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INITIAL HYDROGEN ATTACK KINETICS IN A CARBON STEEL

The Ohio State University

PH.D.

1979

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INITIAL HYDROGEN ATTACK KINETICS
IN A CARBON 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

Marvin Grendel McKimpson, B.S., M.S.

* * * * *

The Ohio State University

1979

Reading Committee:

Paul G. Shewmon
John P. Hirth
Robert A. Rapp

Approved By

A handwritten signature in dark ink, appearing to read "P. G. Shewmon", is written over a horizontal line.

Paul G. Shewmon
Department of
Metallurgical Engineering

VITA

June 11, 1954.....	Born - Elgin, Illinois
1976.....	B.S. Met. E. Iowa State University, Ames, Iowa
1976-1979.....	Research Associate, Metallurgical Engineering Department, The Ohio State University, Columbus, Ohio
1978.....	M.Sc., The Ohio State University, Columbus, Ohio

PUBLICATIONS

N. P. Lillybeck, M. G. McKimpson, R. T. Wimber and D. W. Donis; "An Evaluation of Graphite-Shape Consistency in Compact-Flake-Graphite Iron from Mechanical Property Data." AFS Transactions, Vol. 87, pp. 129-132, 1977.

R. Pishko, M. McKimpson and P. G. Shewmon: "The Effect of Steelmaking on the Hydrogen Attack of Carbon Steel." Metallurgical Transactions A, Vol. 10A, pp. 887-894, July 1979.

TABLE OF CONTENTS

	Page
VITA.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
 Chapter	
I. INTRODUCTION.....	1
II. LITERATURE REVIEW.....	4
1.0 The Incubation Period.....	6
1.1 Metallographic Results.....	7
1.2 Phenomenological Correlations.....	9
2.0 Bubble Growth Models.....	14
2.1 Grain Boundary Diffusion.....	16
2.2 Power Law Creep.....	18
3.0 Applications to Hydrogen Attack.....	22
3.1 Shewmon's Analysis.....	23
3.2 Numerical Simulations.....	25
3.3 Experimental Results.....	31
III. BUBBLE GROWTH PROCESSES.....	34
1.0 General Results.....	34
2.0 Equilibrium P_{CH_4} Models.....	37
3.0 Formation-Limited P_{CH_4} Models.....	42
3.1 Surface Reaction Limited P_{CH_4}	46
3.2 Carbon Diffusion Limited P_{CH_4}	47
IV. EQUIPMENT AND PROCEDURE.....	49
1.0 Equipment.....	49
1.1 The Cage.....	52
1.2 The Pressure Vessel.....	55

	Page
2.0 Specimen Preparation.....	57
3.0 Procedure.....	58
3.1 Data Reduction.....	60
3.2 Sources of Error.....	63
V. EXPERIMENTAL RESULTS.....	65
1.0 Time Dependence.....	65
2.0 Microstructural Development.....	70
3.0 Incubation Period Kinetic Results.....	74
3.1 Transients.....	77
3.2 Temperature and Pressure Dependences...	81
4.0 Rapid Attack Kinetic Results.....	90
VI. DISCUSSION.....	93
1.0 Incubation Time Calculations.....	93
2.0 Incubation Period Growth Mechanisms....	96
2.1 Grain Boundary Diffusion.....	97
2.2 High Temperature, Low Pressure Region..	101
2.3 High Pressure, Low Temperature Region..	104
2.4 Alternate Growth Models.....	109
2.5 Summary.....	111
3.0 Rapid Attack Expansion Mechanisms.....	114
VII. CONCLUSIONS.....	119
APPENDIXES	
A. Equilibrium Methane Pressure Calculations...	123
B. Reduced Data.....	136
C. Material Parameters.....	148
LIST OF REFERENCES.....	149

LIST OF TABLES

Table		Page
1.	Predicted Time, Temperature and Hydrogen Pressure Dependences of the Methane Bubble Expansion Rate for Various Growth Models	43
2.	Temperature Jump Transients Observed During the Incubation Period (Run 5)	79
3.	Pressure Jump Transients Observed During the Incubation Period (Run 5)	80
4.	Temperature and Pressure Dependences Observed During Rapid Hydrogen Attack	91

LIST OF FIGURES

Figure	Page
1. Incubation Times for Rapid Hydrogen Attack.....	13
2. Size Dependence of Bubble Growth Rate for Grain Boundary and Creep Growth Models.....	19
3. Apparent Activation Energy Q_m of Methane Pressure in Equilibrium with Fe_3C	39
4. Hydrogen Pressure Exponent p of Methane Pressure in Equilibrium with Fe_3C	40
5. Dilatometric Apparatus.....	50
6. Cage Assembly.....	53
7. Observed Expansion Rate as a Function of Time (Run 6).....	66
8. Semi-Log Plot of Expansion Rate as a Function of Time (Run 6).....	69
9. ESR Steel Specimen Exposed to Hydrogen at 17.2 MPa and 400°C for 58 Hours.....	71
10. ESR Steel Specimen Exposed to Hydrogen at 17.2 MPa and 400°C for 99 Hours.....	72
11. ESR Steel Specimen Exposed to Hydrogen at 17.2 MPa and 400°C for 123 Hours.....	73
12. ESR Steel Specimen Exposed to Hydrogen at 6.4 MPa and 450°C for 153 Hours.....	75
13. Hydrogen Attack Rate Vs. Temperature-High Temperature, Low Pressure Region (Run 5).....	82
14. Hydrogen Attack Rate Vs. Pressure High Temperature, Low Pressure Region (Run 5).....	83

Figure		Page
15.	Hydrogen Attack Rate Vs. Temperature High Pressure, Low Temperature Region (Run 2).....	85
16.	Hydrogen Attack Rate Vs. Pressure High Pressure, Low Temperature Region (Run 7).....	86
17.	Calculated Constant Rate Curves for Hydrogen Attack in A516 Steel.....	88
18.	Hydrogen Attack Rate Pressure Dependence at High Pressure - High Temperature, Low Pressure Region (Run 3).....	89
19.	Transition Pressures for Methane Bubble Growth.....	99
20.	Calculated Methane Pressures in Equilibrium with Fe_3C	128

INTRODUCTION

Hydrogen attack is a form of internal decarburization which occurs in carbon and low alloy steels exposed to hot, high-pressure hydrogen. The phenomena is distinguished from hydrogen embrittlement in that hydrogen attack occurs above about 200°C^1 and in that the material damage caused by it cannot be reversed with a low temperature annealing treatment. Hydrogen attack has been a problem in both the petroleum and synthetic ammonia industries for a number of years. Accordingly, these industries have developed a set of empirical design curves--called the Nelson Curves¹--showing the hydrogen temperatures and pressures necessary for hydrogen attack in various plain carbon and alloy steels. These Nelson Curves are widely recognized within the industry and it is generally acknowledged that the curves, if properly used, do permit safe engineering design of pressure vessels for hydrogen service.

In recent years, considerable emphasis has been placed on developing alternative sources of energy. Several of these emerging technologies, especially coal gasification and geothermal energy, may operate under conditions in which hydrogen attack of the containment materials may be a significant problem. The experience gained in the

petroleum and ammonia industries, however, may not be directly applicable to these new environments. The new energy technologies will utilize materials in different hydrogen environments and under different types of loading than those currently used in the petroleum industry. At present, the factors controlling hydrogen attack are not well enough understood to enable one to confidently predict how such changes will affect hydrogen attack kinetics in a particular material.

Recently, a number of basic studies have been carried out to gain additional information about the rate-controlling factors for hydrogen attack. These studies, however, have concentrated on the theoretical and microstructural aspects of hydrogen attack; very few experimental kinetic studies have been made of the initial stages of attack. Yet, the kinetics of methane bubble formation during these initial stages is one of the major factors determining the hydrogen attack resistance of a steel.

Accordingly, this research was undertaken to study the kinetics of methane bubble growth during the initial stages of hydrogen attack. It was directed toward investigating three basic questions: 1) What processes are responsible for methane bubble expansion during the early stages of attack? 2) What factors control the internal methane pressures of these bubbles? and 3) What changes

occur at the end of the classical hydrogen attack incubation period to initiate fissure formation? Hopefully, the information gained from investigating these questions can provide additional understanding of the overall hydrogen attack process.

LITERATURE REVIEW

The macroscopic effects of hot, high-pressure hydrogen on carbon steels are reasonably well documented.¹ At high temperatures (above 500°C) and low hydrogen partial pressures, surface decarburization generally occurs. This decarburization causes slight losses in strength and hardness, and a slight increase in ductility. It is not accompanied by internal fissuring, which suggests that decarburization occurs only at the external surface of the metal. Current theories indicate that the rate of decarburization is primarily controlled by the rate of carbon diffusion to this external surface.^{1,2}

At lower temperatures (but above 200°C) and higher hydrogen pressures, internal decarburization, or hydrogen attack, is more likely to occur. When a steel is first exposed to hot, high-pressure hydrogen, one observes an initial incubation period during which no significant changes occur in the macroscopic properties of the metal. On continued exposure, internal intergranular fissures begin to develop. In normalized carbon steels, these fissures form near pearlite colonies and may or may not be associated with MnS or other inclusions.³ During this

'rapid attack' the metal shows a marked volumetric expansion and a drastic loss in mechanical properties. The process continues until a rather extensive network of decarburized fissures has developed in the steel. The rate of attack then tapers off and eventually approaches zero. After a carbon steel has undergone complete attack, one typically finds that its volume has been increased by 5 to 10%,³ its tensile strength has been reduced by about 1/3 and its ductility has been sharply decreased.⁴

It is generally agreed that hydrogen attack initially proceeds through the formation and growth of small, high-pressure methane bubbles along interior grain boundaries of a steel. Monatomic hydrogen diffuses into the iron and then reacts with cementite (either directly or by carbon transport through an α -Fe boundary layer) according to the overall reaction:

The methane molecules formed through this reaction accumulate at the reaction site since methane, because of its size, has a very low diffusivity in iron. This methane buildup results in a network of small gas-filled bubbles along grain boundaries. Very high methane pressures soon develop inside these bubbles, causing them to expand by either diffusional or dislocation creep. This process of

bubble nucleation and growth occurs throughout the incubation period preceding rapid hydrogen attack. Eventually the voids begin to coalesce, forming the elongated, intergranular fissures characteristic of rapid hydrogen attack.

A number of investigators have detected the methane gas which forms during hydrogen attack. Podgurski⁵ first demonstrated that methane was present in cold worked steels exposed to hydrogen at 300°C and that this methane was not present in steels which had been charged with hydrogen at 25°C. Since then, a number of investigators have detected methane in both hydrogen attacked steel^{6,7} and in effluent gases.^{8,9} Thus, it is well established that hydrogen attack is actually associated with methane formation.

1.0 The Incubation Period

The rapid attack stage of hydrogen attack has been studied by a number of investigators. The incubation period preceding this attack, however, has received far less attention. The bubble growth processes which occur during this interval are not well characterized. Nevertheless, metallographic studies have clearly established that methane bubble nucleation and growth does, in fact, occur during this period. In addition, some attempts have been made to model methane bubble growth kinetics during this interval.

1.1 Metallographic Results

Vitovec¹⁰ first suggested that discrete methane bubbles coalesced to form the large, intergranular fissures associated with rapid attack, and an early paper¹¹ from his research group contains several photographs clearing showing intergranular methane bubbles spaced about 1 μm apart in a 0.5% Mo steel. Since then, Hasegawa and Nomura⁶ have reported networks of intergranular bubbles spaced about 3 μm apart on both polished and fracture surfaces of a 0.05% and 0.15 wt % C steel exposed to hydrogen at 20.3 MPa and 380°C. Shih and Johnson¹² noted discrete bubbles ranging from 0.5 to 6 μm on intergranular fracture surfaces of 1020 steel exposed to hydrogen at 10.3 MPa and 600°C and observed regions where these bubbles had begun to coalesce into fissures. Somewhat similar findings were reported by Pishko et al.¹³ who observed networks of methane bubbles spaced about 1 μm apart on both polished and fracture surfaces of low carbon steel exposed to hydrogen at 6.5 MPa and 450°C. Recently, Natan⁷ has observed very small (10-150 nm) intergranular methane bubbles in hydrogen attacked 1020 and Ferrovac E steels using transmission electron microscopy. Sagues¹⁴ has reported discrete methane bubbles in hydrogen attacked Ferrovac 1020 steel, although these bubbles were somewhat larger (3-30 μm) and more widely spaced (about 65 μm) than those observed in the commercial materials.

The literature indicates that these methane bubbles usually form along some heterogeneity on grain boundaries. Allen et al.³ observed that hydrogen attack fissures in 1020 steel usually nucleated along either MnS inclusions near pearlite colonies or along pearlite-ferrite interfaces. Scanning electron microscopy studies confirm that bubble nucleation occurs preferentially at these sites. Shih and Johnson,¹² for example, reported that methane bubbles formed primarily on small MnS particles in 1020 steel exposed to hydrogen at 600°C. Hasegawa and Nomura⁶ exposed low carbon steels to hydrogen at 380°C and 20.3 MPa and found that bubbles in these materials formed preferentially on grain boundary carbides. Pishko et al.¹³ also observed bubbles primarily on carbide particles in steels exposed at 450°C and 6.5 MPa. Somewhat surprisingly, Sagues¹⁴ observed that methane bubbles in Ferrovac 1020 often formed away from pearlite colonies. He offered no explanation for this somewhat anomalous result.

From these metallographic investigations, one can conclude the networks of discrete methane bubbles are, in fact, the precursors of hydrogen attack fissures. The bubbles in these networks generally have spacings ranging from about 1 to 5 μm and are usually associated with carbide particles or inclusions. Any satisfactory theoretical

model for describing methane bubble growth during the incubation period must be consistent with these observations.

1.2 Phenomenological Correlations

A number of studies have also been carried out to determine how the length of the incubation period varies as a function of hydrogen temperature and pressure in carbon steels. The earliest investigations of this time preceding rapid attack were primarily alloy development studies directed toward determining the most suitable materials for service in hot, high-pressure hydrogen. Most of these early studies have been summarized by Fletcher and Elsea.¹⁵

Weiner¹⁶ was probably the first to specifically study the length of the hydrogen attack incubation period as a function of exposure conditions. He measured the time for rapid attack in a commercial steel containing 0.15 wt% C at temperatures of 427 to 538°C and hydrogen pressures from 3.1 to 6.6 MPa. He found that this incubation time, t_i , in hours, was approximately given by:

$$t_i = .456P_{H_2}^{-3} e^{+(61.1 \text{ kJ/RT})} \quad 1$$

where P_{H_2} is the hydrogen pressure in MPa and RT has the usual meaning. Both spheroidization and an increase in grain size increased t_i whereas the addition of 0.1 wt% Al decreased it. Weiner noted that the incubation time

appeared to increase significantly above 538°C and that it was independent of both section thickness and the presence or absence of surface oxides. Several recent investigators^{14,17} have reported incubation times similar to those predicted by Eqn. 1.

A short time later, Allen et al.⁴ measured the time for rapid hydrogen attack in both commercial 1020 and Ferrovac 1020 steels. They found that the time for attack in the commercial steel was given by:

$$t_r = .195 P_{H_2}^{-2} \exp \left(\frac{63.6 \text{ kJ}}{RT} \right) \quad 2$$

where t_r is the number of hours required for 50% hydrogen attack. The Ferrovac 1020 showed similar kinetic behavior except that rapid attack consistently occurred at slightly shorter exposure times. Equation 2 was found to be valid at temperatures from 371 to 538°C and at pressures between 2.8 and 9.6 MPa. The authors also noted that t_r appeared to become less dependent on hydrogen pressure below 371°C.

About 10 years ago, the American Petroleum Institute collected the results of all of the various laboratory investigations of hydrogen attack behavior in carbon steel. They combined these data with operating experience from the petroleum and synthetic ammonia industries and used the results to develop a family of curves similar to the Nelson Curves. These curves, which are shown in Fig. 1,

give the expected time required for rapid hydrogen attack in carbon steel as a function of hydrogen temperature and pressure. Temperature-pressure combinations above a given time line correspond to hydrogen attack in less than the given time, whereas temperature-pressure combinations below the line correspond to no rapid attack in the given time interval.

These curves are very useful for engineering applications because they characterize the minimum expected service life of carbon steel in a hydrogen environment. The form of the curves also illustrates that there are, in fact, two limiting regimes of hydrogen attack behavior. At high temperatures and low hydrogen pressures, the time for attack depends strongly on hydrogen pressure, but it is relatively independent of temperature. On the other hand, at high pressures and low temperatures, the incubation time varies strongly with temperature but is relatively independent of hydrogen pressure. As pointed out by Shewmon,¹⁸ this suggests possible differences in the kinetics of methane bubble formation in the two regions.

Such curves, however, do not provide much information about the details of methane bubble growth in steels during the incubation period. Since the curves are based largely on engineering data, they represent the composite behavior of a wide variety of steels exposed to hydrogen under a

wide range of conditions. Accordingly, they do not provide detailed information about the bubble growth in any one steel subjected to a particular state of stress. The laboratory investigations of Weiner¹⁶ and Allen et al.⁴ were restricted to specific steels and stress states, but the studies were limited to relatively low pressures (9.6 MPa maximum) and contain slight ambiguities associated with the use of mechanical property criteria for identify the incubation time. More importantly, the studies only provide the time for rapid attack in the steel and this time need not be simply related to the rate of bubble growth. There are at least two possible reasons for this. First, the average methane bubble spacing may vary with hydrogen exposure conditions. At high temperatures and low hydrogen pressures, the methane supersaturation for bubble nucleation (assuming classical nucleation and growth processes) is low, so methane bubble spacings may be large. Thus, bubbles may have to grow a great deal before they being to coalesce. Conversely, at low temperatures and high hydrogen pressures, the methane supersaturation for nucleation is high and average methane bubble spacings may be much lower. In this case, only a small amount of growth need occur before coalescence.

Second, the relative size required for rapid bubble coalescence may vary with the internal methane pressure.

Fig. 1. Incubation Times for Rapid Hydrogen Attack¹

At low internal pressures (high temperatures and low hydrogen pressures) equally spaced bubbles may have to be quite large before the stress fields of the individual bubbles interact enough to promote coalescence. At high internal pressures (low temperatures and high hydrogen pressures) bubbles having the same spacing may begin to interact at a much smaller size. This effect should reinforce the bubble density effect. Together they make it unlikely that a simple correlation would exist between the time required for rapid hydrogen attack under various exposure conditions and the rate of bubble growth.

2.0 Bubble Growth Models

Researchers have also studied the early stages of hydrogen attack using mathematical models to investigate methane bubble growth. This was first done by Weiner,¹⁶ who sought to explain the incubation period for hydrogen attack in terms of the time required to reduce grain boundary oxides by hydrogen. In retrospect, his suggestion does not appear feasible since subsequent investigators have found no evidence to support such a model and because the thermodynamics of the necessary reactions are not favorable. Later Allen et al.³ developed a comprehensive theory of methane fissure growth based on the kinetics of methane formation. Their treatment, however,

arbitrarily assumed that the time derivative of the internal methane pressure was proportional to $P_{H_2}^2$. This assumption is probably not realistic, since it neglects the effect of fissure expansion on the internal methane pressure. In addition, it conflicts with recent experimental work¹⁹ showing that the rate of the methane generation surface reaction on ferrite is proportional to $P_{H_2}^{1.5}$.

More recent models for methane bubble growth have been developed using numerical simulation techniques. These attempt to characterize the growth of internally pressurized bubbles during hydrogen attack by examining the growth of a 2-dimensional infinite array of evenly spaced voids along a planar grain boundary. The treatments assume this array nucleates at time zero, although the models could be generalized to include time-dependent nucleation effects. The center-to-center spacing of bubbles in this array is taken to be $2d$, so that the array consists of $2d$ by $2d$ cells, each containing a growing bubble at its center. From symmetry, each cell must behave identically, so one need only consider the growth of one bubble. Then, by assuming the steel matrix is incompressible, one can calculate the bulk expansion of a sample as the product of the volumetric expansion of one bubble times the number of bubbles in that sample. This number of bubbles is usually estimated by assuming a homogeneous distribution of bubbles

on all grain boundaries of the sample. Under these assumptions, the modelling problem then reduces to that of describing the growth of a single intergranular bubble during hydrogen exposure.

As first suggested by Vitovec,⁹ a methane bubble is likely to expand through either grain boundary diffusion of iron atoms away from the bubble or by power law creep of the surrounding matrix. (Following Shewmon,²⁰ one can readily show that lattice diffusion should not play a major role in bubble growth.) This expansion may be driven either by internal methane pressures which are nearly those in equilibrium with Fe_3C or by pressures which are much lower than equilibrium, depending on the relative rates of bubble expansion and methane generation. Each of these possibilities can be investigated numerically. Ultimately, one should be able to determine what process provides the rate-determining step for bubble growth.

2.1 Grain Boundary Diffusion

Bubble expansion by grain boundary diffusion has been treated by a number of authors since it was first suggested by Hull and Rimmer.²¹ Raj and Ashby,²² (as modified by Raj et al.²³ to include internally pressurized bubbles) provide one of the more recent and complete treatments of the problem. They assume the 2d by 2d array described

earlier and take the chemical potential at the surface of each methane bubble to be $(P_{\text{CH}_4} - \frac{2\gamma}{r})\Omega$, where P_{CH_4} is the internal methane pressure, γ is the surface energy of the metal at the surface of the bubble, r is the bubble radius and Ω is the atomic volume. Surface diffusion inside the bubble is assumed to be rapid, so this potential is independent of position. The chemical potential gradient at a distance d from the center of the bubble is taken to be zero to insure that no net flux of atoms leaves the element. Atoms are assumed to flow from the bubble out into the grain boundary and are plated out at a uniform rate over the remaining boundary area. This rate of deposition (and hence the rate of bubble expansion) can then be calculated using the additional constraint of mechanical equilibrium.

From this analysis, one obtains that the bubble growth rate $\dot{V}_{\text{gb}}$ is given by:

$$\dot{V}_{\text{gb}} = \frac{2\pi D_{\text{gb}} \delta (P_{\text{CH}_4} - \frac{2\gamma}{r})}{kT} \frac{1-x^2}{x^2 (1 - \frac{x^2}{4}) - \frac{3}{4} - \ln x} \quad 3$$

where $X = \frac{r}{d}$, k is Boltzman's constant and $D_{\text{gb}} \delta$ is the product of the grain boundary diffusion coefficient and the grain boundary thickness. (Speight and Beere²⁴ derive a slightly different form of Eqn. 3. At the small bubble sizes of primary interest here, however, the difference

between the two results is very small and can be neglected.) Equation 3 predicts that the bubble expansion rate will vary linearly with the effective internal methane pressure ($P_{CH_4} - \frac{2\gamma}{r}$). Also, aside from this pressure term, only the diffusion coefficient D_{gb} varies strongly with temperature. Thus, at constant pressure, the activation energy for this growth process would be simply Q_{gb} , the activation energy for grain boundary diffusion in Fe. Assuming P_{CH_4} is constant, the bubble size dependence of the growth rate is given by the last term on the right-hand side of Eqn. 3. This quantity, called $F(X)$, is shown in Fig. 2 as a function of the relative bubble size X . At very small bubble sizes, $F(X)$, and hence $\dot{V}_{gb}$, is nearly independent of X . Only as the bubbles begin to coalesce ($X \rightarrow 1$) does $\dot{V}_{gb}$ become a strong function of bubble size.

2.2 Power Law Creep

Theoretical models for the growth of pressurized bubbles through power law creep have also been developed. The growth rate of a single bubble embedded in an infinite medium was first calculated by Finnie and Heller,²⁵ although their published results contain misprints. Since then, several authors, including Wilkinson and Ashby²⁶ and Shih²⁷ have treated the more useful problem of the creep expansion

Fig. 2. Size Dependence of Bubble Growth Rate for Grain Boundary and Creep Growth Models

of an internally pressurized spherical shell having a finite thickness (Wilkinson and Ashby²⁶ actually dealt with the reverse problem of pressure sintering by creep, but their results can be readily generalized to the current problem.)

The derivation of the power law bubble growth expression is quite straightforward, but it does require the assumption that the appropriate constitutive equation for bubble growth is a generalized form of the power law creep expression, namely:

$$\dot{\epsilon}_r = B(\sigma_r - \sigma_\theta)^n = \frac{AD_1 b}{kTG^{n-1}} (\sigma_r - \sigma_\theta)^n \quad 4$$

where $\dot{\epsilon}_r$ is the radial strain rate, σ_r and σ_θ are the radial and tangential shear stresses, and B and n are constants. The second equality follows from the expression for B given by Mukherjee, Bird and Dorn,²⁸ where A is a dimensionless constant, D_1 is the lattice self diffusion coefficient, G is the shear modulus and b is the magnitude of the appropriate Burgers vector. Such an expression is clearly valid for macroscopic creep phenomena. It may not, however, be appropriate for characterizing the growth of submicron bubbles spaced only a few microns apart. This possibility has not been critically discussed by the investigators using the expression.

The derivation begins by considering the grain boundary array of methane bubbles to be an array of internally pressurized thick-walled spherical vessels, each having an inner radius r and an outer radius d . One combines the strain compatibility conditions for such a vessel with a volume conservation constraint to determine the radial and tangential strain rates as a function of position. This expression contains an integration constant which must be evaluated using Eqn. 4, mechanical equilibrium and appropriate pressure boundary conditions. One then obtains an expression for the radial strain rate $\dot{\epsilon}_r$ at the inner surface of the vessel, which can be converted to the expansion rate of the bubble $\dot{V}_{\text{creep}}$ by the relation:

$$\dot{V}_{\text{creep}} = 4\pi r^2 \frac{dr}{dt} = 4\pi r^2 \cdot r \dot{\epsilon}_r \quad 5$$

Substituting $\dot{\epsilon}_r$ and rewriting the equation in terms of X one obtains that:

$$\dot{V}_{\text{creep}} = \frac{2\pi A D_1 b}{d^3 k T G^{n-1}} \left[\frac{3}{2n} (P_{\text{CH}_4} - \frac{2\gamma}{r}) \right]^n \frac{1}{(X^{-3/n} - 1)^n} \quad 6$$

This expression is similar to that given by Shih²⁷ except that the cavity volume used in Shih's expression has been rewritten in terms of X and, following Wilkinson and Ashby,²⁶ a surface energy correction has been inserted into the pressure term.

Ignoring the weak linear temperature dependences of T and G in this expression, the overall activation energy for the creep process (at constant P_{CH_4}) will be Q_1 , the activation energy for lattice self diffusion in Fe, and the pressure exponent will be the power law exponent n . The bubble size dependence $G(X)$ is given by the last term on the right-hand side of Equation 6. This quantity is shown as a function of X in Figure 2. Note that $G(X)$, unlike its counterpart for grain boundary diffusion, depends very strongly on X at all bubble sizes. Also, from Eqn. 6, note that $\dot{V}_{\text{creep}}$, unlike $\dot{V}_{\text{gb}}$, depends explicitly on the bubble half-spacing d as well as on the normalized bubble size.

3.0 Applications To Hydrogen Attack

These expressions for bubble growth by grain boundary diffusion (Eqn. 3) and power law creep (Eqn. 6) can be used to predict the expansion rate of methane bubbles during hydrogen attack. The diffusion coefficients and other material parameters required in the equations are known, at least for high-purity iron. Unfortunately, the internal methane pressure and the true bubble size during the early stages of growth are not generally known. Accordingly, one must assume values for these two quantities in order to use the growth expressions. Different

investigators have assumed different values and have therefore arrived at different conclusions about methane bubble growth.

3.1 Shewmon's Analysis

Shewmon¹⁸ was the first to proceed in this manner. He began by considering whether or not the methane pressure inside a growing bubble might be limited by the kinetics of methane formation. He pointed out that the growth of a methane bubble on a ferrite-ferrite boundary involved five steps, any of which could be rate determining:

- 1) Transport of hydrogen to the surface of the growing bubble.
- 2) Dissociation of Fe_3C into Fe and dissolved C atoms.
- 3) Diffusion of C atoms to the surface of the growing bubble.
- 4) Reaction of C and H at the surface to form methane.
- 5) Transport of Fe atoms away from the growing bubble.

From a diffusion analysis, Shewmon found that Step 1 should not be rate determining for thin (~ 25 mm) samples. Also, from available data he concluded that Fe_3C dissolution was probably diffusion rather than interface controlled, so that Step 2 should not be rate determining.

He observed that if Step 5 was rate determining then the methane pressure inside a bubble would be nearly that

in equilibrium with Fe_3C at the given temperature and pressure and could be estimated from thermodynamic data.

Shewmon did this by assuming a linear relationship between methane fugacity and pressure at high pressures and then inserted this estimate into the diffusional growth model of Raj and Ashby (Eqn. 3). He found that such a model predicted temperature and pressure dependences for the incubation time to rapid attack which were similar to those reported by Weiner¹⁶ provided the bubble density was high and temperature independent. From this, Shewmon concluded that methane bubbles forming at high temperatures and relatively low hydrogen pressures probably did contain nearly equilibrium pressures.

He recognized, however, that this analysis was not likely to apply at the lower temperatures and higher pressures more typical of industrial applications. In this region, the incubation times predicted from Weiner's work¹⁶ are much shorter than those obtained from Fig. 1. Shewmon noted that this suggests that some new process retards methane bubble growth in this region. This process might be either methane formation kinetics (Step 4) or carbon diffusion (Step 3). Not enough information, however, was available to make a choice between the two.

Thus, Shewmon's analysis indicated that methane bubble growth during hydrogen attack probably does occur

through grain boundary transport of Fe atoms away from the bubble. At high temperatures and low hydrogen pressures, this growth is driven by near-equilibrium internal methane pressures. At high pressures and low temperatures, however, the internal methane pressures are probably significantly below equilibrium due to either carbon diffusion or methane surface reaction kinetics.

3.2 Numerical Simulations

Other investigators have attempted to substantiate Shewmon's conclusions using numerical simulation models. These models attempt to actually calculate the methane pressure inside a growing bubble using two coupled first order differential equations: one for bubble expansion and one for methane generation. By numerically integrating this system of equations, one can determine the molar density of methane inside the bubble as a function of time. This molar density can then be converted to a methane pressure using an appropriate equation of state. The pressure can then be used to determine the rate of bubble expansion.

The models assume that bubble expansion occurs through either grain boundary diffusion or creep. That is, they take the differential equation for bubble expansion to be the sum of Eqns. 3 and 6. Thus, as a byproduct of the

model, one can readily determine whether diffusional or creep growth dominates.

The rate of methane generation in these models is assumed to be controlled by the kinetics of the methane decarburization surface reaction. Carbon diffusion kinetics are neglected since estimates²⁷ show that the relaxation time for this process should be relatively small. Grabke and Martin¹⁹ have studied the rate of methane formation on high-purity Fe foils in atmospheres containing various CH₄/H₂ ratios. The experiments were done at temperatures ranging from 500 to 800°C and hydrogen pressures up to 0.1 MPa. In this region, they found that the rate of methane generation $\dot{n}$ per unit area of surface was given by:

$$\dot{n} = K_f [C] P_{H_2}^{3/2} - K_b P_{CH_4} P_{H_2}^{-1/2} \quad 7$$

where K_f is a forward reaction rate constant having a value of $1.73 \times 10^{-12} \exp(-\frac{56.9 \text{ kJ}}{RT}) \text{ ms}^{-1} \text{ Pa}^{-1.5}$ and K_b is carburization rate constant having a value of $4.15 \times 10^4 \exp(-\frac{213.4 \text{ kJ}}{RT}) \text{ mole m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1.5}$. The symbol [C] represents the carbon concentration at the reacting surface. If carbon diffusion is assumed to be rapid, [C] will be approximately the carbon concentration in equilibrium with Fe₃C. By extrapolating these kinetic results to commercial steels exposed to hydrogen at much higher

pressures and somewhat lower temperatures, one can thus write an equation for the rate of methane formation on the surface of a spherical bubble embedded in ferrite.

The first simulation study using these coupled differential equations for bubble growth and methane generation was done by Sagues et al.¹⁴. These researchers used a modified ideal gas law to calculate the methane pressure and also employed a limiting form of Eqn. 6 corresponding to very large bubble spacings. The model was then used to investigate the growth of relatively large ($>3 \mu\text{m}$) widely spaced ($\sim 60 \mu\text{m}$) bubbles at hydrogen pressures up to 3.1 MPa and temperatures up to 500°C . These somewhat restrictive parameters were chosen so that the predictions of the model could be compared with experimental measurements obtained under similar conditions.

They found that bubble growth kinetics under these conditions could be divided into three distinct regions:

1) Low Temperatures and/or High P_{H_2}

Here, methane pressures were much lower than those in equilibrium with Fe_3C . Cavities grew predominantly by power law creep and methane production at the cavity surface was rate controlling. In this region the model predicted an apparent activation energy for bubble growth of 157.7 kJ.

2) Intermediate Temperatures and P_{H_2}

In this region, bubbles contained the equilibrium methane pressure, but deformation still occurred by creep rather than grain boundary

diffusion. Accordingly, the cavity volume increased almost exponentially with time. Since the equilibrium pressure raised to the 6.9 power decreases sharply with increasing temperature, the rate of bubble expansion decreased with increasing temperature.

3) High Temperatures and Low P_{H_2}

Here, as predicted by Shewmon,¹⁸ methane was present at low equilibrium pressures and bubble growth did occur primarily by grain boundary diffusion.

Regions 1 and 2 were found to span most of the exposure conditions typical of industrial applications. Thus, the investigators concluded that bubble growth during hydrogen attack occurred primarily through power law creep rather than grain boundary diffusion. The simulation showed that this bubble growth could be driven by either equilibrium or below equilibrium methane pressures, depending on the exposure conditions. One should bear in mind, however, that these conclusions apply primarily to the growth of large, widely spaced bubbles, since these were the only type of bubbles investigated.

Shih²⁷ obtained similar results using a somewhat more detailed simulation program. His treatment used a more exact equation of state for methane (that proposed by Sevast'yanov and Zykov²⁹) and also incorporated the general power law growth expression given as Eqn. 6 rather than the limiting case used by Sagues et al.¹⁴ The study also

investigated the growth of bubble arrays having a variety of initial bubble sizes and spacings. Shih found that bubble growth under all exposure conditions proceeded initially by grain boundary diffusion but later became creep-dominated. The initial grain boundary diffusion interval, however, constituted an insignificant fraction of the total bubble growth except at very high temperatures and low hydrogen pressures. His model also showed that the internal methane pressure varied inversely with temperature but that it never attained the equilibrium value. It also illustrated that variations in cavity size only affect the initial stages of growth. Changes in bubble density on the other hand, primarily affect the later stages of bubble development since they influence the amount of growth required for coalescence.

Shih did not use his simulation to tabulate the expected time, temperature and hydrogen pressure dependences of his creep-dominated growth model. One can, however, estimate the predicted time and temperature dependences from various graphs contained in his thesis. The model clearly predicts that the rate of bubble expansion increases rapidly with time. Indeed, the amount of total sample expansion appears to be about a cubic function of

exposure time. The apparent activation energy for the expansion process decreases with increasing temperature, but looks to be roughly 140 kJ between 300 and 400°C.

The most recent simulation work has been done by Oldfield et al.² This study differs substantially from the previous ones in several respects. First, rather than assuming that the methane bubble spacing is independent of exposure conditions, they allowed this spacing to decrease linearly with increasing equilibrium methane pressure. Second, these investigators included a $\frac{2\gamma}{r}$ surface energy correction term in calculating the internal methane pressure driving both creep and grain boundary diffusion. This surface energy term was justifiably neglected by Sagues et al.,¹⁴ since they only investigated the growth of large bubbles. Shih²⁷ had inserted the surface energy term when calculating the driving force for grain boundary diffusion but did not use it when calculating the driving force for creep.

Third, Oldfield et al. wrote the rate of the methane decomposition reaction in Eqn. 7 in terms of the internal methane fugacity rather than the internal methane pressure. This change makes Eqn. 7 consistent with the proper high-pressure form of the methane equilibrium constant. Although accurate measurements of methane fugacities at very high pressures are generally not available, these authors

pointed out that such values could be estimated from existing equations of state for methane gas. Using such an estimate based on a modified ideal gas law, Oldfield et al. found that methane fugacity/pressure corrections were, in fact, substantial and that they greatly reduced the actual equilibrium methane pressures which could be attained inside a bubble. By incorporating these fugacity corrections into their simulation, they found that growing bubbles would, in fact, contain nearly equilibrium pressures under most exposure conditions of interest. Furthermore, these equilibrium pressures were low enough that bubble expansion occurred primarily by grain boundary diffusion rather than power law creep.

3.3 Experimental Results

Unfortunately, there is little experimental evidence which can be used to support any of these theoretical growth models. As mentioned above, hydrogen incubation period data is not very well suited for this purpose. Aside from these studies, however, there have been only two investigations which specifically studied methane bubble growth under hydrogen attack conditions.

The first of these was done by Westfal and Worzala.¹⁷ They exposed samples of Ferrovac E and Ferrovac 1020 steels to hydrogen at several different temperatures and pressures

and then used thin foil transmission electron microscopy to study the size of the methane bubbles as a function of time. Unfortunately, their results were confined to intragranular bubbles because of difficulties in specimen preparation. Accordingly, even these data cannot provide quantitative information about intergranular methane bubble growth during hydrogen attack.

The second study is a dilatometric investigation of bubble growth done by Sagues et al.¹⁴ They measured the hydrogen attack expansion rate of Ferrovac 1020 samples at temperatures ranging from 275 to 475°C and hydrogen pressures ranging from 0.79 to 6.20 MPa. Over this range, they found that the sample expansion rate increased approximately exponentially with time. In addition, it showed an exponential temperature dependence with an activation energy of 170 ± 20 kJ. The authors pointed out that this activation energy was similar to that predicted by their simulation model¹⁴ for bubble growth by creep at low temperatures and high hydrogen pressures. These kinetic measurements were made only on relatively pure steels which had already undergone significant amounts of hydrogen attack (>0.1% total expansion). In addition, the Ferrovac steel contained methane bubbles which were substantially larger and more widely spaced than those

generally found in commercial materials. Accordingly, the kinetic behavior observed by Sagues et al. may not be representative of that found during the initial stages of methane bubble growth in commercial steels.

Clearly, there is a definite need for additional kinetic studies of methane bubble growth during hydrogen attack. Since the theoretical aspects of the problem have been investigated in reasonable detail, it would appear that the most pressing need is for additional experimental studies of bubble growth. By looking at how the bubble growth rate varies as a function of time, temperature and hydrogen pressure, one should be able to determine whether bubble growth occurs predominantly by power law creep or by grain boundary diffusion. One may also be able to use these experimentally measured dependences to determine whether the internal methane pressures driving bubble growth are essentially equilibrium pressures or whether they are significantly below equilibrium and hence controlled primarily by methane formation kinetics. Then, by comparing these results with various theoretical models such as those described above, one should be able to gain additional insights about the assumptions incorporated into these models.

BUBBLE GROWTH PROCESSES

The dilatometric investigations of hydrogen attack described in the following sections were undertaken to provide additional experimental information about the kinetics of methane bubble growth in steels. The dilatometric apparatus permits in-situ measurements of the rate of bulk sample expansion during hydrogen attack as a function of time, temperature and hydrogen pressure. In order to study methane bubble growth processes, however, one must be able to relate such measurements to the growth rate of a single bubble.

1.0 General Results

As suggested by the numerical simulation studies, the easiest way to make this connection is to simply assume that all methane bubbles in the specimen behave identically. This assumption will be adopted for this investigation. It is clearly an oversimplification. Nevertheless, if applied with caution, it can be quite useful. It should be reasonably applicable for describing the expansion of samples which have been given a nucleation pretreatment to insure complete bubble nucleation at time zero. Even if

all the bubbles in such samples do not behave identically, one should be able to approximate their growth in terms of an array of "average" identical bubbles. Furthermore, the assumption allows one to directly compare experimental bubble growth results with those predicted by the numerical simulations.

Using the identical bubbles assumption, the time, temperature and hydrogen pressure dependences of the sample expansion rate will be the same as those for the growth of an individual bubble. That is, if the bulk sample expansion rate $\dot{V}_s$ is given by some expression:

$$\dot{V}_s = C_1 \exp\left(-\frac{Q}{RT}\right) P_{H_2}^m H(t) \quad 8$$

where C_1 is a constant, then Q , m and $H(t)$ will be, respectively, the apparent activation energy, the hydrogen pressure exponent and the time dependence for both sample expansion and methane bubble growth. The value of C_1 will depend on a number of things, including the bubble growth process and the density of methane bubbles in the specimen.

Next, one would like to relate the experimentally observable quantities Q , m and $H(t)$ for methane bubble growth to those predicted by the growth models of Eqns. 3 and 6. To do this, one must relate the internal methane pressure P_{CH_4} to the external hydrogen pressure P_{H_2} in Eqn.

8. This relationship will vary depending on whether P_{CH_4} is limited primarily by equilibrium considerations or by formation kinetics. Nevertheless, by analogy with other chemical systems, one can say that:

$$P_{CH_4} = C_2 \exp\left(-\frac{Q_m}{RT}\right) P_{H_2}^p \quad 9$$

where C_2 is a proportionality constant and Q_m and p are parameters which may vary with exposure conditions and the amount of sample expansion. One can then insert Eqn. 9 back into Eqns. 3 and 6 to obtain these expressions in terms of the external hydrogen pressure. Then, by inspection one can determine the predicted values of Q and m in terms of the parameters of the different models. For voids growing by grain boundary diffusion, one obtains that:

$$Q = Q_m + Q_{gb} \quad 10a$$

$$m = p \quad 10b$$

For voids growing by power law creep, one finds that:

$$Q = Q_m + nQ_1 \quad 11a$$

$$m = n p \quad 11b$$

where all symbols have been previously defined.

2.0 Equilibrium P_{CH_4} Models

Next, one must determine the appropriate values of Q_m and p for the different bubble growth models. Only the two limiting cases--equilibrium and methane formation control--will be considered. For the case of equilibrium methane pressures, one can find Q_m and p purely from thermodynamic data. One can first write an equilibrium constant K for reaction (i), namely:

$$K = \frac{a_{Fe} f_{CH_4}}{a_{Fe_3C} f_{H_2}^2} \quad 12$$

Then, assuming unit activity for the solid phases Fe and Fe_3C and, because of the relatively low pressures involved, equating the hydrogen pressure to its fugacity, one obtains:

$$f_{CH_4} = K P_{H_2}^2 \quad 13$$

Inserting the methane fugacity coefficient γ and rearranging, one obtains:

$$P_{CH_4} = \frac{K P_{H_2}^2}{\gamma} \quad 14$$

At low methane fugacities, $\gamma \rightarrow 1$ and:

$$P_{CH_4} \approx f_{CH_4} = K P_{H_2}^2 \quad 15$$

In this case, $p = 2$ and Q_m is simply the standard enthalpy change associated with methane formation. It can easily be determined from the temperature dependence of the

equilibrium constant. Using values of this equilibrium constant calculated from the data in Ref. 30 and 31, one finds that Q_m is approximately -114 kJ between 327 and 427°C.

At high equilibrium methane pressures, γ cannot be neglected. As pointed out by Oldfield et al.² it can be estimated from existing equations of state for methane. Although the calculations of Oldfield et al.² were done using a modified ideal gas law, their approach can be applied to more detailed equations of state using numerical techniques. Once γ has been estimated, it can be substituted back into Eqn. 14 to calculate equilibrium methane pressures. Approximate values of Q_m and p can then be determined at different temperatures and hydrogen pressures. Such calculations have been carried out using the semi-empirical equation of state for methane recently proposed by Sevast'yanov and Zykov.²⁹ The calculations are detailed in Appendix A and the results are shown in Figs. 3 and 4. Note that methane gas behaves ideally only at quite low pressures, so one must consider nonideality corrections over most of the region of interest in hydrogen attack. Also observe that even if methane bubbles do contain nearly equilibrium methane pressures, one should not expect Q_m and p to be constant over a wide exposure region.

These values of Q_m and p , in conjunction with Eqns. 10 and 11 and the material parameters of Appendix C can be used to predict the values of Q and m one would observe for

Fig. 3. Apparent Activation Energy Q_m of Methane Pressure in Equilibrium with Fe_3C

Fig. 4. Hydrogen Pressure Exponent p of Methane Pressure in Equilibrium with Fe_3C

bubble growth driven by near-equilibrium internal methane pressures. The resulting numbers, calculated at two representative exposure conditions, are shown in Table 1. The values of Q and m obtained for grain boundary diffusion are substantially different from those predicted by Shewmon,¹⁸ primarily because the former do include detailed fugacity/pressure corrections. Also note that the predicted negative Q for bubble growth by creep is consistent with the simulation results of Sagues et al.¹⁴

One can also estimate a time dependence for bubble growth under these conditions. Since a near-equilibrium internal pressure will not vary with time, the time dependence of bubble growth will be only that caused by the $F(X)$ and $G(X)$ terms in Eqns. 3 and 6. From Fig. 2, $F(X)$ increases by only a factor of two as the bubble radius increases by an order of magnitude. Thus, the rate of bubble expansion should be nearly constant as the bubble enlarges. $G(X)$, on the other hand, is roughly proportional to bubble volume at small bubble sizes and is an even stronger function of bubble size for large bubbles. It increases by more than three orders of magnitude as X increases by one order of magnitude. This means that the expansion rate of a bubble growing by creep must increase rapidly as the bubble expands. Indeed, the simulation results of Sagues et al.¹⁴ showed that bubbles growing

under these conditions expand exponentially with time. These time dependence estimates are also shown in Table 1.

These predicted time, temperature and hydrogen pressure dependences are clearly estimates. Among other things, they assume that growing bubbles contain equilibrium rather than near-equilibrium methane pressures and that the high-purity iron parameters of Appendix C are applicable to the commercial steels used in this investigation. In this respect, the value of the creep stress exponent n is particularly suspect, both because lower values have been reported for iron²⁸ and because the form of the power law expression itself may change at very high stresses.³²

3.0 Formation-Limited P_{CH_4} Models

The case of methane formation kinetics control would occur when the methane pressure inside a growing bubble is far below the equilibrium pressure. Under these conditions, one would expect to eventually reach a quasi-steady-state in which the increase in methane pressure due to methane formation would just balance the decrease in pressure due to bubble expansion. Thus, the pressure inside the bubble would remain nearly constant. In this case, one can write that:

$$\dot{V} = \frac{V}{n_{CH_4}} \dot{n} S$$

Table 1. Predicted Time, Temperature and Hydrogen Pressure Dependences of the Methane Bubble Expansion Rate for Various Growth Models

Factor Controlling Internal P_{CH_4}	Grain Boundary Diffusion	Power Law Creep
Near-Equilibrium Methane Pressure		
High T, Low P_{H_2} (450°C, 3 MPa)	$Q = 132 \text{ kJ}^a$ $m = 0.7^a$ Very weak time dependence	$Q = -32 \text{ kJ}$ $m = 4.8$ $\dot{V}_s \propto e^t$
High P_{H_2} , Low T (380°C, 20 MPa)	$Q = 156 \text{ kJ}$ $m = 0.3$ Very weak time dependence	$Q = 170 \text{ kJ}$ $m = 1.8$ $\dot{V}_s \propto e^t$
Formation Limited Methane Pressure		
Surface Reaction Controlled	$Q = 154 \text{ kJ}$ $m = 0.7^b$ $\dot{V}_s \propto t^2$	$Q = 149 \text{ kJ}$ $m = 1.3^b$ $\dot{V}_s \propto t^2$
Carbon Diffusion Limited	$Q = 129 \text{ kJ}$ $m \approx 0$ Weak time dependence	$Q = 105 \text{ kJ}$ $m \approx 0$ Weak time dependence

^a Q and m are defined by $\dot{V}_s = C_1 e^{(-\frac{Q}{RT})} P_{H_2}^m H(t)$ (Eqn. 8)
where $\dot{V}_s$ is the bulk sample expansion rate.

^bAssuming constant internal methane pressure.

where $\dot{V}$ is the volumetric bubble expansion rate, V is the bubble volume, n_{CH_4} is the number of moles of methane inside the bubble, $\dot{n}$ is the rate of methane generation per unit area and S is the surface area of the bubble. Furthermore:

$$\frac{V}{\dot{n}} = \frac{z R T}{P_{\text{CH}_4}} \quad 17$$

where z is the compressibility factor for methane. Equation 17 and appropriate expressions for $\dot{n}$ and $\dot{V}$ can then be substituted back into Eqn. 16. The resulting expression can be solved for P_{CH_4} as a function of P_{H_2} . Then, by neglecting the relatively weak dependence of z on temperature and methane pressure, one can determine the appropriate values of Q_m and p .

The values of Q_m and p will thus depend on both the bubble expansion process and the kinetic process limiting methane formation. Indeed, it is probably easiest to carry out the analysis described above by saying that the bubble deformation process $\dot{V}$ has some arbitrary activation energy Q_{def} and methane pressure exponent q . Likewise, the rate determining process for methane generation can be said to have some apparent activation energy Q_{gen} and hydrogen pressure exponent s . In addition, since the analysis is only being used to estimate Q_m and p observed during

temperature and pressure jumps, the bubble size dependences of both the deformation and methane generation processes can be neglected. Then, proceeding as above, one finds that:

$$P_{CH_4} = [Z RT]^{\frac{1}{q+1}} \exp\left(-\frac{Q_{gen} - Q_{def}}{q + 1}\right) P_{H_2}^{\frac{s}{q+1}} \quad 18$$

Thus, by inspection:

$$Q_m = \frac{Q_{gen} - Q_{def}}{q + 1} \quad 19a$$

$$p = \frac{s}{q + 1} \quad 19b$$

Then, after inserting appropriate values of Q_{def} and q , one can substitute these expressions back into Eqns. 10 and 11 to obtain expressions for Q and m . For bubbles growing by grain boundary diffusion, one obtains that:

$$Q = \frac{Q_{gen} + Q_{gb}}{2} \quad 20a$$

$$m = \frac{p}{2} \quad 20b$$

For bubbles growing by creep:

$$Q = \frac{n Q_{gen} + Q_l}{n + 1} \quad 21a$$

$$m = \frac{n P}{n+1} \quad 21b$$

The values of Q_{gen} and s will depend on the process limiting methane formation. Following Shewmon,¹⁸ this process may be either the methane surface reaction or carbon diffusion.

3.1 Surface Reaction Limited P_{CH_4}

Consider first the surface reaction case. If one assumes that Eqn. 7 can be extrapolated as necessary, then Q_{gen} and s can be found directly from that expression. Since P_{CH_4} would be far below equilibrium, the back reaction can be neglected. Thus, $s = 1.5$ and Q_{gen} will be the sum of the activation energy of the forward rate constant (56.9 kJ^{19}) and the heat of solution of cementite in α -Fe (77.4 kJ^{30}) or 134 kJ . Using these numbers one can readily predict the values of Q and m for bubble growth. Also, the rate of bubble expansion should increase significantly with time under these conditions. If the internal methane pressure does remain nearly constant then, by Eqn. 16 the volumetric bubble expansion rate will be proportional to the surface area of the bubble available for methane generation. If the bubble grows as a sphere on a ferrite-ferrite boundary, $\dot{V}$ will be proportional to x^2 and the cavity volume will increase as a cubic function of time.

These estimated temperature, hydrogen pressure and time dependences for bubble growth are given in Table 1. The estimates are only as valid as Eqn. 7 at the temperatures and hydrogen pressures of interest, but better data are not available. Even if the extrapolation is not reasonable, though, the values of m should be upper estimates since the rate determining processes for methane generation can only

become less dependent on P_{H_2} at high hydrogen pressures.³³ It is also encouraging to note that the temperature and time dependences for bubble growth by creep given in Table 1 are very similar to those obtained by Shih²⁷ using his detailed simulation program. The predicted Q for creep is also close to the value of 157.7 kJ obtained by Sagues et al.¹⁴

3.2 Carbon Diffusion Limited P_{CH_4}

If, on the other hand, methane generation is limited by the rate of carbon diffusion to the surface of a growing bubble, then Q_{gen} should simply be the activation energy for carbon diffusion in ferrite, or about 84 kJ.³⁴ The rate of methane generation in this case should be nearly independent of the external hydrogen pressure (except at very low hydrogen pressures) since the carbon diffusion gradient will be essentially independent of this quantity. Thus, s (see Eqn. 8) should be approximately zero. These values can then be used to calculate Q and m . The time dependence of the bubble growth rate will be less than that for the surface reaction limited case because the carbon diffusion gradient at the surface of the bubble is likely to decrease with increasing bubble size. One could estimate this time dependence more precisely using a diffusion analysis, but it hardly seems necessary in light of the

microstructural and kinetic results given in subsequent sections. These predicted temperature, hydrogen pressure and time dependences for carbon diffusion limited bubble growth are also given in Table 1.

One can now experimentally measure the temperature, hydrogen pressure and time dependences of the expansion rate of a sample undergoing hydrogen attack and compare the results obtained with those predicted for the cases of Table 1. Such a comparison should enable one to identify the dominant rate determining processes responsible for bubble growth. Furthermore, differences between the observed and predicted results can suggest deficiencies in the existing theoretical models.

EQUIPMENT AND PROCEDURE

The time, temperature and hydrogen pressure dependences of sample expansion during the earliest stages of hydrogen attack were measured using an in-situ capacitance bridge dilatometer. The apparatus is similar to that initially described by White,³⁵ but contained several modifications necessary for making measurements in hot, high pressure hydrogen. The equipment is shown schematically in Fig. 5. The dilatometer is about one order of magnitude more sensitive than previous dilatometers used to study hydrogen attack¹⁴ and can generally measure linear strain rates of about 10^{-7} hr^{-1} in a 25 mm high sample.

1.0 Equipment

The heart of the apparatus is the capacitance transducer assembly located inside the pressure vessel. It consists of a dumbbell-shaped hydrogen attack specimen about 25 mm high, a cylindrical cage assembly and a fixed top electrode. Both the top electrode and the sample are electrically insulated from the cage by high-purity alumina washers. Together, the sample and top electrode form a parallel plate capacitor which is shielded by the cage

Fig. 5. Dilatometric Apparatus

assembly. The initial gap between the sample and top electrode varied from run to run, but was typically about 0.1 mm. This transducer fits inside a small, externally heated, austenitic stainless steel pressure vessel.

As a sample was exposed to hot, high pressure hydrogen in the dilatometer, it began to expand. This expansion decreased the gap between the two capacitor plates and increased the capacitance between them. This increase was measured using a General Radio Model 1615-A capacitance bridge. A 17 V, 1 kHz AC signal from the audio oscillator was used to drive the bridge circuit, and the lock-in amplifier (Ortec Model 9501) served as the detector in that circuit. The output of the amplifier was then fed to the strip-chart recorder. Coaxial cables were used throughout the system, and all components of the capacitance circuit were grounded only to the pressure vessel. This vessel, in turn, was grounded to the house electrical ground. Temperature measurements were made using a Type K chromel-alumel thermocouple located inside the cage assembly as close to the sample as possible.

The role of the amplifier and chart recorder in this circuit warrants a brief comment. Bridge circuits are generally designed to make discrete measurements of component impedance at null signal. For the long-term tests (>1000 hrs) of this study, however, it was much more

desirable to have a continuous impedance vs. time record. A self-balancing bridge would have been ideal for this purpose, but it was not available. Both experiment and equivalent circuit analysis, however, showed that deviations from null signal in the bridge circuit were linearly proportional to the impedance difference between the standard and unknown arms of the bridge. Accordingly, for small changes in capacitance, one could continuously record the output voltage from the detector and then use this trace to determine the unknown capacitance as a function of time. The bridge and chart recorder were used in this manner throughout the investigation.

1.1 The Cage

The transducer assembly is probably the most critical part of the entire apparatus. It is shown in more detail in Fig. 6. The insulators were made by cutting thin wafers from alumina tubes having appropriate diameters. Stainless steel screws were used to fasten the capacitance lead to the specimen and the specimen to the cage bottom. Similar screws (not shown) were used to fasten the cage assembly together. The cage body contained four large (12 mm x 12 mm) equally spaced cut-outs which are also not shown. These windows allowed free hydrogen entry into the cage and

Fig. 6. Cage Assembly

provided convenient feed-throughs for the capacitance and thermocouple leads.

Two different cage assemblies were actually used during the investigation. Both had the geometry shown in Fig. 6, but the cage and top electrode in the first assembly were made of decarburized carbon steel, whereas those in the second assembly were made of 316 stainless steel. The decarburized cage, since it was metallurgically similar to the specimen, minimized both thermal noise in the transducer and transients after temperature and pressure jumps. Unfortunately, it could potentially undergo a small amount of hydrogen attack expansion after long exposure times. The stainless steel cage was clearly inert but had different thermal expansion and hydrogen solubility characteristics than the specimen. These differences reduced the overall sensitivity of the apparatus and compounded the difficulties involved in interpreting transient expansion data. Nevertheless, most runs were done with the stainless steel cage.

Particular care was needed to insure that the top surface of the specimen and the bottom surface of the top electrode in the cage were nearly parallel for each dilatometric run. Since the cage completely surrounded the capacitor plates after assembly, one could only do this by making each of the critical components as nearly

parallel as possible before assembly. This was done as follows: First, the top electrode and appropriate insulators were fastened to the cage top and the unit was ground until the bottom surfaces of the electrode and the cage top were coplanar. Next, the cage body was ground until micrometer measurements showed that its top and bottom surfaces were within 5 μm of being parallel. The alumina insulator separating the sample from the cage bottom was then cut to the same thickness tolerance using a low speed diamond wafering saw and the top surface of the cage bottom was ground flat. All grinding was done through 600 grit paper using standard metallographic techniques. Finally, the top electrode surface was polished using 1 1/4 μm diamond paste. This preparation insured that the top electrode surface was reasonably parallel to the top of the alumina insulator resting on the cage bottom. Then, by making sure that the sample was parallel, one could insure that the top of the sample would be parallel with the top electrode.

1.2 The Pressure Vessel

The transducer assembly of Figure 6 fit inside a 0.3 l capacity 316 stainless steel pressure vessel manufactured by High Pressure Equipment Co. of Erie, PA. The lower part of this vessel was heated externally by a furnace containing two semi-circular heating elements having a combined

maximum output of 1.5 kW. Maximum power to these elements was controlled by a manually adjustable variac. Furnace temperatures were regulated by a Barber-Coleman Model 543B time-proportioning controller. Prepurified tank hydrogen (nominally 99.95% H₂, dew point <-60°C) was supplied to the pressure vessel through a 316 stainless piping system. This system could also be used to backfill the vessel with low-pressure nitrogen or to evacuate it with a mechanical pump.

The transducer was suspended in the hot zone of this pressure vessel using a small stainless steel bracket fastened to the vessel lid. Coaxial leads running from the transducer to this lid were made by stringing ceramic beads over chromel wire and then threading this insulated wire through grounded stainless steel tubes. Separate Conax electrical conductor sealing glands containing Teflon sealants were then used to run the leads out of the vessel. A similar Conax transducer gland was used as a pressure feed-through for the thermocouple wires. These three Conax fittings were raised up off the top of the vessel using 50 mm hex long nipple extensions to avoid overheating the sealants. Once outside the vessel, the capacitance leads were connected to conventional coaxial cables using rigid aluminum junction boxes securely fastened to each Conax fitting.

2.0 Specimen Preparation

All dilatometric runs were carried out using samples of fully normalized electroslag refined A516 steel. The steel was obtained in the form of 50 mm thick plate and had the following composition (in weight %): 0.29% C, 1.04% Mn, 0.21% Si, 0.003% S, 0.14% P, 0.13% Cr, 0.18% Ni, 0.24% Cu, 0.05% Mo, 0.057% Al and 0.002% V. Dumbbell-shaped samples were machined from this steel such that the long axis of the dumbbell was perpendicular to the rolling plane of the plate. This somewhat unusual sample geometry minimized the distances required for hydrogen diffusion while giving adequate capacitor surface area. The top and bottom surfaces of this sample were ground using standard metallographic techniques until micrometer measurements showed that the two surfaces were within 5 μm of being parallel and both surfaces had been finished through 600 grit paper. The top surface was then further polished using 1 $\frac{1}{4}$ μm diamond paste. Next, the specimen was encapsulated in Vycor under about 50 kPa H_2 , austenitized at 920°C for one hour and air cooled in the Vycor capsule. This treatment generally resulted in the specimen having an average ASTM grain size of 8 to 9. After the heat treatment, the top surface of the specimen was briefly polished with 1 $\frac{1}{4}$ μm diamond abrasive to remove surface debris, but was not subjected to any other grinding or machining operations before being installed in the dilatometer.

3.0 Procedure

After the sample and cage assembly had been prepared as described above, they were cleaned ultrasonically in ethanol and assembled. Particular care was taken to insure that the electrode and all mating surfaces remained clean during assembly. A small amount of Fel-Pro lubricant was used on the screws holding the cage top and bottom to the cage body, but no lubricant was used on either of the screws touching the specimen. The cage assembly was then fastened to its support bracket, the pressure vessel capacitance leads were connected and the thermocouple was positioned inside the cage. Finally, crinkled aluminum foil was wrapped around the cage body as a convection shield and Fiberfax refractory batting was packed loosely around the foil.

A small amount of titanium sponge was placed in the bottom of the pressure vessel as an oxygen getter. The transducer assembly was then inserted into the vessel, additional Fiberfax insulation was packed into the "dead space" above the cage and the vessel was sealed. After being evacuated and backfilled with nitrogen three times, the vessel was evacuated and pressurized with hydrogen and the system was then checked for leaks using a Taguchi gas sensor.³⁶ If no leaks were found, it was vented to about 0.3 MPa H_2 , heated to about 450°C and held at that

temperature for one hour to allow surface oxides on the specimen to decompose. The temperature and hydrogen pressure were then adjusted as necessary to begin the run.

Two types of experimental runs were carried out with the dilatometer. The earliest studies measured only the rate of sample expansion at a given temperature and hydrogen pressure as a function of time. Different samples were then used to observe the expansion kinetics under different exposure conditions. These experiments clearly demonstrated that hydrogen attack induced sample expansion does occur during the incubation period preceding rapid hydrogen attack. These runs, however, were quite long. In addition, because of possible variations in bubble density between samples, they could not provide very satisfactory information about the temperature and P_{H_2} dependences of the methane bubble growth rate.

Later runs used temperature and pressure jump measurements on a single sample to study bubble growth. These experiments involved measuring the rate of hydrogen attack at some initial temperature and pressure and then rapidly changing the hydrogen temperature or pressure to a new value and measuring the new expansion rate. A number of these jump measurements were carried out on each sample. To insure that the number of methane bubbles did not change appreciably during the jumps, most samples were

given a nucleation pretreatment by exposing them to high pressure, low temperature hydrogen for at least several hours after the deoxidation period. Specific treatments used for each run are given in Appendix B.

3.1 Data Reduction

In both the time dependence and jump runs, the rate of sample expansion during each measurement interval was determined from the capacitance of the transducer assembly and its time derivative. As discussed previously, the chart recorder provided a capacitance vs. time trace for the transducer cell. This trace was calibrated by measuring the pen deflection produced by a known capacitance change on the standard side of the bridge circuit so it could be calibrated using the standard capacitors of the bridge. A visually estimated straight line was then drawn through the trace over various intervals and the slope of this line was used to calculate the rate of capacitance increase due to sample expansion. Since the capacitance trace contained short-term thermal noise, the slope measurements were usually made over at least a five hour period; intervals of up to 10 hours were used whenever possible. The capacitance at the midpoint of each slope interval was also calculated. Thus, the raw data for each run consisted of a number of capacitance slope and

mean capacitance values measured at different times during the run. In the time dependence runs, each of these times represented different amounts of total sample expansion, whereas in the temperature and pressure jump runs the times represented both different exposure conditions and different amounts of expansion.

These data were then used to calculate the expansion rate and the total expansion of the sample. First, the transducer capacitance was used to determine the gap g between the sample and the fixed electrode. White³⁵ has given the following expression for the capacitance C of a circular parallel plate capacitor such as the one used in this investigation:

$$C = \frac{k \epsilon_0 \pi R^2}{g} + \frac{k \epsilon_0 \pi R w}{g + .22w} \left(1 + \frac{w}{2R}\right) \quad 22$$

where k = Dielectric constant

ϵ_0 = Permittivity of free space

R = Radius of the top electrode

w = Gap width between top electrode and surround guard ring

This equation was solved for g as a function of C to obtain:

$$g = -\frac{A}{2} + \frac{D}{2C} + \frac{1}{2} \sqrt{\left(A - \frac{D}{C}\right)^2 + \frac{4A\theta}{C}} \quad 23$$

where $A = .22w$

$$D = \theta \left(1 + \frac{w}{R} + \frac{w^2}{2R^2}\right)$$

$$\theta = k \epsilon_0 \pi R^2$$

Equation 23 was then used to calculate g at each measurement interval. The linear strain rate of the sample $\dot{\epsilon}_s$ was then calculated from g and the capacitance slope $\dot{C}$ using the expression:

$$\dot{\epsilon}_s = \frac{1}{L} \frac{g^2 \dot{C}}{\theta} \quad 24$$

where L is the length of the dilatometer specimen. Aside from the normalizing factor $\frac{1}{L}$, this equation is simply a differential form of the standard parallel plate capacitor expression:

$$C = \frac{\theta}{g} \quad 25$$

Finally, the total amount of sample expansion was found by subtracting the calculated sample-electrode gap from the gap at the beginning of the run.

The computer program used for these calculations did attempt to correct for both the dielectric constant of high pressure hydrogen (using the Clausius-Mossotti equation³⁷) and the thermal expansion of the transducer cage (using data from Ref. 38 for the decarburized cage and data from Ref. 39 for the stainless steel cage). These corrections, though, did not completely compensate for the step function changes in capacitance observed during temperature and pressure jumps. Thus, to calculate total sample expansion during the jump runs, the program assumed that no sample expansion occurred during a jump. This was

clearly an approximation, but, because of the short times involved, it seemed a reasonable one.

The reduced data from the various runs is shown in Appendix B. All of the hydrogen pressures tabulated in this Appendix (and mentioned in subsequent discussions) are absolute rather than gage pressures. This convention was adopted to make the values consistent with the form of Eqn. 9.

3.2 Sources of Error

One would like to assign precise error estimates to the various expansion rate measurements of Appendix B. Unfortunately, the experimental equipment and procedure used to obtain the data makes such estimates difficult, if not impossible. Rather, one can only outline the major sources of error in the investigation and describe the procedures used to control each one. The problem of aligning the specimen relative to the top electrode has already been mentioned and the procedure used to alleviate it has been described. Another problem associated with the transducer was that of controlling short-term temperature fluctuations inside the cage assembly. Optimizing the proportioning band and reset rate on the controller, packing the inside of the pressure vessel with Fiberfax refractory and, whenever possible, insulating the top of

the vessel reduced these fluctuations to a manageable level of about $\pm 0.1^{\circ}\text{C}$ over half an hour. Even at this level, the fluctuations introduced a significant amount of "noise" into the capacitance trace and were the major factor limiting the sensitivity of the dilatometer.

The visual estimating procedure used to average out this thermal noise from the trace was probably a major source of experimental error. Repeated measurements on the same trace suggested that the slope estimates probably had a precision of approximately $\pm 5\%$. In a few cases, errors may have been substantially greater than this due to unusually large amounts of noise in the trace. In addition, slope measurements made during the jump runs may have had a somewhat larger error than this due to the problems of distinguishing between transient and steady-state expansion rates.

The calibration factor for the chart recorder trace also varied noticeably but not systematically with time. This variation was usually about 5% of the mean calibration value, although larger fluctuations (10%) were observed during Run 5. To compensate for this, the calibration factor was measured near each slope interval and this value was used to calculate the expansion rate during the interval. Such a procedure may or may not have satisfactorily corrected for the variation.

EXPERIMENTAL RESULTS

The kinetic data from Appendix B can be used to determine the time, temperature and hydrogen pressure dependences of the earliest stages of hydrogen attack in the ESR steel. The time dependence of the expansion rate was found to be similar in the high temperature, low pressure and the high pressure, low temperature exposure regions, but the temperature and pressure dependences of the expansion rate in the two regions were quite different. Accordingly, the time dependence data will be considered first.

1.0 Time Dependence

Figure 7 shows how the rate of hydrogen attack induced sample expansion was found to vary with time in a specimen exposed to hydrogen at 4.4 MPa H_2 and 455°C. The sample began to expand measurably after only 20 hours exposure and the expansion rate rapidly approached a nearly constant value. The sample continued to expand at this nearly constant but slowing increasing rate for about 220 hours. Then, after the sample had undergone a total linear expansion strain of about 1×10^{-3} , the rate of expansion accelerated sharply, corresponding to the onset of classical

Fig. 7. Observed Expansion Rate as a Function of Time (Run 6)

hydrogen attack behavior. Similar behavior was observed in samples exposed to hydrogen in the high pressure, low temperature region of the Nelson curve, although at high pressures the rapidly accelerating rates initiated at much smaller expansion strains--typically 4 or 5 x 10⁻⁴.

The rapidly accelerating expansion rate shown in the latter portion of Fig. 7 is approximately what one would expect based on the earlier dilatometric studies of hydrogen attack done by Sagues¹⁴ and Westfal and Worzala.⁴⁰ Neither of these investigators, though, reported the initial, nearly constant rate expansion shown in Fig. 7. Presumably, their apparatus did not have the sensitivity necessary to detect it.

This initial sample expansion during the classical "incubation period" for hydrogen attack was observed repeatedly throughout the investigation. All specimens began to expand measurably and at a nearly constant rate shortly after they were exposed to hot, high-pressure hydrogen. In most cases, this expansion began after 20 to 30 hours exposure. Some samples, though, began to show hydrogen attack after only 3 or 4 hours exposure to hydrogen at 17.3 MPa and temperatures above 400°C. Thus, if a true incubation period for hydrogen attack does exist, it must be very short, except, perhaps at very low hydrogen pressures. This observation is similar to that reported by

Sundararajan and Shewmon⁴¹ in HSLA steels. It is also qualitatively consistent with the work of Westfal and Worzala,¹⁷ who found that intragranular methane bubbles in steel appeared to nucleate immediately on exposure to a hydrogen attack environment.

It is worth noting that the transition from the nearly constant to the rapidly accelerating rate shown in Fig. 7 need not correspond to a change in the basic sample expansion process. Probably the easiest way to see this is to replot the data of Fig. 7 on semi-logarithmic axes as shown in Fig. 8. On this graph, note that all of the data for times less than about 330 hours appear to lie on one reasonably straight line. No distinct change of slope occurs at about 220 hours. One could observe the same continuity between the two expansion regions by plotting the expansion rates observed during Run 6 as a linear function of the amount of total expansion. This graph is not shown, but can easily be obtained from the data of Appendix B. Such a graph shows no obvious break in the curve at a sample expansion of 1×10^{-3} . Thus, the form of Fig. 7 may simply result from one sample expansion process which varies weakly but exponentially with time, rather than from two competing expansion processes.

Fig. 8. Semi-Log Plot of Expansion Rate as a Function of Time (Run 6)

2.0 Microstructural Development

Figures 9, 10 and 11 show the development of methane bubbles in a steel specimen given a nucleation pretreatment at 17.2 MPa H_2 and 355°C for 10.5 hours and then exposed to hydrogen at 17.2 MPa and 400°C. The photographs were obtained by repeatedly exposing a single sample to hydrogen in the dilatometer, sectioning it for metallography, and replacing it in the pressure vessel. Each metallographic section was then mechanically polished, etched heavily with Nital, repolished, and etched lightly with 1% Nital. The figures show that one can, in fact, observe methane bubble growth in steels during the initial stages of sample expansion. As shown in Fig. 9, one can begin to see very small methane bubbles (for example at A) after exposure times of only 58 hours and sample expansion strains of only 1.9×10^{-4} . Although these bubbles are not particularly obvious, similar features were not observed in unexposed samples. After 99 hours exposure ($\Delta l/l = 4.1 \times 10^{-4}$) one can clearly see individual bubbles, although most are still quite small. Careful observation of this section also revealed that a few fissures had begun to form after this amount of exposure. This is not surprising since rapidly accelerating expansion rates were usually observed in samples at $\Delta l/l = 4 \times 10^{-4}$ under high pressure exposure conditions. After 123 hours exposure ($\Delta l/l =$

Fig. 9. ESR Steel Specimen exposed to hydrogen at 17.2 MPa and 400°C for 58 hours.

Fig. 10. ESR Steel Specimen exposed to hydrogen at 17.2 MPa and 400°C for 99 hours.

Fig. 11. ESR Steel Specimen exposed to hydrogen at 17.2 MPa and 400°C for 123 hours.

6.5×10^{-4}) methane bubbles in the specimen were quite numerous and obvious. In addition, the polished section showed a rather extensive network of fissures near the exterior surfaces of the specimen, although these are not shown in the micrograph.

These photographs, especially Fig. 11, also illustrate that methane bubbles develop preferentially on cementite particles in the ESR steel. The same trend can be seen in Fig. 12, which shows the bubble structure observed in a specimen exposed to hydrogen at 6.4 MPa H_2 and 450°C for 153 hours. This strong correlation between methane bubbles and cementite (either as pearlite or grain boundary carbides) in this steel has been noted previously,¹³ and it was observed in all of the dilatometric samples investigated. Also, note that Figs. 11 and 12 both correspond to relatively late stages of bubble growth, but show no evidence of decarburized ferrite rings around the bubbles. Thus, if such rings do form during discrete bubble growth, they must be thin enough to have been removed by etching.

3.0 Incubation Period Kinetic Results

The data from the temperature and pressure jump runs can be used to determine the temperature and pressure dependences of the bubble expansion rate during the early stages of growth. Ideally, one could determine the

Fig. 12. ESR Steel Specimen exposed to hydrogen at 6.4 MPa and 450°C for 153 hours.

apparent activation energy Q and hydrogen pressure exponent m for bubble growth simply from the ratio of the sample expansion rates before and after various jumps. In practice, however, this was not very satisfactory since the jump data contained a large amount of fairly random error. Instead, the data were analyzed by assuming that the initial, nearly constant expansion rate observed in a sample was, in fact, independent of the amount of total expansion. This approximation allowed Q and m to be determined by regression analysis. Thus, the assumption actually corresponded to saying that the errors averaged out of the data by the regression analysis were larger than those introduced by the expansion-independent rate assumption.

Except for a few data points specifically mentioned later, all of the jump data were obtained during the incubation period preceding rapid attack. During the jump runs, the sample expansion rate at a given temperature and pressure increased by only a factor of 2 or 3 over the duration of the incubation period. That is, if one measured the initial expansion rate of a sample, then made a number of temperature and pressure jumps and finally returned to the initial exposure conditions just before reaching the onset of rapid attack, there would be only a factor of 2 or 3 difference between the initial and final rates. Accordingly, the error introduced by

assuming a strain independent expansion rate during the incubation period was generally quite small.

Run 3 was an exception to this general behavior. For some reason, the expansion rates observed during this run showed a pronounced sample expansion dependence. In order to normalize out this variation before regression analysis, the expansion rates were assumed to vary linearly with expansion strain and the expansion rates observed at 1.93 MPa H_2 were used to evaluate the constants in this linear function. Accordingly, the expansion rates plotted in Fig. 18 are actually normalized values. The actual measured expansion rates are given in Appendix B.

3.1 Transients

Before considering the results obtained from the jump experiments, a brief comment should be made about transients. Nearly constant sample expansion rates were sometimes not observed immediately after a change in hydrogen exposure conditions during the jump runs. In these cases, the observed expansion rate varied with time but slowly approached the steady state value characteristics of the new exposure conditions. These transient intervals sometimes lasted up to two days and were a particular problem at low sample expansion rates. They were most noticeable in the high temperature, low pressure exposure region. The types

of transients typically observed are shown in Tables 2 and 3. The shape of the transients shown on these tables represents the shape of the capacitance vs. time trace after a jump. As expected, the trace was roughly convex after a jump to exposure conditions resulting in a slower expansion rate and concave after a jump to exposure conditions resulting in a faster expansion rate. The ratio of the expansion rate before to that immediately after a jump was generally about one, although in some cases the capacitance actually decreased immediately after the jump. Also, from Table 3, note that the observed expansion rate increased slightly near the end of the transients caused by pressure drops. This acceleration, though slight, was consistently observed.

The source of these transients was not established. They may have indicated that some part of the hydrogen attack process cannot rapidly adjust to changes in the external environment. Alternatively, they may have been associated with some part of the transducer assembly other than the specimen. During later runs, for example, they may have been caused by the slow equilibration of the stainless steel cage with the hydrogen atmosphere.

The reduced data of Appendix B contains both transient and steady-state expansion data. A conscientious attempt was made to include only the post-transient data

Table 2. Temperature Jump Transients Observed During the Incubation Period (Run 5)

Initial Temp (°C)	Final Temp (°C)	P _{H2} (MPa)	Length (hrs)	Shape	Ratio ^a
450	467	2.51	(No Obvious Transient)		
467	430	2.51	16		1.15
430	448	2.51	19(?)	b	.
449	430	2.51	.	b	1.50
431	408	2.51	35		1.15
407	431	2.51	5		.
431	451	2.51	(No Obvious Transient)		

^aRatio is the ratio of the expansion rate observed before the jump to that observed immediately after the jump.

^bThe transient was not particularly evident.

Table 3. Pressure Jump Transients Observed During the Incubation Period (Run 5)

Initial Pressure (MPa)	Final Pressure (MPa)	Temperature (°C)	Length (hrs)	Shape	Ratio ^a
2.86	3.20	450	22.5		.
3.20	3.89	449	12.5		1.38
3.89	4.41	448	5.8		.79
4.38	3.89	448	20.		.80
3.89	3.20	450	50.		1.07
3.20	2.51	449	46.		.96
2.51	1.83	449	(Transient Hard to Determine)		
1.83	2.51	449	7.5		.
2.51	3.20	449	(No Obvious Transient)		
3.20	3.89	450	5.8		.71
3.89	4.45	450	(No Obvious Transient)		
4.45	2.51	450	20+		1.11

^aRatio is the ratio of the expansion rate observed before the jump to that observed immediately after the jump.

in the results presented in the next section. Unlike the transients, these steady-state rates were fairly reproducible and the measured rate at a given temperature and pressure was nearly the same when approached using jumps from higher and lower expansion rates.

3.2 Temperature and Pressure Dependences

The temperature and pressure dependences observed in the high temperature, low pressure region of the Nelson curve are shown in Figs. 13 and 14. Each point on the graph represents the steady-state expansion rate after making a jump in the hydrogen exposure conditions. Pairs of points at one exposure condition generally mean that the condition was approached using jumps from both higher and lower expansion rates. Both of these figures are based on data from Run 5, although other data obtained during Run 4 did indicate similar values for Q and m . Figure 13 shows that at 2.5 MPa H_2 and temperatures between 400 and 470°C the hydrogen attack process had an apparent activation energy Q of 115 ± 9 kJ. (The $\pm$ value on this and succeeding regression parameters represents the calculated standard error of the regression estimate.) Systematic studies were not carried out above 470°C, but one measurement made at 480°C during Run 4 did suggest

Fig. 13. Hydrogen Attack Rate Vs. Temperature-High Temperature, Low Pressure Region (Run 5)

Fig. 14. Hydrogen Attack Rate Vs. Pressure
High Temperature, Low Pressure Region
(Run 5)

that Q may decrease fairly rapidly at higher temperatures. Figure 14 shows that the rate of hydrogen attack expansion in this region is also proportional to $P_{H_2}^{1.9}$, where the standard error of the estimate on this exponent was found to be 0.2. As indicated, this value was obtained on a sample exposed to hydrogen at 450°C and pressures ranging from 1.7 to 4.3 MPa.

A much higher value of Q and a much lower value of m were observed in the high pressure, low temperature exposure region. Figure 15 shows the temperature dependence of the expansion rate which was observed between 365 and 450°C at 17.3 MPa during Run 2. The apparent activation energy in this region, 210 ± 13 kJ was almost twice that found at higher temperatures and low hydrogen pressures. Similar high values of Q were observed at both 10.4 and 17.3 MPa H_2 during Run 4. The hydrogen pressure dependence observed at 385°C in this high pressure region during Run 7 is shown in Fig. 16. At pressures above 5 MPa, the rate of sample expansion was found to be proportional to $P_{H_2}^{0.6}$. At lower pressures, the expansion rate was a somewhat stronger function of hydrogen pressure and was proportional to $P_{H_2}^{1.2}$. The increased pressure dependence in this region is to be expected. It simply shows that at low hydrogen pressures one moves back into the high temperature, low pressure exposure region of hydrogen attack.

Fig. 15. Hydrogen Attack Rate Vs. Temperature
High Pressure, Low Temperature Region
(Run 2)

Fig. 16. Hydrogen Attack Rate Vs. Pressure
High Pressure, Low Temperature Region
(Run 7)

Probably the easiest way to summarize the regression analyses of the previous four figures is to use them to calculate a set of constant expansion rate curves as a function of hydrogen temperature and pressure. Such curves are shown in Fig. 17. They show sample expansion rate contours for the A516 steel at various temperatures and pressures. The high temperature, low pressure curves were calculated by combining the regression results shown in Figs. 13 and 14 into one expression, and the high pressure, low temperature curves were obtained by similarly combining the results shown in Figs. 15 and 16.

The grey line represents the separation between the high temperature, low pressure and high pressure, low temperature regions of the diagram. It was calculated simply by equating the two expansion rate expressions. Accordingly, the contour lines are not particularly accurate near this dividing line. The position of the line is somewhat surprising, since it indicates that the high temperature, low pressure region extends over to very high pressures at high temperatures. Nevertheless, this result is consistent with experimental observations. Figure 18 shows the hydrogen attack expansion rates observed at 443°C during Run 3 as a function of hydrogen pressure. As expected, the expansion rate is a strong function of hydrogen pressure at low pressures. Note, though, that the pressure dependence only

Fig. 17. Calculated Constant Rate Curves for Hydrogen Attack in A516 Steel

Fig. 18. Hydrogen Attack Rate Pressure Dependence at High Pressure - High Temperature, Low Pressure Region (Run 3)

decreases slightly at pressures above 3 MPa. Consistent with Fig. 17, the rate is still proportional to $P_{H_2}^{1.4}$ even at 17.3 MPa. The position of the grey division line on Fig. 18 is also reasonably consistent with the lower temperature data of Fig. 16. This figure indicates that the actual transition between the high and low pressure region should occur at about 4 MPa H_2 at 385°C. Figure 17 predicts this transition at 5 MPa H_2 .

4.0 Rapid Attack Kinetic Results

In addition to the incubation period bubble growth data just presented, a limited amount of kinetic data was obtained during the rapidly accelerating portion of the expansion rate vs. time curve. These results are shown in Table 4. Unlike those of the preceding section, these values of Q and m were calculated directly from the observed rates immediately before and after a change in exposure conditions. This method was adopted because the expansion rates in this region clearly varied with time and because transients were generally not observed. (When obvious transients were noticed, they were simply disregarded and the calculations were based on the rate immediately after the transient.)

Although the data show a large amount of scatter, the high pressure, low temperature results clearly indicate a

Table 4. Temperature and Pressure Dependences Observed During Rapid Hydrogen Attack.

Temperature Jumps				
Run	Hydrogen Pressure (MPa)	Initial Temperature (°C)	Final Temperature (°C)	Q (kJ)
4	2.5	471	449	130
7	17.3	410	386	104
7	17.2	385	358	119
7	10.4	358	387	160
7	10.4	387	359	182
7	10.4	359	386	145
7	17.3	386	358	163
Mean Value =				145

Pressure Jumps				
Run	Temperature (°C)	Initial Pressure (MPa)	Final Pressure (MPa)	m
4	471	2.5	4.9	2.3
4	471	4.9	2.5	1.8
4	449	2.5	1.5	2.4
4	468	1.5	3.5	2.4
4	358	17.3	10.5	1.7
7	387	10.4	17.3	2.2
7	387	17.3	10.4	2.3
7	386	10.4	17.3	1.8
7	358	17.7	10.4	1.8
7	359	10.4	7.0	2.0
Mean Value =				2.1

stronger pressure dependence and a somewhat lower apparent activation energy than that observed during the incubation period. The high pressure, low temperature activation energy of approximately 145 kJ is comparable to that observed by both Sagues¹⁴ (170 ± 20 kJ) and Sundararajan and Shewmon⁴¹ (160 kJ) during rapid attack. Because of the large scatter shown in Table 4, one clearly cannot say that the value obtained in this study is substantially different from those obtained by the earlier investigators.

DISCUSSION

The kinetic data in the previous section can provide information about a number of aspects of methane bubble growth during the early stages of hydrogen attack. A comparison of the bubble growth data with earlier incubation period studies such as those of Weiner¹⁶ illustrates how the dilatometric data can be used to predict incubation times for rapid attack. The dilatometric results also provide useful information about the kinetic processes controlling the early stages of bubble growth during hydrogen attack.

1.0 Incubation Time Calculations

If the linear expansion strain required to initiate rapid hydrogen attack in a given steel were independent of hydrogen temperature and pressure, one could calculate the incubation time for rapid attack directly from the constant rate curves developed in the previous section. It would be given simply by the strain for rapid attack divided by the predicted expansion rate at the temperature and pressure of interest. Unfortunately, this expansion strain is not a constant. In the A516 steel, it varied from about

4×10^{-4} at high pressures and low temperatures to about 1.3×10^{-3} at high temperatures and low hydrogen pressures.

This investigation did not include a systematic study of this rapid attack expansion strain variation. Such data could be obtained quite easily, though, with the dilatometer and would be a useful supplement to the constant rate curves of Fig. 17.

This variation of the rapid attack strain with exposure conditions is hardly surprising. It probably means that either the average bubble growth required for coalescence or the average methane bubble spacing varies with hydrogen exposure conditions. Bubbles having high internal methane pressures will probably coalesce at an earlier stage of growth than bubbles containing lower pressures. Since high hydrogen pressures and low temperatures favor high internal methane pressures,⁷ one would expect coalescence to occur more rapidly in the high pressure region. High equilibrium methane pressures (corresponding to high hydrogen pressures and low temperatures) may also promote high bubble densities because of the increased supersaturation for bubble nucleation. Since closely spaced bubbles will coalesce at a lower $\frac{\Delta V}{V}$ than widely spaced bubbles, variations in bubble density may also lead to variations in the expansion strain preceding rapid attack.

Shewmon¹⁸ used an analysis based on the incubation time studies of Weiner¹⁶ to conclude that the methane bubble density was essentially constant throughout the high temperature, low pressure region of the Nelson curve. This analysis assumed that methane bubble growth in this region was driven by near-equilibrium internal methane pressures, but it did not include detailed fugacity/pressure corrections such as those described in Appendix A. If his analysis is redone using such corrections, one finds that the predicted bubble density will vary by at least an order of magnitude across this region. More importantly, Shewmon's analysis says nothing about methane bubble density in the high pressure, low temperature exposure region. Accordingly, it does not apply for predicting differences in bubble density between the two exposure regions of the Nelson curve. Thus, it is not inconsistent with Shewmon's work to postulate that samples exposed to hydrogen at high pressures and low temperatures will have a significantly different bubble density than those exposed at high temperatures and low pressures.

No attempt was made to determine whether the observed variations in the strain to rapid attack were due primarily to differences in the growth required for coalescence or to variations in bubble density. Such studies would have

involved a large amount of additional work and the results were not essential to the investigation.

2.0 Incubation Period Growth Mechanisms

The dilatometric data also provide information about methane bubble growth processes during the early stages of hydrogen attack. One can finally compare the observed time, temperature and hydrogen pressure dependences of bubble growth with those predicted by the various theoretical models to determine which appear most satisfactory.

Before beginning this comparison, it is appropriate to make a few comments on methane bubble distribution. All of the theoretical growth models assume that a regular array of grain boundary bubbles nucleates at time zero. The microstructures of Figs. 9 through 12 hardly suggest such an array. The bubbles in these photographs appear to be randomly distributed and their number seems to increase with time. On the other hand, arrays of closely spaced bubbles have been reported on fracture surfaces in this same steel,¹³ suggesting that the array model is reasonable.

Also, the dilatometric results indicate that the methane bubble density remained substantially constant during the early stages of attack. The observed sample expansion rate remained nearly constant throughout the incubation period. If the methane bubble density had

increased substantially during this period then the expansion rate per methane bubble would have had to decrease with increasing exposure time. Of the growth models listed in Table 1, only the carbon diffusion limited P_{CH_4} model predicts such behavior. But carbon diffusion should not be rate controlling when methane bubbles form on Fe_3C particles and show no evidence of local decarburization. In addition, the predicted values of Q and m for this rate determining process do not match those observed experimentally. Therefore, the observed sample expansion behavior can be consistent with the theoretical growth models only if the methane bubble density does not increase substantially with time. Both this and the fractographic results suggest that the methane bubble arrays assumed in the theoretical treatments do provide a reasonable first approximation for describing bubble growth in the A516 steel.

2.1 Grain Boundary Diffusion

The kinetic data indicates that the earliest stages of methane bubble growth occur through grain boundary diffusion rather than power law creep. The grain boundary diffusion model predicts that the rate of expansion should be nearly independent of bubble size during the early stages of growth but should accelerate during the later stages of growth. This is the same type of behavior as

that observed during the early stages of hydrogen attack; the sample first expands at a nearly constant rate, but this expansion rate accelerates as bubbles coalesce into fissures. On the other hand, the power law creep models predict that the expansion rate of a bubble should be nearly proportional to the volume of that bubble. Such a strong dependence of the expansion rate on the expansion strain is clearly not in accord with hydrogen attack expansion data such as that shown in Fig. 7.

It is quantitatively reasonable for the initial stages of bubble growth to occur by grain boundary diffusion rather than creep. Probably the easiest way to see this is to use Eqns. 3 and 6 to calculate a transition pressure between the two growth mechanisms. To determine this pressure, one need only equate the two expressions and solve for P_{CH_4} . At pressures lower than the transition value, bubble growth will occur predominantly by grain boundary diffusion, whereas at higher pressures it will occur through power law creep. This transition pressure has been calculated at 350 and 450°C as a function of relative bubble size X using the material parameters of Appendix C. The results are shown in Figure 19.

To use this plot, one must estimate both the bubble size and the internal methane pressure during the early stages of growth. The maximum possible pressure is the

Fig. 19. Transition Pressures for Methane Bubble Growth

equilibrium methane pressure estimated from Appendix A. This pressure at two representative exposure conditions (350°C, 20 MPa H₂ and 450°C, 3 MPa H₂) is also shown on the graph. At 350°C and 20 MPa H₂, Fig. 19 shows that bubbles should grow by grain boundary diffusion at relative bubble sizes less than 0.035 and at 450°C they should grow by grain boundary diffusion until $X = 0.14$. Taking the bubble half-spacing d to be 1 μm , these correspond to bubble radii of 35 and 140 nm respectively.

These transition radii are larger than the initial bubble radius assumed by Shih²⁷ for his simulation work (22 nm) and they are about an order of magnitude larger than the "critical radius" $\frac{2\gamma}{P_{\text{CH}_4}}$ for a stable bubble. In addition, they are on the upper end of the size distribution for discrete methane bubbles (15-100 nm) observed by Natan⁷ in 1020 steels. Furthermore, the transition radii are themselves lower estimates since they assume equilibrium methane pressures and ignore the possible difficulties involved in applying the power law constitutive relation to very small bubbles. Therefore, it is reasonable to expect bubble expansion to occur by grain boundary diffusion during the early stages of growth.

This conclusion agrees with the simulation results of Oldfield et al.,² which also showed that grain boundary diffusion would account for a significant amount of bubble

growth. The result is qualitatively similar to that obtained by Shih,²⁷ although his calculations indicated that the initial grain boundary diffusion interval was too short to account for a significant amount of bubble growth. Shih's model, for example, indicated that the transition radius for bubbles having an initial radius of 21.2 nm would be only 21.3 nm at 350°C and 20 MPa H₂. Two factors appear responsible for this discrepancy between the two results. First, Shih's study did not include detailed fugacity/pressure corrections such as those from Appendix A. Accordingly, bubbles in his model could develop higher internal pressures, which made them more likely to expand by creep. Second, Shih's simulation did not include a surface energy correction term when calculating the driving force for creep. This omission would cause the rate of creep expansion to be overestimated at small bubble sizes.

2.2 High Temperature, Low Pressure Region

The time dependence of the hydrogen attack expansion rate clearly suggests that the initial stages of bubble growth occur by grain boundary diffusion rather than creep, and this is consistent with the expansion rate predicted by Eqns. 3 and 6. Can the observed temperature and hydrogen pressure dependences for bubble growth be explained using this model?

A quick comparison of the experimental results in both the high temperature, low pressure and high pressure, low temperature exposure regions with those predicted in Table 1 shows that the observed and predicted results do not match very well for either the near-equilibrium or surface reaction controlled case. (The carbon diffusion case was previously ruled out, primarily on metallographic evidence.) The experimental results, though, show even less correlation with the power law creep predictions.

Since the observed values of Q and m do not match either of the predicted values for grain boundary diffusional growth, one must determine which of the two cases, if either, is most appropriate. Consider first the high temperature, low pressure exposure region. Here, the observed hydrogen pressure exponent of 1.9 is much larger than the predicted value of 0.7 for surface reaction control. Since 0.7 should be a maximum value if the methane generation surface reaction on ferrite is rate controlling, this process does not appear to be rate determining.

Similar difficulties with surface reaction control are encountered if one hypothesizes that the methane formation reaction occurs on cementite rather than ferrite. From stoichiometry, it is unlikely that the expression for the rate of methane generation of Fe_3C would have a hydrogen pressure exponent greater than 2 since the ratio of the

forward and backward reaction rates must reduce to the equilibrium constant. Thus, by Eqn. 20b, the exponent n for bubble growth would still be ≤ 1.0 . In addition, if methane formation occurred on cementite rather than ferrite one would expect to see some evidence of preferential cementite dissolution around a growing bubble. This dissolution was not observed. Thus, the internal methane pressure driving bubble growth does not appear to be controlled by surface reaction kinetics in this region.

By default, this implies that the methane pressure inside a bubble growing in this exposure region must be a near-equilibrium pressure. Why, then, do the observed and predicted values differ as much as they do? Possibly the actual methane pressure inside a bubble is significantly lower than that in equilibrium with pure Fe_3C at a given temperature and hydrogen pressure. The pressure must be somewhat below the equilibrium value simply because the bubble expands at a finite rate. In addition, the carbon activity in the A516 steel may be significantly below that in equilibrium with pure Fe_3C since the commercial steel contains a number of alloying and tramp elements having a strong affinity for carbon. This reduced activity would significantly lower the equilibrium pressure which could be attained in the A516 material.

If the methane pressure is less than the equilibrium value for pure Fe - C alloys, the necessary nonideality corrections for methane gas will be reduced. This will raise the predicted value of m and decrease the predicted value of Q . In the limit of very low internal pressures, these values will become those predicted for ideal gas behavior, namely $m=2.0$ and $Q=60$ kJ. The observed temperature and pressure dependences do clearly fall between the values given in Table 1 and this limiting case of very low internal pressures. Admittedly, a slight discrepancy still exists between theory and experiment, since the observed pressure exponent suggests a very low internal pressure whereas the apparent activation energy suggests a somewhat higher pressure. Nevertheless, the data are reasonably consistent with a growth model in which bubble expansion occurs primarily by grain boundary diffusion and is driven by "near-equilibrium" methane pressures significantly below those in equilibrium with pure Fe_3C . Such pressures would be time-independent, so the model would also be consistent with the observed time dependence.

2.3 High Pressure, Low Temperature Exposure Region

The weak time and hydrogen pressure dependences observed for bubble growth in this exposure region again suggest that the early stages of bubble growth occur

primarily through grain boundary diffusion. As before, however, the observed results do not match either of the two predicted cases given in Table 1, so one must inquire which, if either, is most appropriate. Shewmon¹⁸ originally suggested that internal methane pressures in this region must be below equilibrium simply because the equilibrium pressures would be extremely high. Using the fugacity/pressure corrections of Appendix A, though, one finds that the equilibrium pressures may not be reasonably large. Thus, this possibility should not be ruled out a priori.

The observed time dependence of the bubble expansion rate in this region is most consistent with a near-equilibrium growth model. One could rationalize the observed dependence in terms of a surface reaction controlled model by saying that the internal methane pressure dropped rapidly enough with time to result in a nearly constant bubble expansion rate. The observed time dependence, however, follows directly from the near-equilibrium model without additional assumptions. Furthermore, it seems unlikely that one would observe the same time dependence of the sample expansion rate in the high pressure, low temperature and high temperature, low pressure regions if the methane pressures in the two regions were controlled by entirely different processes.

If internal methane pressures in this exposure region

are in fact controlled by methane formation kinetics, then the observed and predicted hydrogen pressure dependences would agree quite nicely. The observed value of Q is substantially higher than that predicted by the model. This discrepancy, though, could be rationalized by saying that either the activation energy for grain boundary transport of iron or the activation energy of the methane generation surface reaction must be underestimated. This is very possible. The use of Grabke and Martin's data¹⁹ for predicting the activation energy of the surface reaction did require a large extrapolation to hydrogen attack exposure conditions. The commercial A516 steel also contains impurities such as sulfur and phosphorous which may segregate to growing bubbles. If such segregation does occur, it will retard the methane formation surface reaction⁴² and may change its activation energy substantially. In addition, the methane generation reaction may have occurred on cementite rather than ferrite in this high pressure region. Thus, the observed kinetic dependences for bubble growth can be rationalized in terms of a surface reaction controlled growth model if one assumes that: 1) the rate determining process for bubble growth differs in the two exposure regions of the Nelson curve, 2) the internal methane pressure drops rapidly enough with time

to result in a nearly constant expansion rate and 3) the apparent activation energy for the expansion process is seriously underestimated in Table 1.

It is also possible, though, that the methane pressures driving bubble growth in this exposure region are, in fact, near equilibrium. In this case, one must again assume that the actual pressures driving growth are significantly less than those in equilibrium with pure Fe_3C in order to reconcile the observed and predicted hydrogen pressure dependences. For example, if the actual methane pressure inside a bubble is only 1/5 of that in equilibrium with pure Fe_3C , then the predicted value of m for such a model increases to about 0.8. A decrease in methane pressure alone, though, will still not explain the difference between the observed and predicted values of Q . From Fig. 3, Q_m decreases with decreasing methane pressure. Since the observed Q is already larger than Q_{gb} , reducing the postulated methane pressure inside a bubble will only compound the discrepancy between the observed and predicted Q 's. Accordingly, one must also assume that Q_{gb} , the activation energy for grain boundary transport of iron atoms is significantly underestimated in Table 1. This is possible, since the A516 steel used in this investigation contained various alloying elements and impurities which may have increased the activation energy

for grain boundary diffusion in this material. Since methane bubbles formed on carbide particles, it is also possible that iron diffusion away from the bubbles occurred primarily along ferrite-cementite interfaces. The activation energy for such transport may be substantially different than that for diffusion along ferrite-ferrite boundaries.

If one assumes that the true activation energy for iron transport in the A516 steel is about 230 kJ rather than 173.5 kJ and that the actual methane pressures driving bubble growth are about $\frac{1}{5}$ those in equilibrium with pure Fe_3C , then the predicted Q for bubble growth increases from 156 kJ to 182 kJ. In addition, if these estimated parameters of $Q_{\text{gb}}^{\text{A516}} = 230 \text{ kJ}$ and $P_{\text{CH}_4}^{\text{A516}} = \frac{1}{5} P_{\text{CH}_4}^{\text{Fe}_3\text{C}}$ have any physical basis, they should also apply for bubble growth in the high temperature, low pressure region of the Nelson curve. Using these parameters, coupled with Eqns. 10a and 10b, to predict values of Q and m in the high temperature region, one finds that $Q^{\text{Pred.}} = 144 \text{ kJ}$ and $m^{\text{Pred.}} = 1.5$ at 450°C and 3.0 MPa H_2 . The agreement with the experimental values of $Q = 115 \pm 9 \text{ kJ}$ and $m = 1.9 \pm 0.2$ is not particularly good. Nevertheless, it is noteworthy that one can assume two parameters ($Q_{\text{gb}}^{\text{A516}}$ and $P_{\text{CH}_4}^{\text{A516}}$) and then use the near-equilibrium pressure bubble growth model to obtain moderately good predictions of the time, temperature

and hydrogen pressure dependences of bubble growth in both the high temperature, low pressure and high pressure, low temperature regions of the Nelson curve.

2.4 Alternate Growth Models

Admittedly, the grain boundary diffusional growth model, even with bubble expansion driven by near-equilibrium internal methane pressures, does not provide a totally satisfactory explanation for the observed bubble growth kinetics. A possible explanation for this is that the simple bubble growth model represented by Eqn. 3 may not be totally applicable for describing bubble growth during hydrogen attack. Several authors, including Edward and Ashby⁴³ and Burton⁴⁴ have pointed out that grain boundary cavity growth in real polycrystalline materials requires strain accommodation in the surrounding grains. Eqn. 3 tacitly assumes that this accommodation occurs rapidly so that it can be neglected. This, however, may be a bad assumption. Perhaps the experimental data represent some mixture of bubble growth and strain accommodation kinetics.

Equation 3 also assumes that diffusion of Fe atoms along the surface of a growing bubble is rapid, so that the rate of bubble expansion is determined by the rate of atom transport into the boundary. Chuang et al.,⁴⁵ though, have pointed out that if the ratio of the surface to the

grain boundary diffusivity is small and the applied stresses are large then the surface diffusion step may control the rate of bubble expansion. In this case, the bubble will grow in a crack-like manner and the activation energy for the expansion process will be that for surface diffusion in the material. Such growth should have a stress exponent of either 1.5 or 3.0, depending on the applied stress and the ratio of the surface and boundary diffusion coefficients.

It is unlikely that surface diffusion completely dominates bubble expansion during the early stages of hydrogen attack. Chuang et al.⁴⁵ find that the applied stresses necessary to cause surface diffusion limited bubble growth increase very sharply with decreasing cavity size for small cavities. Accordingly, it is questionable whether the very early stages of growth are likely to be controlled by this process. Furthermore, Geguzin et al.⁴⁶ have reported the activation energy for surface diffusion in iron to be 130 kJ at temperatures between 547 and 857°C. This value, if it can be extrapolated to the somewhat lower temperatures of interest for hydrogen attack, is lower than that required to be consistent with the observed data in either exposure region. It is possible, though, that the observed data represent some mixture of grain boundary and surface

diffusion control. In this case, the relative importance of each process would probably vary with temperature, and one could not expect a simple grain boundary diffusion model to fit the data very well.

2.5 Summary

The kinetic results obtained during this investigation clearly suggest that the earliest stages of bubble growth in the high temperature, low pressure region occur by grain boundary diffusion and are driven by near-equilibrium internal methane pressures. The earliest stages of bubble growth in the high pressure, low temperature exposure region probably also occur through grain boundary diffusion. The observed temperature and hydrogen pressure dependences for bubble growth in this region can be rationalized with either a surface reaction controlled P_{CH_4} or near-equilibrium P_{CH_4} model. The near-equilibrium case has the advantage that one model can then be used to describe bubble growth in both regions of the Nelson curve. This model fits the observed data in both exposure regions moderately well if one assumes that the methane pressures driving growth in the A516 steel are about 1/5 of those in equilibrium with Fe_3C and that the activation energy for Fe transport in the steel is about 230 kJ.

Recent work by Natan⁷ provides additional evidence

that methane bubbles growing during the initial incubation period of hydrogen attack do, in fact, contain near-equilibrium pressures. He was able to measure the methane pressures which actually developed inside Ferrovac E and SAE 1020 steels during hydrogen attack by determining the density loss and amount of methane generated in these steels.

His results showed that very high methane pressures actually do develop inside bubbles during the early stages of growth in the 1020 steels. For example, he observed methane pressures of about 1500 MPa in samples exposed to 10 MPa H_2 at 500°C and pressures of almost 5000 MPa in steels exposed to 10 MPa H_2 at 400°C. These high pressures were observed only during the very early stages of sample expansion. At density losses greater than about 0.2%, the internal pressures dropped sharply with increasing density loss, but then began to level off at density losses greater than about 1.0%. In addition, he found that the internal methane pressure was a strong function of alloy composition; two different 1020 steels having different residual element compositions showed methane pressures which differed by almost a factor of three.

From his results, Natan concluded that the methane pressures driving hydrogen attack were almost always below those in equilibrium with Fe_3C , even during the early

stages of growth. This conclusion, though, was based on estimates of the equilibrium methane pressure obtained simply by dividing the equilibrium methane fugacity by the compressibility factor obtained from the equation of state for methane given by Sevast'vanov and Zykov.²⁹ As pointed out earlier, one can obtain a better estimate of equilibrium methane pressures by integrating a function of the compressibility factor over pressure as was done in Appendix A.

If one compares the experimentally measured pressures given by Natan to those calculated in Appendix A, one finds that the methane pressures measured at very small density changes are not substantially below the calculated equilibrium pressures. In fact, some of the pressures are substantially higher than the calculated values from Appendix A. This discrepancy is probably due to both the relatively crude numerical technique used for calculating the equilibrium pressures and to the formidable experimental difficulties involved in measuring high methane pressures at very small hydrogen attack expansions. Nevertheless, Natan's results do provide experimental support for the claim that near-equilibrium methane pressures can develop inside methane bubbles during the very early stages of hydrogen attack. In addition, his work shows that it is

probably not unreasonable for the A516 steel to develop methane pressures 1/5 of those in equilibrium with pure Fe_3C .

3.0 Rapid Attack Expansion Mechanisms

The limited amount of kinetic data obtained during the rapid attack phase of hydrogen attack showed that the mechanism of sample expansion operating during this interval was clearly different than that responsible for bubble growth during the incubation period. Such a difference is to be expected, since metallographic studies,^{3,4} have shown that sample expansion during this interval is primarily associated with bubble coalescence and fissure propagation rather than with discrete bubble growth. These coalescence and fissure propagation processes are undoubtedly complex, since they must involve interactions between pressurized bubbles and fissures and between the bubbles themselves. In addition, the methane pressures driving bubble expansion probably vary with time, both because the size of the fissures changes markedly and because some of the internal methane is vented to the surface during the later stages of attack.⁷ Together, these factors would make any analytical model of sample expansion during this period extremely complex, much more complex than any of the discrete bubble growth models considered in Table 1.

Nevertheless, it is noteworthy that the experimentally observed time, temperature and hydrogen pressure dependences for sample expansion in this region are similar to those predicted for power law creep expansion of bubbles driven by surface reaction controlled internal methane pressures. This good agreement is probably not entirely coincidental. One would expect internally pressurized fissures to expand predominantly by creep simply because of their large size. Furthermore, the values of Q and m given in Table 1 should not be very sensitive to deformation geometry since they were derived without reference to it. The observed value of m is somewhat larger than that predicted by the simple growth model. The discrepancy between the two values, however, is not too great, and probably just reflects the complex interaction processes suggested above.

It is also reasonable to expect that methane formation kinetics would control the internal pressure during rapid hydrogen attack. During the incubation period, the total volume of methane bubbles is small and the surface/volume ratio of these bubbles is high, so these bubbles can be quickly pressurized to near-equilibrium internal pressures. During bubble coalescence and fissure propagation, though, the amount of void volume increases rapidly and the rate of methane generation may not be able to keep pace with this increase. Furthermore, some of the methane

which does form is vented to the surface and lost.⁷ Both of these processes should lead to a decrease in the average methane pressure driving sample expansion during the later stages of hydrogen attack, and Natan⁷ has observed such a decrease in both Ferrovac E and SAE 1020 steels. This decrease means that the driving pressures must be below equilibrium and hence controlled by formation kinetics.

The conclusion that sample expansion during rapid hydrogen attack occurs primarily through methane formation limited creep is also consistent with the work of previous investigators. Shih⁴⁷ reported observing subgrain formation around growing fissures, suggesting that these fissures expand by creep. In addition, his simulation showed that if a fissure or large bubble expands by creep, the rate of methane generation on ferrite surfaces in that void will not be fast enough to maintain near-equilibrium internal pressures.

The dilatometric study of Sagues et al.¹⁴ also showed that bubble growth in Ferrovac 1020 during the rapidly accelerating stage of attack occurred primarily through power law creep and appeared to be driven by surface reaction controlled internal pressures. Admittedly, these investigators did not report incubation period kinetics preceding this creep-dominated bubble growth interval. Nevertheless, their data must clearly represent rapid

attack rather than incubation period kinetics. The expansion rates which they observed increased sharply with time, which is much more characteristic of rapid attack than incubation period kinetics. The data were also obtained on samples which had undergone prior hydrogen attack expansions of at least 10^{-3} . Finally, although the specimens used for the dilatometric work did contain discrete bubbles rather than fissures, these bubbles were quite large (3 - 30 μm) and had a mean spacing of 65 μm . Thus the relative bubble size X for this work ranged from about 0.05 to 0.5, which is much larger than that estimated for bubbles during the incubation stage of hydrogen attack.

Thus, it appears that sample expansion during rapid attack occurs predominantly by creep, with internal methane pressures being determined by the rate of methane generation. Since this growth process is entirely different than that observed during the incubation period, one might conclude that the end of the incubation period occurs when individual bubbles begin to expand by creep rather than grain boundary diffusion. Based on Fig. 19, one would even expect such a transition at large bubble sizes. Unfortunately, the results of Fig. 8 and similar experiments do not indicate a sharp change in the bubble growth mechanism at the end of the incubation period. Accordingly, it is possible that the end of the incubation period occurs when

bubbles begin to coalesce by grain boundary diffusion into fissures. Then, once these fissures form they expand by creep. Not enough data was obtained in the very early stages of the rapid attack period to make a definite choice between these two possibilities.

CONCLUSIONS

Methane bubble growth clearly did occur during the classical "incubation period" preceding rapid hydrogen attack in normalized A516 steel. This bubble growth attained a nearly constant rate shortly after the steel was exposed to hot, high-pressure hydrogen and continued at this nearly constant rate throughout the incubation period. At the end of the incubation period, the rate of bubble growth accelerated markedly, corresponding to the onset of bubble coalescence and classical hydrogen attack behavior.

The expansion strain at which bubble coalescence (accelerated growth) began was found to vary with exposure conditions. At high hydrogen pressures and low temperatures, it was observed at linear expansion strains of 4 or 5×10^{-4} , whereas at high temperatures and low hydrogen pressures it was found to begin at strains of about 1×10^{-3} . This suggests that either a smaller average methane bubble spacing or a higher bubble internal pressure decreases the amount of bubble expansion required to initiate coalescence in the high pressure region. It probably also explains why the temperature and pressure

dependences observed for bubble growth in this study were not the same as those predicted from the incubation time data of others.

The temperature and pressure dependences for bubble growth during the incubation period were found to be significantly different than those observed during the later rapid attack stage. During the incubation period, the rate of bubble expansion in the high temperature, low pressure region of the Nelson curve was found to be proportional to $P_{H_2}^{1.9 \pm 0.2}$ and to have an apparent activation energy of 115 ± 9 kJ. In the high pressure, low temperature region, the rate of bubble expansion was found to be proportional to $P_{H_2}^{0.62 \pm 0.07}$ and to have an apparent activation energy of 210 ± 13 kJ during the incubation period. Only limited data were obtained during the rapidly accelerating portion of the sample expansion curve, but the expansion rate in this region appeared to have a hydrogen pressure exponent of about 2.1 and an apparent activation energy of roughly 145 kJ at both high and low hydrogen pressures.

The time, temperature and hydrogen pressure dependences of the sample expansion rate during the incubation period strongly suggest that methane bubble growth during this period occurs predominantly by grain boundary diffusion. The very weak time dependence of the expansion rate

at both high and low hydrogen pressures is much smaller than that predicted by power law creep models, but is similar to that predicted for diffusive growth by grain boundary transport. At high temperatures and low hydrogen pressures, the observed temperature and pressure dependences are most compatible with a grain boundary diffusion model in which bubble growth is driven by near-equilibrium methane pressures. The model fits quite well if one assumes that the driving pressures are significantly below those in equilibrium with Fe_3C . Such lower pressures might be expected both because the bubble expands continuously and because the carbon activity in the A516 steel is probably lower than that in equilibrium with pure Fe_3C .

At high hydrogen pressures and low temperatures, bubble growth probably also occurs by grain boundary diffusion, but the processes controlling the internal methane pressure could not be unambiguously identified. Either a near-equilibrium or a surface reaction controlled growth model would explain the observed low pressure dependence, but neither explains the high activation energy. If one assumes that the activation energy for grain boundary diffusion in the A516 steel is about 230 kJ and that the actual methane pressure driving bubble growth is 1/5 that in equilibrium with pure Fe_3C , then the near-equilibrium

diffusional growth model provides a moderately good fit to the observed kinetic results in both regions of the Nelson curve.

The rapid attack data obtained suggest that sample expansion during this interval occurs primarily by methane formation limited creep expansion. The rapidly accelerating expansion rate, higher hydrogen pressure dependence and intermediate activation energy are all consistent with this possibility, and it is in accord with the work of previous investigators. It could not be determined whether the rapid attack phase of hydrogen attack begins when methane bubbles begin to expand by creep rather than grain boundary diffusion or whether fissures simply start to expand by creep after bubble coalescence occurs.

APPENDIX A

Equilibrium Methane Pressure Calculations

The methane fugacity f_{CH_4} in equilibrium with pure cementite at a given temperature and hydrogen pressure can be readily calculated from thermodynamic data. In order to relate this fugacity to the methane pressure during bubble growth, one must also know the fugacity coefficient $\gamma_{\text{CH}_4} = \frac{f_{\text{CH}_4}}{P_{\text{CH}_4}}$. γ_{CH_4} in turn, can be calculated as a function of P_{CH_4} using an appropriate equation of state for methane.

The fugacity of a gas is given by the isothermal relation:

$$RT \, d \ln f = V \, dP \quad \text{A.1}$$

where P and V are, respectively, the pressure and molar volume of the gas and by the condition that f approaches P as the pressure approaches zero. Rearranging Eqn. A.1:

$$\frac{d \ln f}{dP} = \frac{V}{RT} = \frac{z}{P} \quad \text{A.2}$$

where the second equality follows from the definition of the compressibility factor z . But, from the definition of γ :

$$\frac{d \ln f}{dP} = \frac{d \ln \gamma}{dP} + \frac{1}{P} \quad \text{A.3}$$

Substituting A.3 back onto A.2 and rearranging:

$$d \ln \hat{\gamma} = \frac{Z-1}{P} dP \quad A.4$$

Then, integrating both sides and recalling that $\hat{\gamma} \rightarrow 1$ as $P \rightarrow 0$:

$$\ln \hat{\gamma} = \int_0^P \frac{Z-1}{P} dP \quad A.5$$

Oldfield et al.² used this equation, coupled with the equation of state for methane used by Sagues et al.,¹⁴ to estimate equilibrium methane pressures in their study.

Recently, Sevast'yanov and Zykov²⁹ have proposed a semi-empirical equation of state for methane which has been experimentally verified at temperatures up to 400°C and pressures up to about 10^3 MPa. Accordingly, use of this equation of state should provide a better estimate of methane fugacity coefficients than that used by Oldfield et al.² For temperatures greater than twice the critical temperature, the Sevast'yanov-Zykov equation has the form:

$$Z = \frac{\exp\left(\frac{-5y}{3}\right)}{(1-y)^4} - \rho b_O F - \frac{1}{(T^*)^2} \left[1 - \frac{1.5}{(T^*)^2}\right] (\rho b_O)^2 + \frac{(\rho b_O)^4}{2(T^*)^2} \quad A.6$$

where $T^* = T/T_{\text{critical}}$ ($T_{\text{critical}} = 190.9^\circ\text{K}$ for CH_4)

$b_O = 0.0615 \text{ l/m}$ (for CH_4)

ρ = Molar gas density

$y = .25 b_O (B^* + f)$

B^* = Second reduced virial coefficient

$$F = 2.128/(T^* - 0.245)$$

This expression is somewhat cumbersome and it cannot be readily used to calculate γ_{CH_4} by Equation A.5. Accordingly, Eqn. A.6 was approximated by a quadratic expression:

$$z = A(P_{\text{CH}_4})^2 + B(P_{\text{CH}_4}) + C \quad \text{A.7}$$

at each temperature of interest. To do this, Eqn. A.6 was first used to calculate both z and P_{CH_4} at 16 evenly spaced values of ρ corresponding to methane pressures less than about 2000 MPa. A , B and C were then determined by regression analysis of these 16 points. This was done at nine evenly spaced temperatures from 325 to 525°C. The correlation coefficient of each of the 9 regressions was 0.9998. Individual residual errors were generally less than about 5% and were largest at very low methane pressures.

The simple form of Eqn. A.7 enabled it to be substituted back into Eqn. A.5 to obtain an analytic expression for γ_{CH_4} . This analytic expression was used to calculate both γ_{CH_4} and f_{CH_4} for a series of methane pressures at each temperature. The hydrogen pressure in equilibrium with each methane fugacity was then determined using equilibrium constants for methane formation from Fe_3C calculated using the thermodynamic data given in Refs. 30 and 31. These calculations resulted in a table containing

the hydrogen pressures in equilibrium with given methane pressures at each of the nine temperatures of interest. The results of these calculations at three temperatures-- 350, 400 and 450°C--are shown in Figure 20. Note that at high hydrogen pressures the equilibrium methane pressure becomes nearly independent of the external hydrogen pressure. Oldfield et al.² also observed such behavior.

The table of equilibrium methane pressures and corresponding hydrogen pressures was then used to estimate the hydrogen pressure exponent p and apparent activation energy Q_m of the equilibrium methane pressure as a function of temperature and P_{H_2} . At each temperature, an average value of p was calculated over each methane pressure interval using a finite difference expression, and this value was assigned to the (geometric) mean hydrogen pressure over that interval. The values of p obtained in this manner at 350, 400 and 450°C are shown in Figure 4. In order to find Q_m , the equilibrium methane pressure corresponding to given hydrogen pressures of 0.2, 1.0, 3.0, 10 and 20 MPa were first determined from the table using linear interpolation. The average apparent activation energy at each of these pressures was then calculated over each of the eight temperature intervals and was assigned to the temperature at the midpoint of each interval. The results of these calculations are shown in Fig. 3.

The computer programs used to carry out these calculations are given in the last portion of this Appendix. Both were written using the Statistical Analysis System software package developed by SAS Institute Inc. of Raleigh, North Carolina. The first program to calculate the regression coefficients A, B and C is quite straightforward and requires only the temperature T and second virial coefficient BSTAR at each temperature of interest as input data. The second program is somewhat more involved. It requires the equilibrium constant K, the regression coefficients A, B and C, the temperature TEMP and a plotting symbol CODE at each desired temperature as input. It uses these values to build two data sets, MASTER and REGR. MASTER contains methane pressures PCH4, associated equilibrium hydrogen pressures PH2 and the hydrogen pressure exponent p (called N in the program) at each temperature. REGR contains the interpolated methane pressures PCH4R at each hydrogen pressure PCHECK needed to calculate Q_m . LAGPCH4, LAGPH2, CH4LAG and PLAG are lagged variables used for calculating N and PCH4R. Values of Q_m (called SLOPE in the program) are calculated as data set ACT is built from the values contained in REGR. OLDP and OLDT are the lagged variables needed to evaluate SLOPE. The data-check variable CURVE insures that the program does not calculate SLOPE values between points at different hydrogen pressures.

Fig. 20. Calculated Methane Pressures in Equilibrium with Fe_3C

PROGRAMS USED FOR METHANE PRESSURE CALCULATIONS

1. PROGRAM FOR CALCULATING COEFFICIENTS A,B AND C

* PROGRAM TO CALCULATE QUADRATIC Z-PCH₄ CURVES FROM RUSSIAN EQUATION;

DATA MASTER;

INPUT T BSTAR;

TSTAR=(T+273)/190.85;

FCON=2.128/(TSTAR-0.245);

RD=0;

LOOP1: RB=RD*61.5;

Y=0.25*RB*(BSTAR+FCON);

Z=EXP(-1.667*Y**3)/(1-Y)**4-RB*FCON-(TSTAR**2)*(1-1.5/(TSTAR**2))

*RB**2+0.5*(TSTAR**2)*(RB**4);

PCH₄=Z*RU*(T+273)*8.314;

OUTPUT;

RU=RD+0.0025;

IF PCH₄>2000 THEN RETURN;

KEEP T Z PCH₄;

GO TO LOOP1;

CARDS;

325 .1131

350 .1420

375 .1687

400 .1921

425 .2141

450 .2346

475 .2529

500 .2702

525 .2862

TITLE1 REGRESSION ANALYSIS FOR RUSSIAN P-V EQUATION FOR METHANE;

PROC SORT; BY T;

PROC GLM DATA=MASTER; BY T;

MODEL Z=PCH4*PCH4 PCH4;

OUTPUT OUT=NEW PREDICTED=ZHAT RESIDUAL=RESID;

PROC PRINT DATA=NEW; BY T;

PROC PLOT DATA=NEW; BY T;

PLOT Z*PCH4 ZHAT*PCH4=*/O;

LABEL ZHAT=PREDICTED VALUE;

PROGRAMS USED FOR METHANE PRESSURE CALCULATIONS

II. PROGRAM FOR CALCULATING APPARENT ACTIVATION ENERGIES AND PRESSURE DEPENDENCES

* PROGRAM TO CALCULATE EQUILIBRIUM METHANE PRESSURES USING A QUADRATIC;
* POLYNOMIAL FOR Z;

*;

DATA MASTER(KEEP=TEMP CODE PCH4 GAMMA PH2 LPCH4 N SPOT)

REGR(KEEP=TEMP PCHECK PCH4R LPCH4R RTEMP);

INPUT K A B C TEMP CODE;

FILE PRINT;

* THIS PRINTS THE INPUT DATA;

IF _N_=1 THEN LINK TOP;

PUT TEMP 20-25 @32 A : E8.1 @51 B : 9.8 @71 C : 9.8 @90 K : 8.2;

PCH4=1;

PCHECK=.2;

LAGPCH4=.;

LAGPH2=.;

LINK CALC;

PCH4=0;

* LOOPS 1 AND 2 INCREMENT PCH4;

LOOP1: PCH4=PCH4+10;

LINK CALC;

IF PCH4<95 THEN GO TO LOOP1;

LOOP2: PCH4=PCH4+50;

```

LINK CALC;
IF PH2=. THEN RETURN;
IF PCH4<1490 THEN GO TO LOOP2;
RETURN;
CALC: GAMMA=EXP(A/2*PCH4**2+B*PCH4+(C-1)*LOG(PCH4));
PH2=SQRT(GAMMA*PCH4/K);
IF PH2>24 THEN PH2=.;
LPCH4=LOG10(PCH4);
LPH2=LOG10(PH2);
N=(LPCH4-LAGPCH4)/(LPH2-LAGPH2);
SPOT=10**MEAN(LPH2,LAGPH2);
LAGPCH4=LPCH4;
LAGPH2=LPH2;
IF PCHECK>21 THEN GO TO BACK;
IF PH2<=PCHECK THEN LINK LOW;
IF PH2>PCHECK THEN LINK HIGH;
BACK: OUTPUT MASTER;
RETURN;

* LINKS HIGH AND LOW ARE USED TO INTERPOLATE PCH4;

LOW: CH4LAG=PCH4;
PLAG=PH2;
RETURN;
HIGH: PCH4R=(PCHECK-PLAG)/(PH2-PLAG)*(PCH4-CH4LAG)+CH4LAG;
LPCH4R=LOG10(PCH4R);
RTEMP=1/(TEMP+273);
OUTPUT REGR;
IF 4.1<PCHECK THEN PCHECK=PCHECK+5.0;

```

```

IF .96<PCHECK<= 4 THEN PCHECK=PCHECK+2.0;
IF .1<PCHECK<.95 THEN PCHECK=PCHECK+.4;
RETURN;
TOP: PUT ' ' ;
PUT @45 'VALUES USED FOR CALCULATIONS';
PUT @30 'A B AND C ARE ARE COEFFICIENTS IN  $Z=A*PCH4^{**2} + B*PCH4 + C$ ';
PUT ' ' ;
PUT @22 'TEMP' @36 'A' @55 'B' @75 'C' @94 'K';
RETURN;
CARDS;
11997 -5.0E-7 .00597212 .94462550 325 1
4800 -4.7E-7 .00572542 .95400301 350 2
2061 -4.4E-7 .00549964 .96273869 375 3
942. -4.2E-7 .00528812 .96994173 400 4
455.7 -3.9E-7 .00509392 .97686440 425 5
231.7 -3.7E-7 .00491426 .98334895 450 6
123.3 -3.5E-7 .00474520 .98885029 475 7
68.32 -3.4E-7 .00458838 .99415016 500 8
39.29 -3.2E-7 .00444149 .99898083 525 9
PROC SORT DATA=MASTER; BY TEMP;

* THESE STATEMENTS OUTPUT MASTER IN VARIOUS FORMS;

PROC PRINT DATA=MASTER; BY TEMP;

TITLE1 VALUES FOR N DETERMINATION;
LABEL TEMP=TEMPERATURE-DEGREES C;
PROC SORT DATA=MASTER; BY PH2;
PROC PLOT DATA=MASTER;

```

```

TITLE1 EQUILIBRIUM METHANE PRESSURE AS A FUNCTION OF HYDROGEN PRESSURE;
PLOT PCH4*PH2=CODE;
TITLE3 1=325C 2=350C 3=375C 4=400C 5=425C 6=450C 7=475C 8=500C 9=525C;
LABEL PCH4=METHANE PRESSURE-MPA;
LABEL PH2=HYDROGEN PRESSURE-MPA;
PROC PLOT DATA=MASTER;
PLOT N*SPOT=CODE;
TITLE1 APPARENT PRESSURE EXPONENT OF EQUILIBRIUM METHANE PRESSURE;
TITLE2 1=325C 2=350C 3=375C 4=400C 5=425C 6=450C 7=475C 8=500C 9=525C;
LABEL N=PRESSURE EXPONENT;
LABEL SPOT=HYDROGEN PRESSURE - MPA;
PROC SORT DATA=REGR;
BY PCHECK TEMP;

```

* DATA SET ACT CALCULATES APPARENT ACTIVATION ENERGIES;

```

DATA ACT;
SET REGR;
IF PCHECK=.2 THEN SYMBOL='A';
IF PCHECK=.6 THEN SYMBOL='B';
IF .9<PCHECK<1.02 THEN SYMBOL='C';
IF 2.9<PCHECK<3.1 THEN SYMBOL='D';
IF 4.9<PCHECK<5.1 THEN SYMBOL='E';
IF 9.9<PCHECK<10.1 THEN SYMBOL='F';
IF 14.9<PCHECK<15.1 THEN SYMBOL='G';
IF 19.9<PCHECK<20.1 THEN SYMBOL='H';
RETAIN OLDP OLDT CURVE;
IF CURVE=PCHECK THEN OLDT=.;
SLOPE=-.01915*(LPCH4R-OLDP)/(RTEMP-OLDT);

```



```

VALUE=2/(OLDT+RTEMP)-273;
FORMAT VALUE 5.1;
DROP CURVE;
OUTPUT;
OLDP=LPCH4R;
OLDT=RTEMP;
CURVE=PCHECK;
PROC SORT DATA=ACT;
BY PCHECK VALUE;

```

* THESE STATEMENTS OUTPUT ACT IN VARIOUS FORMS;

```

PROC PRINT DATA=ACT;
TITLE1 VALUES FOR ACTIVATION ENERGY DETERMINATION;
LABEL PCHECK=HYDROGEN PRESSURE-MPA;
BY PCHECK;
PROC PLOT DATA=ACT;
PLOT LPCH4R*RTEMP=SYMBOL;
TITLE1 TEMPERATURE DEPENDENCE OF EQUILIBRIUM METHANE PRESSURE;
TITLE2 AT VARIOUS HYDROGEN PRESSURES;
TITLE4 A=.2MPA B=.6MPA C=1MPA D=3MPA E=5MPA F=10MPA G=15MPA H=20MPA;
LABEL LPCH4R=LOG METHANE PRESSURE;
LABEL RTEMP=RECIPROCAL TEMPERATURE;
PROC PLOT DATA=ACT;
PLOT SLOPE*VALUE=SYMBOL;
TITLE1 APPARENT ACTIVATION ENERGY FOR METHANE FORMATION;
TITLE3 A=.2MPA B=.6MPA C=1MPA D=3MPA E=5MPA F=10MPA G=15MPA H=20MPA;
LABEL SLOPE=APPARENT ACTIVATION ENERGY-KJ;
LABEL VALUE=TEMPERATURE-C;

```

APPENDIX B
Reduced Data

RUN 1

NO NUCLEATION PRETREATMENT USED

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
33.6	450.0	6.58	0.00E+00	1.56E-06
39.2	450.0	6.58	1.57E-05	2.37E-06
46.6	450.0	6.58	2.47E-05	2.53E-06
52.1	450.0	6.58	4.34E-05	2.79E-06
57.8	450.0	6.58	5.35E-05	2.68E-06
67.7	450.0	6.58	8.69E-05	2.91E-06
75.2	450.0	6.58	1.16E-04	3.14E-06
78.1	450.0	6.58	1.21E-04	3.73E-06
83.7	450.0	6.58	1.45E-04	3.32E-06
88.8	450.0	6.58	1.59E-04	3.90E-06
94.2	450.0	6.58	1.64E-04	4.07E-06
100.0	450.0	6.58	2.06E-04	4.77E-06
107.4	450.0	6.58	2.43E-04	4.75E-06
112.6	450.0	6.58	2.69E-04	5.26E-06
117.3	450.0	6.58	2.76E-04	5.05E-06
123.8	450.0	6.58	3.31E-04	5.44E-06
126.6	450.0	6.58	3.35E-04	5.58E-06
131.3	450.0	6.58	3.70E-04	5.86E-06
137.5	450.0	6.58	4.07E-04	6.24E-06
140.5	450.0	6.58	4.12E-04	6.21E-06
147.8	450.0	6.58	4.73E-04	6.95E-06
152.4	450.0	6.58	5.14E-04	7.19E-06

RUN 2

NO NUCLEATION PRETREATMENT USED

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
2.7	406.0	17.34	0.00E+00	0.00E+00
11.4	406.0	17.34	3.58E-05	5.60E-06
15.7	406.0	17.34	5.91E-05	6.24E-06
21.0	406.0	17.34	9.23E-05	6.53E-06
26.9	406.0	17.34	1.30E-04	7.09E-06
38.6	406.5	17.34	2.11E-04	7.74E-06
40.3	406.5	17.34	2.25E-04	7.76E-06
41.9	388.5	17.34	2.25E-04	2.96E-06
47.7	386.0	17.34	2.45E-04	2.75E-06
49.4	367.0	17.34	2.45E-04	8.75E-07
56.9	367.5	17.34	2.50E-04	8.73E-07
61.1	367.5	17.34	2.54E-04	6.00E-07
62.0	386.0	17.34	2.54E-04	1.97E-06
65.7	386.0	17.34	2.60E-04	1.96E-06
66.5	404.5	17.34	2.59E-04	6.54E-06
74.8	404.0	17.34	3.09E-04	6.01E-06
84.0	404.0	17.34	3.59E-04	5.74E-06
85.3	373.5	17.34	3.59E-04	1.35E-06
95.8	373.0	17.34	3.74E-04	1.45E-06
97.0	404.0	17.34	3.74E-04	4.43E-06
107.4	404.0	17.34	4.19E-04	5.34E-06
111.9	404.0	17.34	4.43E-04	6.56E-06
113.3	371.0	17.34	4.43E-04	1.02E-06
123.6	370.0	17.34	4.48E-04	8.48E-07
132.2	375.0	17.34	4.50E-04	8.60E-07
134.6	404.5	17.34	4.50E-04	5.66E-06
136.8	405.5	17.34	4.63E-04	5.63E-06
139.2	432.0	17.34	4.62E-04	2.53E-05

RUN 3

NO NUCLEATION PRETREATMENT USED

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
4.6	442.5	18.10	0.00E+00	2.47E-05
90.0	442.0	1.93	6.26E-05	6.24E-07
140.8	443.0	1.00	5.19E-05	4.37E-08
185.7	444.0	1.93	7.07E-05	5.89E-07
210.6	443.5	3.55	1.43E-04	2.91E-06
221.0	443.5	5.27	2.07E-04	5.94E-06
258.2	443.0	3.55	3.33E-04	3.43E-06
263.5	443.5	7.00	3.88E-04	1.06E-05
277.5	444.0	5.27	4.93E-04	8.44E-06
280.7	444.0	5.27	5.21E-04	8.90E-06
317.3	444.0	1.93	5.95E-04	1.19E-06
329.0	443.5	1.93	6.10E-04	1.25E-06
331.6	443.5	10.44	6.70E-04	2.44E-05
334.5	444.0	17.34	7.97E-04	6.36E-05
336.2	444.0	17.34	9.24E-04	8.59E-05
341.7	444.0	7.00	1.04E-03	2.14E-05
389.1	443.0	1.93	1.17E-03	1.96E-06
402.6	443.5	1.93	1.20E-03	2.12E-06
498.6	442.0	1.93	1.30E-03	1.94E-06

RUN 4

NUCLEATION PRETREATMENT: 108 HRS AT 375 C AND 17.3 MPA
HYDROGEN

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
0.0	377.9	17.34	0.00E+00	.
15.8	377.7	17.34	1.29E-05	8.56E-07
17.5	400.6	17.34	1.29E-05	.
26.3	401.0	17.34	3.95E-05	3.95E-06
28.1	355.6	17.34	3.95E-05	.
50.5	354.0	17.34	6.08E-05	4.30E-07
87.2	354.1	17.34	6.96E-05	2.56E-07
91.5	374.3	17.34	6.96E-05	.
134.0	373.1	17.34	1.16E-04	9.40E-07
140.6	380.0	13.89	1.16E-04	.
157.8	379.5	13.89	1.40E-04	1.38E-06
160.6	379.2	10.62	1.40E-04	.
168.6	379.4	10.62	1.51E-04	1.62E-06
169.7	386.1	10.62	1.51E-04	.
181.6	386.7	10.62	1.68E-04	1.89E-06
185.4	374.5	17.34	1.68E-04	.
213.3	376.4	17.34	1.76E-04	8.95E-07
216.5	386.1	17.34	1.76E-04	.
230.3	388.3	17.34	1.99E-04	2.06E-06
231.5	388.3	10.44	1.99E-04	.
241.8	388.9	10.44	2.22E-04	2.55E-06
243.1	388.7	7.00	2.22E-04	.
254.1	387.4	7.00	2.53E-04	2.16E-06
256.9	387.4	3.55	2.53E-04	.
265.9	386.8	3.55	2.74E-04	1.97E-06
281.7	387.8	1.83	2.74E-04	.
307.1	387.3	1.83	3.39E-04	8.43E-07
307.6	387.4	3.55	3.39E-04	.
336.7	387.4	3.55	3.47E-04	3.90E-07
337.8	387.2	17.34	3.47E-04	.
374.3	389.6	17.34	3.72E-04	2.05E-06

. DENOTES VALUES NOT MEASURED FROM THE TRACE

RUN 4 - CONTINUED

141

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
374.7	386.8	1.48	3.72E-04	.
422.6	385.9	1.48	4.64E-04	9.27E-07
424.8	413.3	1.48	4.64E-04	.
447.3	412.0	1.48	4.80E-04	0.00E+00
449.8	414.7	17.34	4.80E-04	.
457.8	414.6	17.34	5.78E-04	1.17E-05
458.0	413.8	10.44	5.78E-04	.
469.4	414.7	10.44	6.76E-04	8.63E-06
470.8	415.7	17.34	6.76E-04	.
471.5	415.7	17.34	6.96E-04	2.06E-05
472.5	415.0	17.34	7.22E-04	2.32E-05
472.6	414.2	10.44	7.22E-04	.
473.5	414.5	10.44	7.27E-04	1.19E-05
474.7	387.5	10.44	7.28E-04	.
493.8	387.1	10.44	7.81E-04	2.54E-06
495.5	413.3	10.44	7.80E-04	.
500.2	414.3	10.44	8.18E-04	9.70E-06
500.6	424.3	7.00	8.18E-04	.
517.3	424.9	7.00	1.02E-03	1.25E-05
519.8	436.8	4.24	1.02E-03	.
524.8	437.1	4.24	1.08E-03	1.36E-05
524.9	437.2	2.86	1.08E-03	.
544.3	437.2	2.86	1.23E-03	6.83E-06
553.6	459.3	1.48	1.23E-03	.
576.8	457.9	1.48	1.30E-03	2.79E-06
578.5	440.1	1.48	1.30E-03	.
618.7	440.0	1.48	1.12E-03	1.66E-06
637.2	479.6	1.48	1.12E-03	.
665.1	480.1	1.48	1.17E-03	1.98E-06

RUN 5

NUCLEATION PRETREATMENT: 8 HRS AT 360 C AND 16.6 MPA
HYDROGEN

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
139.9	447.6	3.20	0.00E+00	0.00E+00
163.8	448.9	3.20	1.80E-06	5.02E-07
164.6	448.9	3.89	1.80E-06	.
184.6	448.5	3.86	1.84E-05	1.12E-06
200.3	448.4	3.89	3.78E-05	1.24E-06
205.9	448.4	3.89	4.51E-05	.
206.3	448.4	4.45	4.51E-05	.
225.1	442.9	4.41	1.12E-04	2.09E-06
231.8	442.9	4.41	1.29E-04	2.48E-06
249.8	447.8	4.38	1.49E-04	2.36E-06
251.1	447.8	3.89	1.49E-04	.
272.6	450.4	3.89	1.77E-04	2.32E-06
280.8	450.2	3.89	2.01E-04	2.90E-06
280.9	450.0	3.20	2.01E-04	.
304.6	451.1	3.20	2.24E-04	1.70E-06
321.4	453.6	3.20	2.42E-04	.
335.3	449.5	3.20	3.11E-04	.
349.3	448.8	3.17	3.50E-04	2.29E-06
349.4	448.8	2.51	3.50E-04	.
391.6	448.5	2.51	4.09E-04	1.42E-06
416.9	448.7	2.51	4.37E-04	1.51E-06
418.1	448.7	2.51	4.37E-04	.
424.6	450.1	1.93	4.37E-04	.
453.1	449.2	1.83	4.64E-04	6.36E-07
453.3	449.2	2.51	4.64E-04	.
472.4	449.0	2.51	4.81E-04	1.05E-06
493.8	449.5	2.48	5.00E-04	1.04E-06
494.1	449.4	3.20	5.00E-04	.
513.4	449.4	3.17	5.33E-04	1.95E-06
513.6	449.5	3.89	5.33E-04	.
535.6	449.6	3.86	5.88E-04	2.61E-06

. DENOTES VALUES NOT MEASURED FROM THE TRACE

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
535.9	449.6	4.45	5.88E-04	.
561.3	449.9	4.41	6.75E-04	3.79E-06
561.6	449.8	2.51	6.75E-04	.
588.8	449.7	2.53	7.30E-04	1.46E-06
636.3	449.4	2.51	7.93E-04	1.17E-06
640.9	467.3	2.51	7.93E-04	.
669.8	467.2	2.51	8.51E-04	2.08E-06
681.3	466.8	2.51	8.81E-04	2.15E-06
684.3	430.8	2.51	8.82E-04	.
716.8	430.5	2.51	9.21E-04	1.11E-06
731.3	430.4	2.51	9.35E-04	.
733.8	448.3	2.51	9.34E-04	.
754.3	448.2	2.51	9.62E-04	1.34E-06
760.4	449.4	2.51	9.58E-04	.
777.4	449.0	2.51	9.86E-04	1.44E-06
782.4	429.7	2.51	9.87E-04	.
801.4	429.9	2.51	1.00E-03	1.04E-06
850.3	430.6	2.48	1.03E-03	8.21E-07
853.8	407.6	2.48	1.03E-03	.
899.4	407.3	2.48	1.06E-03	4.14E-07
902.3	431.1	2.48	1.06E-03	.
920.9	430.8	2.48	1.07E-03	7.90E-07
924.3	450.7	2.48	1.07E-03	.
945.4	450.6	2.48	1.10E-03	1.34E-06
950.4	450.1	2.48	1.11E-03	.
952.4	472.7	2.51	1.11E-03	.
968.8	471.8	2.48	1.15E-03	2.66E-06
970.1	472.1	2.47	1.17E-03	3.04E-06
1001.3	471.9	2.48	1.24E-03	2.99E-06
1023.8	471.6	2.51	1.32E-03	2.98E-06
1023.9	471.3	4.93	1.32E-03	1.45E-05
1041.4	471.4	4.86	1.58E-03	1.52E-05
1064.2	471.2	4.89	2.01E-03	2.21E-05
1064.6	471.0	2.51	2.01E-03	.
1112.7	471.0	2.51	2.33E-03	6.34E-06
1116.1	449.1	2.51	2.34E-03	.
1120.8	449.2	2.51	2.35E-03	3.37E-06
1168.1	448.7	2.51	2.50E-03	3.05E-06

. DENOTES VALUES NOT MEASURED FROM THE TRACE

RUN 5 - CONTINUED

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
1168.4	449.2	1.48	2.50E-03	.
1190.8	449.2	1.48	2.53E-03	8.14E-07
1208.4	448.3	1.48	2.55E-03	8.69E-07
1212.3	468.3	1.48	2.55E-03	.
1240.1	468.6	1.48	2.57E-03	1.06E-06
1240.4	468.6	1.48	2.58E-03	1.35E-06
1280.4	468.7	1.48	2.62E-03	1.40E-06
1307.1	468.4	1.48	2.66E-03	1.40E-06
1330.8	468.1	1.48	2.69E-03	1.34E-06
1331.1	468.0	3.55	2.69E-03	1.19E-05
1364.4	467.4	3.48	3.08E-03	1.24E-05
1369.1	467.4	3.48	3.10E-03	1.46E-05

RUN 6

NO NUCLEATION PRETREATMENT USED

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
18.5	454.0	4.36	0.00E+00	0.00E+00
46.8	454.0	4.36	2.27E-05	5.46E-07
66.8	454.0	4.31	5.31E-05	1.61E-06
89.3	454.0	4.29	1.05E-04	2.33E-06
115.7	453.0	4.34	1.88E-04	2.97E-06
119.3	453.0	4.34	2.02E-04	4.02E-06
142.8	454.5	4.31	2.90E-04	4.08E-06
161.2	456.0	4.34	3.71E-04	5.08E-06
191.0	456.0	4.34	5.37E-04	5.80E-06
210.9	455.0	4.31	6.78E-04	6.34E-06
215.2	455.0	4.38	7.07E-04	6.22E-06
257.4	455.0	4.31	1.07E-03	9.49E-06
263.5	455.0	4.38	1.14E-03	1.25E-05
285.0	455.0	4.34	1.39E-03	1.56E-05
311.7	455.0	4.38	1.77E-03	1.96E-05
334.3	454.0	4.36	2.20E-03	2.49E-05
357.7	454.0	4.36	2.82E-03	4.10E-05
376.4	454.0	4.31	3.54E-03	5.31E-05
383.1	456.0	4.31	3.82E-03	6.11E-05
383.2	456.0	4.38	4.22E-03	7.37E-05
389.0	456.0	4.38	4.66E-03	7.71E-05
407.5	456.0	4.34	5.66E-03	8.42E-05

RUN 7

NUCLEATION PRETREATMENT: 29 HRS AT 378 C AND 20.7 MPA
HYDROGEN + 15.5 HRS AT 350 C AND 20.1 MPA HYDROGEN

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
0.0	380.9	20.65	0.00E+00	0.00E+00
46.3	381.2	20.48	3.59E-05	2.41E-06
51.8	384.6	17.51	3.59E-05	1.95E-06
69.8	384.6	17.34	7.54E-05	1.93E-06
70.9	384.8	13.89	7.54E-05	.
93.3	384.9	13.96	1.22E-04	2.04E-06
93.4	384.4	10.44	1.22E-04	.
145.6	385.2	10.44	1.95E-04	1.30E-06
145.8	385.4	20.79	1.95E-04	.
166.0	384.4	20.51	2.66E-04	2.13E-06
166.2	384.5	13.89	2.66E-04	.
237.3	384.9	13.89	3.73E-04	2.02E-06
237.5	385.2	7.00	3.73E-04	.
313.3	385.4	7.00	4.97E-04	1.18E-06
313.3	385.4	10.44	4.97E-04	.
360.8	385.4	10.41	5.68E-04	1.70E-06
371.0	384.5	5.27	5.68E-04	.
437.0	384.6	5.27	6.55E-04	9.49E-07
437.3	384.6	7.00	6.55E-04	.
479.9	384.3	7.00	6.91E-04	1.04E-06
480.0	384.3	3.55	6.91E-04	.
551.0	385.3	3.55	7.50E-04	6.48E-07
551.5	385.3	5.27	7.50E-04	.
608.0	385.6	5.24	7.92E-04	1.12E-06
608.6	385.6	2.17	7.92E-04	.
719.8	385.9	2.24	8.18E-04	3.51E-07
719.8	385.9	3.55	8.18E-04	.
795.8	385.4	3.51	8.62E-04	6.62E-07
795.8	385.4	1.14	8.62E-04	.
1005.1	385.5	1.17	9.09E-04	1.58E-07
1005.2	385.5	2.17	9.09E-04	.

. DENOTES VALUES NOT MEASURED FROM THE TRACE

TIME HRS	TEMPERATURE CELSIUS	HYDROGEN PRESSURE (MPA)	EXPANSION STRAIN	EXPANSION RATE (PER HR)
1128.5	386.8	2.14	9.32E-04	3.17E-07
1132.6	385.9	10.44	9.32E-04	.
1201.5	385.8	10.44	1.07E-03	2.60E-06
1204.0	409.2	10.44	1.07E-03	.
1274.5	410.3	10.44	1.64E-03	1.57E-05
1275.1	409.9	17.34	1.64E-03	5.83E-05
1280.3	409.6	17.34	1.96E-03	6.71E-05
1280.3	386.0	17.34	1.96E-03	3.47E-05
1300.2	385.3	17.20	2.69E-03	4.57E-05
1302.2	357.8	17.41	2.69E-03	1.77E-05
1319.0	357.7	17.27	2.98E-03	1.64E-05
1319.5	357.9	10.44	2.98E-03	.
1343.3	357.9	10.51	3.16E-03	7.10E-06
1344.6	387.0	10.44	3.16E-03	2.72E-05
1366.3	387.0	10.44	3.67E-03	2.24E-05
1366.6	386.6	17.34	3.67E-03	6.91E-05
1372.0	386.6	17.27	4.01E-03	6.00E-05
1372.5	386.7	10.44	4.01E-03	.
1390.3	386.7	10.44	4.37E-03	1.90E-05
1391.8	358.8	10.44	4.37E-03	.
1413.5	358.9	10.27	4.46E-03	4.43E-06
1414.6	384.4	10.44	4.46E-03	.
1436.8	386.5	10.44	4.79E-03	1.41E-05
1437.1	386.8	17.34	4.79E-03	.
1444.8	386.0	17.34	5.10E-03	3.57E-05
1447.5	358.4	17.34	5.10E-03	.
1466.8	358.4	17.66	5.28E-03	9.76E-06
1467.1	358.5	10.44	5.28E-03	.
1514.0	358.7	10.44	5.47E-03	3.66E-06
1514.3	358.8	7.00	5.47E-03	.
1558.5	359.0	7.00	5.56E-03	1.64E-06
1560.3	385.7	10.44	5.55E-03	.
1585.1	386.7	10.44	5.77E-03	7.30E-06

APPENDIX C

MATERIAL PARAMETERS

$$A = 7 \times 10^{13} \quad (\text{Ref. 48})$$

$$b = 2.48 \times 10^{-10} \text{ m} \quad (\text{Ref. 48})$$

$$[C] = 2.40 \times 10^6 \exp\left(-\frac{77.35 \text{ kJ}}{RT}\right) \quad (\text{Ref. 30})$$

where $[C]$ = solubility of Fe_3C in ferrite in ppm

$$d = 1.0 \text{ } \mu\text{m} \quad (\text{Assumed, based on metallographic results})$$

$$D_C = 2 \times 10^{-6} \exp\left(-\frac{84.0 \text{ kJ}}{RT}\right) \text{ m}^2 \text{ s}^{-1} \quad (\text{Ref. 34})$$

where D_C is the diffusion coefficient of C in α -Fe

$$D_{gb} = 1.1 \times 10^{-12} \exp\left(-\frac{173.5 \text{ kJ}}{RT}\right) \text{ m}^3 \text{ s}^{-1} \quad (\text{Ref. 49})$$

$$D = 2.0 \times 10^{-4} \exp\left(-\frac{251.1 \text{ kJ}}{RT}\right) \text{ m}^2 \text{ s}^{-1} \quad (\text{Ref. 50})$$

$$G = 6.4 \times 10^{10} (1 - (T - 300) \times 4.5 \times 10^{-4}) \text{ Pa} \quad (\text{Ref. 48})$$

where T = Temperature ($^{\circ}\text{K}$)

$$n = 6.9 \quad (\text{Ref. 51})$$

$$\dot{n} = K_f [C] P_{\text{H}_2}^{1.5} = K_b f_{\text{CH}_4} P_{\text{H}_2}^{-0.5}$$

$$\text{where } K_f = 1.73 \times 10^{-12} \exp\left(-\frac{56.9 \text{ kJ}}{RT}\right) \text{ ms}^{-1} \text{ Pa}^{-1.5}$$

$$K_b = 4.15 \cdot 10^4 \exp\left(-\frac{213.4 \text{ kJ}}{RT}\right) \text{ mole m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1.5}$$

$[C]$ = Carbon concentration (moles m^{-3})

$$\gamma = 0.78 \text{ Jm}^{-2} \quad (\text{Ref. 52})$$

$$\Omega = 1.18 \times 10^{-29} \text{ m}^3 \quad (\text{Ref. 48})$$

LIST OF REFERENCES

1. Steel for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants, American Petroleum Institute Publ. 941, 2nd. ed., 1977.
2. W. Oldfield, G. R. Odette and S. Vagarali: Quarterly Progress Report No. 3 - Department of Energy Contract No. ET-78-S-01-3153, 1979.
3. R. E. Allen, R. J. Jansen, P. C. Rosenthal and F. H. Vitovec: Proc. API 1962, vol. 42, pp. 452-62.
4. R. E. Allen, R. J. Jansen, P. C. Rosenthal and F. H. Vitovec: Proc. API 1961, vol. 41, pp. 74-84.
5. H. H. Podgurski: Trans. TMS-AIME, 1961, vol. 221, pp. 389-94.
6. M. Hasegawa and S. Nomura: J. Iron and Steel Inst. Jap., 1977, vol. 17, pp. 187-93.
7. M. Natan: Ph.D. Thesis, Chapt. 5, Cornell University, 1979.
8. R. J. Steuber and G. H. Geiger: Corrosion, 1969, vol. 22, pp. 309-318.
9. G. H. Geiger and O. F. Angeles: API Pub. 945, 1975.
10. F. H. Vitovec: Proc API, vol. 44, pp. 179-188.
11. P. C. Rosenthal, W. L. Schroeder, and F. H. Vitovec: Proc. API 1963, vol. 43, pp. 98-105.
12. H. M. Shih and H. H. Johnson: Scripta Met, 1977, vol. 11, pp. 151-154.
13. R. Pishko, M. McKimpson and P. G. Shewmon: Met. Trans. A, vol. 10A, pp. 887-894.
14. A. Sagues, B. O. Hall and H. Wiedersich: Scripta Met., 1977, vol. 12, pp. 319-326.

15. E. E. Fletcher and A. R. Elsea: DMIC Report No. 202, Batelle Memorial Institute, Columbus, Ohio, 1964.
16. L. C. Weiner: Corrosion, 1961, vol. 17, pp. 137-43.
17. D. A. Westfal and F. J. Worzala: Hydrogen in Metals, I. M. Bernstein and A. W. Thompson, eds., pp. 78-89, ASM, Metals Park, OH, 1974.
18. P. G. Shewmon: Met. Trans. A, 1976, vol. 7A, pp. 278-86.
19. H. J. Grabke and E. Martin: Arch. Eisenheuttenw., 1972, vol. 44, pp. 837-42.
20. P. G. Shewmon: Diffusion in Solids, p. 181, McGraw-Hill, New York, 1963.
21. D. Hull and D. E. Rimmer: Phil Mag., 1959, vol. 4, pp. 673-87.
22. R. Raj and M. Ashby: Acta Met., 1975, vol. 23, pp. 653-66.
23. R. Raj, H. M. Shih and H. H. Johnson: Scripta Met., 1977, vol. 11, pp. 839-42.
24. M. V. Speight and W. Beere: Metal Sci., 1975, vol. 9, p. 190-191.
25. I. Finnie and W. Heller: Creep of Engineering Materials, pp. 186-7, McGraw-Hill, New York, 1959.
26. D. S. Wilkinson and M. Ashby: Acta Met., 1975, vol. 23, pp. 1277-85.
27. H. M. Shih: Ph.D. Thesis, Chapt. 4, Cornell University, 1978.
28. A. K. Mukherjee, J. E. Bird and J. E. Dorn: ASM Trans., 1969, vol. 62, pp. 155-79.
29. R. M. Sevast'yanov and N. A. Zykov: Teplofizika Vysokekh Temperature, 1972, vol. 10, pp. 979-87.
30. J. Chipman: Met. Trans., 1972, vol. 3, pp. 55-64.
31. JANAF Thermochemical Tables, 2nd Ed., June 1971, NSRDS-NBS-37.

32. P. W. Davies, G. Nelmes, K. R. Williams and B. Wilshire: Metal Sci. J., 1973, vol. 7, pp. 87-92.
33. H. Grabke: Max-Planck-Institut Für Eisenforschung GMBH, Düsseldorf, Germany, private communication, 1979.
34. C. Wert: Phys. Rev., 1950, vol. 79, pp. 601-605.
35. G. K. White: Cryogenics, 1961, vol. 1, pp. 151-158.
36. C. R. Levart: Popular Electronics, Aug. 1976, vol. 10, pp. 46-7.
37. N. E. Hull, W. E. Vaughan, A. H. Price and M. Davis: Dielectric Properties and Molecular Behavior, pp. 191-5, Van Nostrand, New York, 1969.
38. C. J. Smithells, ed., Metals Reference Book, 5th ed., p. 960, Butterworths, Boston, 1976.
39. Metals Handbook, 8th Ed., vol. 1, p. 423, ASM, Metals Park, OH, 1961.
40. D. A. Westfal and F. J. Worzala: Scripta Met., 1971, vol. 5, pp. 43-47.
41. G. Sundararajan and P. G. Shewmon: Ohio State Univ., Columbus, OH, to be published, 1978.
42. H. J. Grabke, E. M. Petersen and S. R. Srinivasan: Surf. Sci., 1977, vol. 67, pp. 501-516.
43. G. H. Edward and M. F. Ashby: Acta Met., 1979, vol. 27, pp. 1505-1518.
44. B. Burton: Vacancies '76, R. E. Smallman and J. E. Harris, eds., pp. 156-169, London, The Metals Soc., 1977.
45. T. J. Chuang, K. I. Kagawa, J. R. Rice and L. B. Sills: Acta Met., 1979, vol. 27, pp. 265-84.
46. Y. E. Geguzin and N. N. Ovcharenko: Doklady Akad. Nauk, 1960, vol. 130, p. 537.
47. H. M. Shih: Ph.D. Thesis, Chapt. 3, Cornell University, 1978.

48. H. J. Frost and M. F. Ashby: *Fundamental Aspects of Structural Alloy Design*, R. Jaffe and B. Wilcocks, eds., pp. 27-58, Plenum Press, New York, 1977.
49. D. W. James and G. M. Leak: *Phil. Mag.*, 1965, vol. 12, pp. 491-503.
50. F. S. Buffington, K. Hirano and M. Cohen: *Acta Met.*, 1961, vol. 9, pp. 434-39.
51. Y. Ishida, C. Cheng and J. Dorn: *Trans. Met. Soc. AIME*, 1966, vol. 236, pp. 964-971.
52. J. P. Hirth and J. Lothe: *Theory of Dislocations*, p. 764, McGraw-Hill, New York, 1968.