH_4 - 2\pi r_b r_t \{((1/r_b) + (1/r_t)) \} \cdots (41)$$

Combining Equations 40 and 41, including a term for any external stresses present, and neglecting $r_t$ compared to $r_b$, we obtain:

$$\int_{r_b}^{\lambda} \frac{3 \Delta \mu(r)}{2 \pi r_b^2} \frac{2 \pi r_b r_t}{r_b}$$

Using the Equations 31, 34, 38 and 42, an expression is obtained for the crack extension rate, $v$, as:

$$v = B \frac{1-d^2}{4Qr_b A} \{1+Q \Delta \Sigma \}^{1/2} - 1 \}^3 \cdots (43)$$

where

$$Q = 1 \ln(1/d) - (3-d^2)(1-d^2)/4$$

$$d = r_b/\lambda$$

$$\Delta = (D_s \delta s)/(D_b \delta b)$$

$$B = (D_s \delta s \gamma_s) / kT$$

$$\Sigma = \frac{4r_b \sigma_\infty + PCH_4 - 2\psi/r_b}{\gamma_s \sin(\psi/2)(1-d^2)^3}$$
Combining Equations 34 and 39, the grain boundary thickening rate is given by:

\[
\frac{\partial \delta}{\partial t} = \frac{2Db\delta_b}{Kt} \left( \frac{r_b}{\lambda^2 - r_b^2} \right) \left( 4\gamma S \sin(\psi/2) \left( \frac{D_s \delta_s}{Db \delta_b} \right) (v/B)^{2/3} \right)
\]

\[
\frac{\partial \delta}{\partial t} = \frac{2Db\delta_b}{Kt} \left( \frac{r_b}{\lambda^2 - r_b^2} \right) \left( 4\gamma S \sin(\psi/2) \left( \frac{D_s \delta_s}{Db \delta_b} \right) (v/B)^{2/3} \right) \quad \ldots \quad (44)
\]

where \( v \) is evaluated from Equation 43. This grain boundary thickening rate is what determines the externally measured swelling rates during HA, and not the crack extension rate. Thus the methane pressure dependence of the experimentally measured HA strain rate, will be as dictated by Equation 44. Previous investigators (8,10) used the equation for the crack extension rate, \( v \), to predict the methane pressure dependence of the HA strain rate, and thus their models will predict erroneous dilatometric results.

To predict the methane pressure dependences, two limiting cases can be considered. In the equation 43 for \( v \), if \( QAE \gg 1 \), then

\[
((1 + QAE^{1/2} - 1)^3 = QAE^{3/2} \quad \ldots \quad (45)
\]

Since \( \Sigma \) varies linearly with methane pressure, the crack extension rate will vary as \( P_{CH_4}^{3/2} \). Since the grain boundary thickening rate varies as \( v^{2/3} \) (Equation 44), we have:

\[
\frac{\partial \delta}{\partial t} = (P_{CH_4} - 2\gamma/r_b) \quad \ldots \quad (46)
\]
Thus for the limiting case where $Q \Delta \Sigma \ll 1$, the HA strain rate is predicted to vary linearly with $P_{CH_4}$. The limiting case of $Q \Delta \Sigma \gg 1$ corresponds to grain boundary diffusion controlled growth, since a large $\Delta$ implies that surface diffusion is much faster than grain boundary diffusion. Since the growth rate is still proportional to $\Delta$, as pointed out by Sundararajan and shewmon (10) this can be considered to be a 'mixed grain boundary diffusion-surface diffusion' controlled growth regime. Thus for the 'mixed grain boundary diffusion-surface diffusion' controlled regime, the methane pressure dependence is predicted to be unity. This is different from the $P_{CH_4}^{3/2}$ dependence used by previous investigators (8,10).

On the other hand, if $Q \Delta \Sigma \ll 1$, then surface diffusion is much slower than grain boundary diffusion and the bubbles will grow under surface diffusion control. For the other limiting case where $Q \Delta \Sigma \ll 1$, we have:

$$ (1 + Q \Delta \Sigma)^{1/2} \approx 1 + \frac{Q \Delta \Sigma}{2} \quad \ldots \quad (47) $$

So $v$ varies as $P_{CH_4}^{3}$ and the grain boundary thickening rate varies as:

$$ \frac{\partial \delta}{\partial t} \sim \left( P_{CH_4} - 2 \gamma / r_b \right)^2 \quad \ldots \quad (48) $$

for the case of surface diffusion limited growth and crack-like bubbles. Once again the pressure dependence
is different from the $P_{CH_4}^3$ dependence used by others, for this limiting case.

The critical methane pressure required for the transition from grain boundary diffusion controlled growth to the surface diffusion controlled growth, is obtained using the criterion given by Chuang et al (11):

$$\frac{r_b^3 (v/B)}{B} > 10 \quad \ldots \quad (49)$$

Using Equation 20 for $(v/B)$, we get:

$$P_{CH_4} + c_\infty - 2\gamma/r_b > \frac{12.9 Q \Delta \Sigma \gamma_s \sin(\psi/2)}{r_b (1-d^2)} \quad \ldots \quad (50)$$

Equation 50 gives the criterion for the change in the mechanism of bubble growth from grain boundary diffusion to surface diffusion.

Finally, the quasi-steady-state stress field between the bubbles is obtained by combining the Equations 31, 34, 38 and 43, as:

$$p(r) = -(P_{CH_4} - 2\gamma \sin(\psi/2)(v/B)^{1/3}) + \frac{r_b}{1 - r_b/(\lambda^2)} \left( \frac{4\gamma_s \sin(\psi/2)}{1 - \frac{r_b}{\lambda^2}} \right)$$

$$\frac{\partial s}{\partial r} (v/B)^{2/3} \times \left( \ln \left( \frac{r}{r_b} \right) - \frac{r_b^2 - r^2}{2\lambda^2} \right) \quad \ldots \quad (51)$$

where $v$ is evaluated from Equation 43.
POWER LAW CREEP

Finnie and Heller (48) have treated the case of steady-state power-law creep of an internally pressurized thick walled sphere. They derived an equation for the volumetric strain rate of the sphere, which is

\[
\frac{1}{V} \frac{dV}{dt} = \frac{3}{2} B \sigma^n \left[ \frac{(3/2n)(R/r)^{3/n}}{(R/r_0)^{3/n} - 1} \right]^{n/2} \quad \ldots \quad (52)
\]

where, \( \frac{1}{V} \frac{dV}{dt} \) is the volumetric strain rate at a radial distance, \( r \) from the center of the sphere, \( R \) is the external radius of the sphere, \( r_0 \) is the internal radius of the sphere, \( \sigma \) is the internal pressure driving creep, \( B \) and \( n \) are creep parameters in the constitutive equation, \( \dot{\varepsilon} = B \sigma^n \).

For the case of hydrogen attack, where the bubbles are preferentially located at the grain boundaries, the local interaction between the creeping bubbles can be modeled as follows. The regions close to the grain boundary, within a distance of half-bubble distance \( \lambda \), can be considered to creep under the methane pressure, while the rest of the grain remains rigid, as shown in Figure 24. Thus spheres of internal radius \( r_b \), and external radius \( \lambda \), can be considered to lie along the grain boundary, creeping under the internal methane pressures, resulting in a volume expansion of the
adjoining grains. The volumetric expansion rate of the material due to one such bubble will be the same as the volumetric expansion rate of a creeping sphere of internal radius $r_b$, external radius $\lambda$, and internal pressure ($P_{CH_4} - 2\gamma/r_b$). Using Equation 52, the volumetric growth rate of each bubble is obtained as:

$$\left(\frac{dV}{dt}\right)_{\text{bubble}} = \left(\frac{4}{3}\pi \lambda^3\right) \frac{3B}{2} \left(P_{CH_4} - 2\gamma/r_b\right)^n$$

$$\times \left\{ \frac{(3/2n)}{(\lambda/r_b)^{3/n}} \right\}^n \ldots \text{(53)}$$

**ACCOMMODATION CONTROLLED GROWTH**

Dyson (43) first analyzed the possibility of accommodation controlled growth of creep cavities under externally applied stress. Since experimentally, only some of the grains are found to be cavitated, he argued that the uncavitated grains would have to creep to accommodate the growth of cavitated grains, and that this creep resistance would lower the growth rate of the cavities. To model this effect, he defined a parameter called 'volume fraction of grains cavitated' as the number of grains in a given volume of the material, each with one of their grain boundaries cavitated, divided by the total number of grains, in a
FIG 24: Interactive growth of bubbles by power law creep
given volume of the material. Using this parameter, he showed that the strain rate could be one tenth that of accommodation free strain rate, for a fraction of grains cavitated of 0.1. When the fraction of grains cavitated is raised to unity, the cavities grow free of accommodation effects.

In hydrogen attack modeling, a parameter called 'fraction of grain boundaries cavitated' is used (10,15), instead of Dyson's parameter. Values from 0.1 to 0.3 have been used (10,15), but 0.15 is a typical value for the fraction of grain boundaries cavitated during hydrogen attack. If we assume that each grain has 14 sides, then the total number of grain boundaries per unit volume is \( \frac{7}{D^3} \), where D is the grain size and 7 is the number of sides that 'belong' to each grain since each side is shared by two grains. For a fraction of grain boundaries cavitated of 0.15, we have \( \frac{0.15 \times 7}{D^3} \) grain boundaries cavitated per unit volume. Thus we have roughly one grain boundary cavitated per grain. This means that each of the grains has two of its 14 sides cavitated. From the analysis of Dyson, this represents a case where there is little restraint from the cage of grains. Hence, in the present analysis, accommodation effects will be neglected.
Nucleation of the methane bubbles during hydrogen attack is not understood yet. Lopez and Shewmon (19) have reported the observations, under TEM, of pre-existing microvoids in a quenched and tempered 2 1/4 Cr-1 Mo steel, and concluded that such voids act as nucleation sites for methane bubbles. This is consistent with Lopez's observation that the bubble density, as measured under TEM (26), remains constant during hydrogen attack of 2 1/4 Cr-1 Mo steel.

However, recent TEM and dilatometric work by Wang (49) on carbon steels, has shown that a very low density (much lower than that in Q&T 2 1/4 Cr-1 Mo steel) of bubbles pre-exist in a normalised carbon steel, and that the bubble density increases (by one to two orders of magnitude) with time, as HA proceeds, even at relatively low methane pressures (400°C-500°C; 2-3MPa). The bubble density however, reaches a saturation value after a particular length of time. Bubbles nucleate preferentially on carbides and/or inclusions, and adjacent to previously
existing bubbles, rather than in a bubble free region. Previous work by Pishko et al. (51) has shown that bubbles nucleate profusely on a cavitated boundary, while the other boundaries remain uncavitated.

These observations on plain carbon steels suggest that regions next to existing bubbles, rather than regions free of bubbles, are favored for further nucleation during hydrogen attack. This cascade nucleation effect has been recognized by Hirth (51), who proposed a possible mechanism based on distribution of vacancy chemical potential near a nucleating and growing void. A somewhat different mechanism is proposed here, to explain the nucleation cascade phenomenon.

Equations have been derived for the stress assisted nucleation of cavities during creep, and the theoretical models for such nucleation result in a reciprocal time (for cavity nucleation) that is of the form (52):

$$\dot{\rho} = \rho_0 \exp\left(-\frac{1}{\sigma_n^2}\right) \ldots \quad (54)$$

where $\sigma_n$ is the stress that assists cavitation. In hydrogen attack, the driving force for nucleation is provided by the thermodynamic free energy of formation of methane per unit volume, $AG_v$. This driving force
exists uniformly throughout the material, if carbon and hydrogen diffuse relatively fast. Nucleation sites such as carbides are also fairly uniformly distributed along the grain boundaries. Hence the presence of a growing bubble should alter the conditions for nucleation nearby, causing the inhomogeneous nucleation of bubbles observed experimentally. Such a change in nucleation rates can be explained as follows.

In the preceding chapter, an equation was derived for the steady-state stress distribution \( p(r) \), between bubbles growing under grain boundary diffusion control. A plot of the Equation 25 is shown in Figure 25. It is seen from the figure that a negative (compressive) stress exists close to the bubble, while a positive (tensile) stress is maintained at the center between two growing bubbles. Since the probability of nucleation, as seen from Equation 54, is a strong function of the stress, the positive stress greatly enhances the nucleation probability of a fresh bubble between any two existing bubbles.

The Equation 25 describes the stress distribution after the steady-state is reached. But even during the transient period over which this stress distribution develops, a similar stress distribution will exist.
FIG 25: The steady-state stress distribution between two bubbles growing by grain boundary diffusion.
Developing equations to describe the transient period is complicated by the fact that the radial distance at which the vacancy chemical potential gradient is zero, changes with time. However the transient period can be qualitatively described as follows. During the transient period, the atom deposition at the grain boundary is non-uniform. The deposition rate is maximum at the bubble surface, and decreases with distance away from the bubble. As described by Shewmon (4), this amounts to inserting a wedge of atoms into the grain boundary from the bubble surface. The wedge results in a compressive stress along the grain boundary over which the atoms have been plated, and a tensile stress ahead of the tip of the wedge, where atom plating has not started yet. As the transient period proceeds, the tip of the wedge moves towards the center between two growing bubbles. Thus during the transient period, a tensile stress forms between any two growing bubbles. But the probability of nucleation at a nucleation site decreases as the time during which a tensile stress exists at the site, decreases; And during the transient period the region over which the tensile stress exists, moves with time towards the center between the bubbles. Thus although tensile stresses are developed during the transient period,
they exist only for a relatively short time over a given nucleation site on the boundary. Hence the probability of nucleation during the transient period is lower than during steady-state.

To determine whether the bubbles nucleate during the transient period or during steady-state growth, it is necessary to make a rough estimate of the order of time required to reach steady-state. This can be approximated by using the formula for the relaxation time for diffusion out of a slab (32), which is:

\[ \text{Relaxation Time} = \frac{4\lambda^2}{\pi^2 DD} \] ... (55)

For a half-bubble spacing of 10 microns, the relaxation time is 160 hours at 450°C and 20 hours at 500°C. From the dilatometric work of Wang, it is found that nucleation starts after an incubation time of 50 to 100 hours. Thus to a first approximation, it can be concluded that bubbles nucleate predominantly during steady-state, rather than during the transient period.

Now, the stress that develops at the center during steady-state, varies with bubble spacing, as seen from Equation 31. A plot of the positive stress at the center versus bubble spacing is shown in Figure 26. The stress increases as the bubble spacing decreases. Thus initially when the bubbles are far apart, the
FIG 26: Variation of the stress at the half-bubble spacing distance with half-bubble spacing, for grain boundary diffusion controlled growth of the bubbles.
nucleation time is long, but as fresh bubbles nucleate the bubble spacing decreases, increasing the stress and thus increasing the nucleation rate. Thus when the bubbles get close enough, the stress ahead of the moving wedge may become so high that nucleation might start even before steady-state is reached. So the nucleation will speed up with time. However, it has been shown by Shewmon (4) that grain boundaries are not capable of acting as heterogenous nucleation sites by themselves, and the presence of a second phase such as carbide or sulfide is required for a bubble to nucleate. This is consistent with the observations of Hasegawa et al (59), who found that the presence of carbides at the grain boundary enhanced hydrogen attack of a low carbon steel. Thus even though the nucleation will speed up with time, eventually all the nucleation sites such as carbides will be used up, and nucleation will be complete. Thus the above analysis would predict an incubation time for nucleation, corresponding to the transient period, and a nucleation cascade at the end of the incubation time. Eventually the nucleation will stop due to exhaustion of nucleation sites. The observations of Wang (49) on carbon steels, agree with such a qualitative prediction.
The above mechanism would also explain why only a certain fraction of the grain boundaries are cavitated during HA. Once a grain boundary is cavitated by the nucleation cascade effect, the growing bubbles would create stresses on some of the adjacent boundaries. These stresses will enhance the bubble nucleation probability at those boundaries that are loaded in tension by the bubble growth, and inhibit nucleation on the boundaries stressed in compression. Thus bubble nucleation on one boundary would tend to make the fissures lie in a plane. This chain reaction will proceed until all the bubbles nucleated grow freely. This amounts to an accommodation free bubble growth.

Using Equation 51, derived for crack-like bubbles, a plot of \( p(r) \) versus \( r \) was made, and the plot was similar to that of Figure 25, but the positive stress at the center was higher. A plot of the positive stress versus bubble spacing is shown in Figure 27. Since nucleation time is a strong function of stress, the higher stress will result in higher nucleation rates compared to the case of spherical bubbles. This will result in a faster cascading effect and thus crack-like bubbles would not only expand rapidly, but also nucleate more crack-like bubbles rapidly, and eventually coalesce to form a single fissure. In the
work by Panda (8), such a mechanism must have been responsible for the sudden change in the controlling mechanism for bubble growth.
FIG 27: Variation of the stress at the half-bubble spacing distance with half-bubble spacing, for surface diffusion controlled growth of the bubbles.
DILATOMETRIC DATA AND MODEL PREDICTIONS

The dilatometric results provide the best means of checking models of hydrogen attack as well as creep. The experimental results are reported as linear external strain rates of the samples subjected to HA at different temperatures and hydrogen pressures. As the temperature and/or hydrogen pressure is changed, the conditions of bubble growth are also changed, as will be seen from the present work. Thus different mechanisms should become operative as the conditions of HA are changed using the same sample.

The predictions of a model are best compared with the dilatometric data in the following manner. The predicted absolute linear strain rates for different HA conditions should be checked against the measured values. Dilatometry has always been conducted by keeping the hydrogen pressure constant and varying the temperature and vice versa. Hence a model can be used to plot the variation of the strain rate with
temperature at a constant hydrogen pressure and vice versa. By plotting on the same graph the experimentally measured values, the model can be checked. The equations for grain boundary diffusion, surface diffusion, and power-law creep controlled growth of bubbles were used to calculate the predicted strain rates. Expressions for the contribution of each of the mechanisms to external linear strain rate were obtained as follows.

DIFFUSIONAL STRAIN RATE

During the diffusional growth of bubbles, atoms are plated on the grain boundary regions between the bubbles. Thus the grains separated by the boundary are pushed apart at a rate equal to the grain boundary plating or thickening rate. Equations 23 and 44 give the thickening rates for the grain boundary diffusion controlled and surface diffusion controlled growths respectively. The volumetric growth rate of one grain due to one cavitated boundary is then given by:

$$\left(\frac{dV}{dt}\right)_{\text{grain}} = g^2 \frac{d\delta}{dt} \quad \ldots \quad (56)$$

where $g$ is the grain size. The linear strain rate per grain is then:

$$\frac{1}{3} \left(\frac{dL}{dt}\right)_{\text{grain}} = \frac{1}{3} \frac{1}{V} \left(\frac{dV}{dt}\right)_{\text{grain}} = \frac{1}{3} \left(\frac{d\delta}{dt}\right)_{\text{grain}} \quad \ldots \quad (57)$$
For a material with a volume fraction of grains cavitaded of unity, the linear external strain rate is the same as that of each grain with one cavitaded boundary, and thus,

\[ \dot{\varepsilon}_{\text{diff}} = \frac{1}{3g} \frac{\partial \varepsilon}{\partial t} \quad \ldots \quad (58) \]

where \( \dot{\varepsilon}_{\text{diff}} \) is defined as the external linear strain rate due to diffusional growth of the bubbles. If the fraction of grain boundaries cavitaded is more than 0.15, then for such a general case,

\[ \dot{\varepsilon}_{\text{diff}} = f \left( \frac{1}{3g} \right) \frac{\partial \varepsilon}{\partial t} \quad \ldots \quad (59) \]

where \( f \) is given by,

\[ f = \frac{\text{(fraction of grain boundaries cavitaded)}}{0.15} \]

For the case where the fraction of grain boundaries cavitaded is significantly lower than 0.15, accommodation controlled growth will have to be considered.

POWER LAW CREEP RATE

Equation 53 gives the volumetric growth rate per bubble due to interactive creep growth of grain boundary bubbles. The contribution of this to the externally measured linear strain rate is the same as the linear strain rate per grain and is given by:

\[ \dot{\varepsilon}_{\text{creep}} = \frac{1}{3} f \left( \frac{8}{n\lambda^2} \right) \frac{1}{3g} \frac{dV}{dt} \text{ bubble} \quad \ldots \quad (60) \]
where \( \frac{dV}{dt} \) bubble is as given by Equation 53.

The externally measured linear strain rate would be predicted using Equations 59 and 60. Since diffusional growth and power law creep growth are parallel processes, the net strain rate is given by:

\[
\dot{\varepsilon} = \dot{\varepsilon}_{\text{diff}} + \dot{\varepsilon}_{\text{creep}}
\]

where \( \dot{\varepsilon} \) is the net external linear strain rate measured in the dilatometric experiments.

MATERIAL CONSTANTS

The thermodynamics of methane formation in steels has been worked out by Geiger and Angeles (36) for the various carbides, as discussed in the first section of this thesis. They related the fugacity of methane to the hydrogen partial pressure through a temperature dependent constant \( K(T) \), as seen from Equation 5. Equation 6 gives the variation of methane fugacity with temperature and hydrogen pressure for a commercially quenched and tempered 2 1/4 Cr-1 Mo steel. For carbon steels, an expression for \( K(T) \) was obtained using the values given for Fe_3C (36,37), and is as given below.

\[
K(T) = 1.6 \times 10^{-6} \exp \left( \frac{113640 \text{ J/mol}}{RT} \right) \text{ MPa}^{-1} \quad \ldots (62)
\]
The fugacities of methane were then converted to partial pressures, using the Equation 7. A plot of the variation of methane pressure with hydrogen partial pressure for different temperatures is given in Figure 28.

Hettitch et al (38) have shown that the lattice self-diffusivity of iron is affected by ferromagnetism. Their results were used by Panda (8) to obtain an expression for the lattice self-diffusion coefficient of α-iron, in the temperature range 500°C to 800°C, as:

$$D_l = 0.21 \exp\left(-\frac{320\text{KJ/mol}}{RT}\right) \text{m}^2/\text{s} \quad \ldots \quad (63)$$

Using the new value of $D_l$, Panda also calculated the true grain boundary self-diffusion coefficient and is given by

$$D_b = 9.8 \times 10^{-12} \exp\left(-\frac{206\text{KJ/mol}}{RT}\right) \text{m}^3/\text{s} \quad \ldots \quad (64)$$

The surface self-diffusion coefficient for iron was taken from the work of Kazuyoshi et al (54) on α-iron in dry hydrogen in the temperature range of 800°C to 900°C. Their expression for the surface diffusivity is:

$$D_s = 10 \exp\left(-\frac{228\text{KJ/mol}}{RT}\right) \text{m}^2/\text{s} \quad \ldots \quad (65)$$

and it agrees with previous work by Blakely et al (54) and Qjostein et al (55).
FIG 28: Methane pressures in equilibrium with Fe₃C as a function of hydrogen partial pressure for different temperatures in the range 300°C to 600°C.
In predicting the effect of creep growth, the creep behaviour of the material within a microscopic region of the order of a micron in diameter has to be known. However experiments on the creep behaviour have been conducted only at macroscopic levels and hence experimental results on carbon or low alloy steels cannot be directly used. However, since the creeping region is extremely small and since the regions near the grain boundary are likely to be free of carbides, the use of empirical creep parameters of pure α-iron for the creep behaviour of the local region, is a fair approximation. This assumption is further justified by the fact that the resulting model works well. Hence the creep constitutive equation obtained by Mukherjee et al (39) for pure iron, was used throughout this work.

The constitutive equation is:

\[ \dot{\varepsilon} = \frac{7 \times 10^{14}}{kT} D_1 b \left( \frac{\sigma}{G} \right)^{6.9} \]  

where \( \dot{\varepsilon} \) is the creep strain rate under the stress \( \sigma \) for a material of grain size \( g \), and shear modulus \( G \).

The other material parameters and constants used for the model predictions are listed in Table 7.
### TABLE 7: Material parameters used in the model

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>SYMBOL</th>
<th>VALUE</th>
<th>UNITS</th>
<th>REF.</th>
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<td>Shear Modulus</td>
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<tr>
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</tr>
<tr>
<td>Surface Diffusion Layer Thickness</td>
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<td>m</td>
<td>11</td>
</tr>
<tr>
<td>Dihedral Angle</td>
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<td></td>
<td>Q_l</td>
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<td>J/mol</td>
<td>38</td>
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McKimpson's Data on A516 Steel

McKimpson (6) studied the kinetics of HA of a carbon steel (A516) in two different methane pressure regimes. He studied the first sample at a high hydrogen pressure (17.3 MPa) and low temperatures (360°C-440°C), and used the same sample to study the hydrogen pressure dependence at 450°C. His second sample was studied at a low hydrogen pressure (2.5 MPa) and high temperatures (400°C-500°C). He used a third sample to measure the pressure dependence at 385°C. The first and second samples were given pre-nucleation treatments at roughly 350°C and 20 MPa hydrogen for 10 hours while the third was treated for nearly 25 hours. From metallography, he found that bubbles nucleated preferentially at grain boundaries and that they had a near equilibrium spherical shape. He reports that only a fraction of the grain boundaries were cavitated, but he gives no other quantitative details. However, from the micrographs of Pishko et al (50), rough values can be obtained for bubble spacings. Bubble spacings of the order of 0.5 to 1 micron were estimated from the pictures. Recently Wang (49) has determined average bubble radii in different carbon steels using TEM replica techniques. She determined the average radii in
A516 steel during the initial stages of hydrogen attack to be around 0.05 to 0.1 microns.

Since the bubbles were nearly spherical, equations derived for grain boundary diffusion controlled growth were used for evaluating the model predictions. For the first two samples, which were given a shorter pre-nucleation treatment, a half bubble spacing of 0.55 microns was used, while for the third sample a value of 0.4 microns was used. A bubble radius of 0.05 micron and a fraction of grain boundaries cavitated of 0.15 were used for all the three samples. Using the observed grain size of 20 microns, the model predictions were evaluated. The experimental data are compared with the predictions in figures 29,30,31. It is seen from the figures that for reasonable values of model parameters, the model predictions agree quite well with the experimental data.

By equating the grain boundary diffusional strain rate, to the power-law creep strain rate, a bubble growth mechanism map could be drawn as shown in figure 32. The map also includes the surface diffusion control regime calculated using Equation 50. The map is useful in predicting the controlling mechanism for different temperature-hydrogen pressure conditions. The
FIG 29: Comparison of model predictions with the data of McKimpson
(A) Temperature dependence (B) Pressure dependence
FIG 30: Comparison of model predictions with the data of McKimpson in the high pressure regime
FIG 31: Comparison of model predictions with the data of McKimpson for the hydrogen pressure dependence at 385°C.
FIG 32: Bubble growth mechanism map for carbon steel with parameters as shown.
conditions used by McKimpson are plotted as horizontal and vertical lines on the map. It is seen that at low methane pressures the bubbles grow under grain boundary diffusion control, while at higher methane pressures, power law creep growth is predominant. This is also consistent with the TEM studies of Yacaman (21), who presents clear evidence of dislocation motion around methane bubbles in a carbon steel. He also reports the association of bubbles with carbides, and bubble sizes of the order of 0.05 microns in radius.

PANDA'S DATA ON AL-KILLED 1020 STEEL

Low And Intermediate Pressu

Panda (8) studied an Al-killed 1020 steel at low methane pressures using a sample which was not given a pre-nucleation treatment. He studied the temperature dependence at 3.45 MPa pressure, between 450°C and 550°C. He discarded the initial transient data as nucleation effects. He studied the pressure dependence at 550°C, between 2 MPa and 6 MPa hydrogen. Using scanning electron microscopy, he did a quantitative analysis of the bubble size and distribution. He found nearly spherical bubbles along the grain boundaries, and reports a bubble spacing of 1.86 microns and a
fraction of grain boundaries cavitated of 0.14. For the study at intermediate pressures he used a sample that was given a pre-nucleation treatment, and measured kinetics at 375°C-450°C and hydrogen pressures of 2 MPa to 6 MPa. His steel had a grain size of nearly 20 microns.

The model predictions were calculated using a spacing of 2 microns for the low pressure regime, and 1.1 microns for the intermediate pressure regime. A bubble radius of 0.05 micron and a fraction of grain boundaries cavitated of 0.15 were used for both the samples. Using a grain size of 20 microns, the model predictions were found to agree quite well with the experimental data. The comparisons are shown in figures 33 and 34. A bubble growth mechanism map was made for a representative bubble spacing of 1.1 microns and the operating regimes of Panda marked on the map, as shown in Figure 35. As seen from the figure, for the low and intermediate methane pressure regimes, he was within the grain boundary diffusion control regime, although at intermediate pressures using 7 MPa hydrogen, the bubbles grow with some contribution from power-law creep.
FIG 33: Comparison of model predictions with Panda's data in the low pressure regime
(A) Temperature dependence  (B) Pressure dependence
FIG 34: Comparison of model predictions with Panda's data in the intermediate pressure regime
(A) Temperature dependence (B) Pressure dependence
FIG 35: Bubble growth mechanism map for Al-killed carbon steel with parameters as shown.
High Pressure Regime: As seen from Figure 35, a
and hydrogen pressure of 7 to 20 MPa, the bubbles are
predicted to grow under surface diffusion control.
Panda studied his Al-killed 1020 steel at these
conditions, and indeed found crack-like bubbles
characteristic of surface diffusion controlled growth.
However, while studying the kinetics of the sample, he
found a change in the temperature and hydrogen pressure
dependences, as he was following the kinetics. He
inferred later from metallography, that the mechanism
changed since the crack-like bubbles had extended over
the entire grain boundary, and further growth occurred
by power-law creep.

Unfortunately, Panda did not observe or report the
size and spacing of the crack-like bubbles during the
surface diffusion controlled growth. He did
metallography after the bubbles formed fissures
extending over the entire grain boundary segment. As
explained in the previous chapter on bubble nucleation,
it is most likely that the bubbles initially nucleated
in the same density as during during the low and
intermediate methane pressure regimes, but the stress
assisted nucleation effect is faster during surface
diffusion controlled growth. As a result, the bubble
density must have increased rapidly with time and
eventually became high enough for coalescence into a single fissure per boundary.

**Surface Diffusion:** In the absence of metallographic details, the model parameters were chosen as follows. Since crack-like bubbles are thin and long, a higher bubble radius was used, and a lower bubble spacing was used since a higher bubble density is expected. The fraction of grain boundaries cavitated used was the same as that reported by Panda. The model predictions for $r_b=0.09$ micron, $\gamma=0.2$ microns, a grain size of 20 microns and a fraction of grain boundaries cavitated of 0.05, are compared with the experimental data in Figure 36. The agreement is excellent for the pressure dependence, but is not good for the temperature dependence. Significant contribution from power-law creep was noted even during the predominantly surface diffusion controlled growth. This is also seen from the Figure 35, where the temperature dependence regime of Panda's study, extends from surface diffusion regime to power-law creep regime.

The excellent agreement between the data and predictions, for the hydrog pressure dependence, confirms the validity of the equations 46 and 48,
FIG 36: Comparison of model predictions with Panda's results in the surface diffusion control regime
(A) Temperature dependence (B) Pressure dependence
derived for the methane pressure dependences. The deviation of the data from the predictions for the temperature dependence, is attributed to the fact that the activation energy for surface diffusion used in the model, was obtained by extrapolation of high temperature data.

Power Law Creep: The modelling of the power-law creep growth of fissures, one on each cavitated boundary, was done as follows. According to the equivalent inclusion method (56) of determining stress distribution, the pressurized crack-like bubble, can be replaced by an equivalent misfitting inclusion, which is equivalent in the extent of dilation in each of the directions. For a crack-like bubble, this will be a flat elliptical inclusion of sufficient thickness or volume to cause the same deformation field. Now applying St.Venant's principle, this flat inclusion can be replaced by a spherical inclusion causing the same deformation field beyond a distance equal to the size of the inclusion itself. This is obtained by using a spherical inclusion of equal volume. Applying the equivalent inclusion principle once again, we get a spherical bubble of the same volume as that of the crack-like bubble, with the same pressure inside.
From the micrographs of Panda (8), bubbles were measured to be of 4 microns in radius, and nearly 0.25 microns thick. An equivalent bubble of spherical shape was calculated to have a radius of 1.4 microns. From the grain size of 20 microns, and the fraction of grain boundaries cavitated of 0.05, the bubble spacing was found to be roughly 25 microns. A half bubble spacing of 13.5 microns was used to obtain the best fit. The external volumetric strain rate is given by the volumetric strain rate of an internally pressurized creeping sphere of internal radius 1.4 microns and external radius of 13.5 microns. Thus using Equation 52, the external linear strain rates were calculated. The predicted results are compared with the experimental data, in Figure 37. The agreement is found to be good.

DATA ON 2 1/4 Cr-1 Mo STEELS

Welding Effects: In the first section of this thesis, dilatometric results on the base metal and weld metal of a quenched and tempered 2 1/4 Cr-1 Mo steel weldment were presented. Metallography revealed that spherical bubbles were formed in both the base metal and the weld metal, but the bubbles were preferentially located at
FIG 37: Comparison of model predictions with Panda's results in the power law creep regime
(A) Temperature dependence (B) Pressure dependence
the grain boundaries in the case of the base metal (Figure 13), while they were homogeneously distributed through the bulk in the case of the weld metal (Figure 14). The weld metal also had a significantly higher density of bubbles than the base metal (figures 13 and 14). TEM replica work by Lopez (27) on the base metal revealed an average bubble radius of 0.049 microns and an areal density of $6 \times 10^{-3}$ per square micron. This areal density is higher than the density measured from Figure 13, which was nearly $2 \times 10^{-3}$ per square micron. In the weld metal, Lopez found an average bubble radius of 0.076 microns and a bubble density of $7 \times 10^{-3}$ per square micron. This bubble density is close to the value of $10 \times 10^{-3}$ per square micron measured from Figure 14. The base metal and the weld metal had a grain size of roughly 50 microns.

Modelling of the base metal was done just as was done for carbon steels with spherical bubbles growing by grain boundary diffusion and power-law creep. Using a bubble radius of 0.05 microns, half-bubble spacing of 6.5 microns, a fraction of grain boundaries cavitated of 0.15, and a grain size of 50 microns, good agreement was obtained between the experimental data and the predictions, as seen from Figure 38. A half-bubble spacing of 6.5 microns with a fraction of grain
boundaries cavitated of 0.15, amounts to \(2 \times 10^{-3}\) per square microns. This is lower than the value obtained by Lopez but is the same as that obtained from Figure 13. The higher value obtained by Lopez is probably due to the fact that Lopez counted all the bubbles on both the grain boundaries and within the bulk, while only bubbles at the grain boundary contribute significantly to the specimen expansion and will show up in the SEM after a long-term exposure. The strain rate due to grain boundary diffusion was more than ten times the contribution by power-law creep.

Mechanistic regimes for the bubble growth in the base metal were plotted on a map, to show the transition from grain boundary diffusion control to power-law creep control. Using the bubble radius and half-bubble spacing values used in the model, the map was drawn as shown in Figure 39. The operating regime of the experiments are well within the grain boundary diffusion regime.

Modelling of the weld metal was done by considering the steady-state creep of internally pressurized bubbles of internal radius of 0.075 microns and external radius of 6 microns. The half-bubble spacing of 6 microns amounts to \(7 \times 10^{-3}\) per square micron, which
FIG 38: Comparison of model predictions with results of the present work on the base metal of the 2 1/4 Cr-1 Mo steel weldment. (A) Temperature dependence (B) Pressure dependence.
FIG 39: Bubble growth mechanism map for the base metal of the 2 1/4 Cr-1 Mo steel weldment
is in excellent agreement with the observations by Lopez and somewhat less than that obtained from Figure 14. From Figure 40, the model predictions are found to be in reasonably good agreement with the experimental results.

The reason for the homogeneous bubble distribution in the weld metal is not clear. It is probably best explained as due to a homogeneous distribution of inclusions which nucleated voids due to welding stresses. The voids became bubbles during hydrogen attack. However, once the bubbles form homogeneously distributed, their growth is characterized by power-law creep growth of spherical internally pressurized bubbles.

A mechanistic control regime map was drawn for the case of the weld metal, in the following way. If all the bubbles in the weld metal were located at the grain boundaries, a transition from grain boundary diffusion control to power-law creep control will be predicted, just as in the case of the base metal. Redistributing a bubble density of 7E-3 per square micron, along the grain boundaries, we have an effective half-bubble spacing (at the grain boundaries) of 4 microns with a bubble radius of 0.075 microns. The mechanistic regime
FIG 40: Comparison of model predictions with the results of the present work on the weld metal of the 2 1/4 Cr-1 Mo steel weldment (A) Temperature dependence (R) Pressure dependence
map for such a bubble distribution is given in Figure 41. Plotting the operating regimes for the weld metal on this map, it is seen that the weld metal was mostly within the power-law creep regime.

**Tempering Effects** : The experimental results obtained in the study of tempering effects, described in the first section, were also checked using the grain boundary diffusion-power-law creep model. The bubble radius was taken to be 0.05 microns (same as that of the base metal), and methane pressures were calculated using the carbon activity values determined in the first section. Taking the base metal to obey Equation 6, the equilibrium methane fugacity of the tempered structures were calculated by multiplying equation 6 with the relative carbon activity of the tempered structure with respect to the base metal, as described in Section I. The fugacities were converted to partial pressures, using Equation 7.

Since bubbles in 2 1/4 Cr-1 Mo steels nucleate in pre-existing voids (26), and such voids sinter shut with time at high temperatures, the bubble density would be expected to decrease with prolonged tempering. Hence the bubble spacings of the samples XT1 and XT2 would be smaller than that of the base.
FIG 41: Bubble growth mechanism map for 2 1/4 Cr-1 Mo steel of bubble radius and density the same as that of the weld metal of the present work.
metal (6.5 micron), and those of the samples XT3 and XT4 would be larger. Accordingly half-bubble spacings of 5.5, 6, 6.5 and 6.7 microns were used for the samples in their order of tempering extent. The model predictions are compared with the dilatometric data in figures 42 and 43, and the agreement is seen to be good. Thus the variation of HA behavior with tempering of 2 1/4 Cr-1 Mo steels, can be explained fully on the basis of carbon activity and bubble density.

Yu's Results: The results of Yu (9) on a quenched and tempered 2 1/4 Cr-1 Mo steel can be explained in a manner similar to that of the base metal. In the absence of metallographic data, a bubble radius of 0.05 micron, half-bubble spacing of 8.5 microns and a fraction of grain boundaries cavitated of 0.15 were used to predict the results. The higher bubble spacing can be explained as due to the lack of residual stresses due to welding, which might have opened up more voids in the base metal compared to the quenched and tempered condition. The model predictions based on the above-mentioned values of the model parameters agree very well with the experimental results, as seen from Figure 44. Thus heat to heat variation in the HA behavior of 2 1/4 Cr-1 Mo steels can be fully explained based on bubble densities alone.
FIG 42: Comparison of model predictions with results of the studies on the tempering effects
(A) Sample XT1  (B) Sample XT2
FIG 43: Comparison of model predictions with the results of the studies on the tempering effects
(A) Sample XT3    (B) Sample XT4
FIG 44: Comparison of model predictions with the data of Yu on 2 1/4 Cr-1 Mo QT steel
(A) Temperature dependence  (B) Pressure dependence
IMPLICATIONS OF THE MODEL

The following implications result from the ability of the model to predict the various dilatometric data obtained on both carbon and low alloy steels.

1) The difference in the hydrogen attack rates between carbon steels and low alloy steels, is basically due to the difference in the carbon activity. Although the carbon activity is just one tenth that of a 2 1/4 Cr-1 Mo steel, the resulting difference in the equilibrium methane pressure causes a significant difference in the bubble density, due to the cascade nucleation effect in carbon steel. Due to lower methane pressures in the 2 1/4 Cr-1 Mo steel, there is negligible nucleation of bubbles during HA.

2) The effects due to welding on the HA behavior, or the heat to heat variations in the HA behavior, of
2 1/4 Cr-1 Mo steels is almost entirely due to the variations in the bubble size and the bubble density. Thus any second phase particles such as sulfide inclusions, with low interfacial strength will result in increased bubble nucleation and thus enhanced hydrogen attack rates. Fabrication stresses or other residual stresses that are likely to open up microvoids, will also enhance the HA strain rates of 2 1/4 Cr-1 Mo steels.

3) For commercially quenched and tempered 2 1/4 Cr-1 Mo steels, the bubbles grow under a diffusion controlled process, for hydrogen pressures up to roughly 25 MPa, at all temperatures of interest (300°C-600°C) for HA. Thus matrix creep strength plays no role in limiting the hydrogen attack strain rates of this steel. However, this is true only if the bubble density is less than 2x10^-3 per square micron. As the bubble density increases, the contribution of power-law creep to the bubble growth increases. For a bubble density of 7x10^-3 per square micron, the controlling mechanism changes from grain boundary diffusion to power-law creep at 15 MPa at 400°C, and at 20 MPa at 550°C. Since the bubble density in 2 1/4 Cr-1 Mo steels, is directly dependent on the density of pre-existing voids, HA of this steel can be
controlled by controlling factors that enhance microvoid formation.

4) Nelson Curves: Using the model, with the model parameters that give the best agreement with the experimental results, safe operating regimes of temperature and hydrogen pressures can be calculated. Taking 20000 hours to be a reasonable life time, for a critical strain of $10^{-3}$ for failure, a strain rate of $5 \times 10^{-8}$ per hour is the critical strain rate below which the material is safe. By calculating the methane pressures required for this critical strain rate, and converting them to hydrogen pressures at that temperature, the safe hydrogen pressure-temperature regimes were obtained. The results are plotted as Nelson Curves in Figure 45. The bubble size and distribution used for carbon steel was the same as that of McKimpson's A516 steel. This steel was electroslag refined and this has a cleaner microstructure and lower sulfur than most of the steels used for the API Nelson Curve. For the 2 1/4 Cr-1 Mo base metal and weld metal, the values that gave the best fit with the data of the present work, were used.

It is worth observing that the Nelson Curves turn backwards at higher temperatures. That is, at higher
FIG 45: Nelson Curves calculated using the model for carbon and 2 1/4 Cr-1 Mo steels
temperatures, higher hydrogen pressures are tolerable, beyond a critical temperature (Note: Decaburization would limit service in this range). This also makes physical sense because the methane pressures generated decrease rapidly at higher temperatures, since the equilibrium constant for methane formation from Fe₃C becomes unity (atm⁻¹) at 600°C, and is less at higher temperatures. Figure 45 also shows the API Nelson curves published in 1977 (57). The deviation at lower temperatures for carbon steels is probably due to the fact that steels used 10-20 years ago had higher sulfur resulting in visible attack at lower temperatures, and that their behavior led to the present API curve. Humphrys and Sorrel (58) have reported cases of this where long stringers near the center line of the pipe wall lead to larger blisters, and thus "failure" at low temperatures and low hydrogen pressures that fell below the API Nelson curve.
CONCLUSIONS

1) The growth of internally pressurized bubbles was analyzed, and equations for diffusive bubble growth under equilibrium and non-equilibrium conditions were rederived, following the treatment of externally applied stress assisted creep cavity growth by Chuang and Rice (11). The rederivation resulted in expressions for the steady-state stress fields between growing bubbles. A positive (tensile) stress exists at the center between two growing bubbles, and the magnitude of this stress increases as the bubble spacing decreases. This analysis was used to explain the nucleation cascade effects observed in carbon steels. A sigmoidal variation of the bubble density with time is predicted during the incubation period, and this is in agreement with the experimental observations of Wang (49).

2) The volumetric growth rate of the bubbles growing under surface diffusion control, is predicted
to have a methane pressure dependence of unity under most conditions of hydrogen attack. This is different from the value of 1.5 predicted by Sundararajan et al (10) and Panda (8). The difference arises due to the fact that the previous investigators used the crack extension rate to predict the volumetric strain rate, thus tacitly assuming the width of the crack-like bubble to remain constant with time.

3) The equations governing the rate of bubble/cavity growth are found to be the same for both internally pressurized growth, and externally applied stress assisted growth. Taking the jacking effect of grain boundary atom plating into account, a modified growth equation is obtained for the volumetric growth rate of the bubble under grain boundary diffusion control. For low ratios of bubble radius to bubble spacing values, the modified expression is nearly the same as that used by Sundararajan et al (10), but there is a marked deviation for higher ratios of bubble radius to bubble spacing.

4) It is felt that geometrical constraint plays no role in limiting bubble growth during HA. An
accommodation free model, using the rederived equations for diffusive growth and those derived by Finnie and Heller (48) for power-law creep growth, was found to predict the dilatometric results reasonably well for both carbon and 2 1/4 Cr-1 Mo steel under various mechanistic growth regimes. Differences in the hydrogen attack strain rates between the carbon and 2 1/4 Cr-1 Mo steel were found to be largely due to a lower carbon activity and lower bubble density, in the alloy steel.

5) Bubble growth maps showing the different mechanistic growth regimes at different temperatures and hydrogen pressures were constructed using the accommodation free model. In carbon steels, bubble growth was found to be grain boundary diffusion controlled below 6.5 MPa hydrogen at 400°C and 10 MPa at 550°C, while power-law creep controlled bubble growth above these hydrogen pressures. Below 300°C, surface diffusion controlled bubble growth is predicted for hydrogen pressures above 2 MPa.

6) 2 1/4 Cr-1 Mo steels in the commercially quenched and tempered condition are predicted to suffer
HA by grain boundary diffusion controlled bubble growth below roughly 25 MPa hydrogen at 450°C, and below about 30 MPa hydrogen at 550°C. Power law creep controlled growth is predicted for higher pressures.

7) The weld metal of a commercially quenched and tempered 2 1/4 Cr-1 Mo steel weldment, suffers HA by power-law creep controlled bubble growth above nearly 18 MPa hydrogen at 500°C, and above 20 MPa hydrogen at 550°C. This is due to the higher bubble size and bubble density found in the weld metal compared to the base metal.

8) The effect of tempering on the HA strain rates were predicted by the model quite well, by taking into account for the decrease in the carbon activity with tempering and taking the bubble spacings to decrease marginally with tempering. The decrease in bubble spacing with tempering time is to be expected since long times at high temperatures will result in sintering shut of some of the pre-existing voids.

9) Nelson Curves drawn using the model predict higher safe hydrogen pressures as temperatures rise
above roughly 550°C. This is due to the decrease in the equilibrium methane pressure as the temperature rises towards 600°C.
APPENDIX I

DILATOMETER CALIBRATION

To convert the measured rate of change of capacitance with time to linear strain rate of the sample, the dilatometer was calibrated as follows. Figure 2 shows a schematic sketch of the dilatometer cell. From the figure it is clear that the thickness of the alumina washer determines the gap between the sample's top surface and the electrode. Since the capacitance of the cell is determined by the gap between the electrodes, by changing the washer thickness the capacitance can be changed.

Using a set of alumina washers of different known thicknesses, the variation of capacitance with washer thickness, and thus the variation of the capacitance with gap width was measured. The variation with gap width was fairly linear between 5 pF and 10 pF. Since variations in capacitances measured were of the order of $10^{-4}$ pF/hr, the variation of capacitance with gap width or specimen length was practically linear, so long as the capacitance stayed within roughly 5 pF to 10 pF.
The rate of change of capacitance with gap width or specimen length was measured for each sample studied. The capacitance-time slope obtained from the plots were then converted to linear strain rates of the sample using the equation,

\[ \dot{\epsilon} = \frac{1}{l} \frac{dl}{dt} = \frac{1}{l} \left( \frac{dC}{dt} \times \frac{dl}{dt} \right) \]

\[ \dot{\epsilon} = \frac{1}{l} \left( \frac{dC}{dt} \frac{dh}{dt} \right) \quad \ldots \quad (67) \]

where \( l \) is the specimen length, \( \frac{dh}{dC} \) is the change in gap width with capacitance, which is equal to \( \frac{dl}{dC} \), the change in specimen length with capacitance, and \( \frac{dC}{dt} \) is the measured rate of change of capacitance.
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