GRAIN BOUNDARY CAVITY GROWTH UNDER APPLIED
STRESS AND INTERNAL PRESSURE

BY

James Frank Mancuso

Ph.D. Thesis
August 1977

Research Group:
Prof. C. Y. Li
MSE

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ACKNOWLEDGMENTS

I would like to thank Professor Che-Yu Li for serving as my thesis advisor and showing me the "ropes" of materials science. I would also like to thank Professor K. B. Cady, my committee chairman, and V. O. Kostroun for their service and guidance, especially in the early decision making stages of my stay at Cornell.

I also acknowledge the Energy Research and Development Administration for its support of my graduate work.

Thanks are also accorded to the Cornell staff for their technical assistance. Among these are B. Addis, G. Chevalier, and R. Shewchuk. Special thanks go to R. Coles and M. Rich for their friendship, encouragement and technical support throughout my stay at Bard Hall. Finally, I am pleased to acknowledge the assistance of R. Keusseyan for his help in the final data taking. I would also like to thank R. Cheney and G. T. E. Sylvania for their assistance in material preparation and the hospitality they extended while I was at their plant.

I would like to thank my entire, extended family and especially Mr. and Mrs. Albert Kikel for their support in this undertaking.

I am also most indebted to my wife, Patricia, who I finally got to type this thesis and who has been a continual

source of support and encouragement throughout my graduate "career". Finally, I would like to acknowledge my two children, Lori and Jamie, for being a joy at all times and for being good kids while I was preparing this manuscript. Additional support was received through the National Science Foundation by the use of the Central facilities of the Materials Science Center.

TABLE OF CONTENTS

<u>Chapter</u>		<u>Page</u>
1	INTRODUCTION.....	1
2	PREVIOUS WORK.....	4
2.1	Cavitation Without Insoluble Gases During Creep.....	6
2.2	Cavitation in the Presence of Insoluble Gases.....	19
2.2.1	Hydrogen Attack.....	20
2.2.2	Grain Boundary Cavitation in the Presence of Helium.....	26
3	MODELS FOR GRAIN BOUNDARY CAVITY GROWTH.....	36
3.1	Models for Vacancy Diffusion Controlled Cavity Growth.....	37
3.1.1	Development and Comparison of Models.....	38
3.1.2	The Significance of the Cavity Growth Model.....	46
3.1.3	Summary of Vacancy Diffusion Model... ..	48
3.2	Cavity Growth Under Applied Stress and Irradiation.....	51
3.2.1	Analysis.....	51
3.2.2	Summary.....	58
3.3	The Normal Stress at the Grain Boundaries During Creep Deformation.....	58
3.3.1	Analysis.....	59
3.3.2	Summary.....	65
4	EXPERIMENT.....	68
4.1	Specimen Examination and Cavity Size Distribution Determination.....	69
4.1.1	Morphological Considerations.....	69
4.1.2	The Stereo SEM Technique.....	72
4.1.3	Cavity Size Determination.....	79
4.2	Specimen Preparation.....	82
4.2.1	Materials.....	82

TABLE OF CONTENTS CONTINUED

<u>Chapter</u>	<u>Page</u>
4.2.2 Hydrogen Charging and Production of bubbles.....	84
4.2.2 Cavity Size Measurement.....	92
4.3 Apparatus for Cavity Growth Experiments Under An Applied Stress.....	98
5 CAVITY GROWTH UNDER INTERNAL PRESSURE.....	103
5.1 Experimental Data and Observations.....	104
5.2 Discussion of the Growth Data.....	105
5.3 Bubble Growth During Hydrogen Charging.....	117
5.4 Summary.....	120
6 GRAIN BOUNDARY CAVITY GROWTH UNDER AN APPLIED STRESS.....	121
6.1 Experimental Data and Observations.....	122
6.2 Discussion.....	133
6.2.1 Cavity Growth by Grain Boundary Sliding.....	136
6.2.2 Vacancy Diffusion Controlled Growth..	136
6.3 Summary.....	145
7 DISCUSSION.....	146
7.1 Summary of Results.....	146
7.2 Practical Implications.....	147
7.3 Suggestions for Further Work.....	148
REFERENCES.....	150
APPENDIX A PROCEDURE FOR DETERMINING GRAIN BOUNDARY ORIENTATION AND CAVITY AREA.....	154
A.1 Stereomicroscopy and Determination of Grain Boundary Orientation.....	154
A.2 Measurement of Bubble Area.....	161
APPENDIX B SOLUTION OF THE MASS BALANCE EQUATION.....	163

TABLE OF CONTENTS CONTINUED

<u>Chapter</u>	<u>Page</u>
APPENDIX C EQUILIBRIUM PRESSURES FOR GAS BUBBLES DURING CHARGING.....	166
C.1 Thermo-Chemical Equilibrium of Methane.	166
C.2 Thermo-Chemical Equilibrium of Hydrogen Sulfide.....	167
APPENDIX D CAVITY SIZE DISTRIBUTIONS FOR CAVITY GROWTH UNDER APPLIED STRESS.....	169

LIST OF TABLES

<u>Table</u>		<u>Page</u>
2.1	Damage Rates in Type 316 Stainless Steel.....	28
4.1	Chemical Analysis of Specimen (Ni 270).....	83
5.1	Estimated Initial and Final Pressure on T-Series Bubbles.....	115
6.1	Data for Cavity Growth under an Applied Stress.	130

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2.1 Example of r-type cavities at grain boundaries.....	7
2.2 Example of a w-type cavity at a grain boundary intersection.....	8
2.3 Schematic diagram of grain boundary cavity nucleation on precipitates and grain boundary ledges.....	10
2.4 Nucleation data showing cavity number density as a function of strain at various strain rates in α iron at 700°C.....	11
2.5 Schematic diagram of the mechanism for grain boundary cavity growth by diffusion.....	13
2.6 Cavity growth in α iron at 700°C showing $w \propto \sigma^{3/2}$	15
2.7 Example of amoeboid shape cavities formed in α iron at 700°C.....	16
2.8 Cavity described in Evan's analysis.....	18
2.9 Nelson Diagram for steel showing incubation times as a function of temperature and hydrogen pressure.....	21
2.10 CTR, EBR II and HFIR flux energy spectra.....	27
2.11 Helium bubbles formed in annealed type 316 stainless steel irradiated to a fluence of 4.2×10^{22} n/cm ²	30
2.12 Helium bubble size distributions before and after the application of an applied stress.....	31
2.13 Helium bubbles in type 316 stainless steel subjected to 1.9×10^{22} n/cm ² in EBR II.....	32
3.1 The radial growth rate, as a function of $2r/a$, for cavities under an applied stress and no internal pressure.....	47
3.2 Cavity cross section vs time for a fixed amount of gas.....	49

LIST OF FIGURES CONTINUED

<u>Figure</u>		<u>Page</u>
3.3	Cavity cross section as a function of time under an applied stress for an initial gas pressure equal to $2\gamma/r$	50
3.4	Profiles of vacancy concentration by a surface during irradiation.....	53
3.5	Typical stress vs strain rate data for type 316 stainless steel at 600°C	61
3.6	Schematic diagram of the shear crack treated by Hart's analysis.....	62
3.7	The qualitative behavior of $\dot{\epsilon}_g/\dot{\epsilon}_m$ as a function of the strain rate.....	64
3.8	Crossman and Ashby's strain rate contours in hexagonal grains for various values of n for free sliding.....	66
4.1	Schematic diagram of expected grain boundary cavity shape.....	70
4.2	Typical fracture surface examined in SEM.....	73
4.3	Schematic diagram of specimen position in holder.....	75
4.4	Relationships between the angles determined in the stereographic analysis.....	76
4.5	Two dimensional diagram of the translation expected after a tilt change.....	77
4.6	Demonstration of the origin of perspective error.....	80
4.7	Example of the variation in cavity size due to suspected variation in carbon concentration....	81
4.8	Examples of grain structure for the various heat treatments.....	85
4.9	Schematic diagram of the autoclave used for hydrogen charging.....	86
4.10	Examples of bubbles after charging at 500°C a) in 3.4 MPa hydrogen for 3 hrs and b) in 10.3 MPa hydrogen for 24 hrs.....	88

LIST OF FIGURES CONTINUED

<u>Figure</u>		<u>Page</u>
4.11	Examples of bubbles given a hydrogen charge of 10.3 MPa at 500° for 1.5 hours a) before and b) after a 124 hr. vacuum anneal.....	90
4.12 a,b	Examples of bubble size distributions for specimens charged at 3.4 MPa for 4 hr. at 500°C.....	91
4.13	Example of transgranular fracture typical at a sample annealed at a high temperature after hydrogen charging.....	93
4.14	Plot of hydrogen charging time versus temperature at a hydrogen pressure of 2.8 MPa.....	95
4.15	Comparison of cavity sizes before and after a recharge at 300°C and 3.4 MPa for 12 hours.....	97
4.16	Schematic diagram of equipment used to produce cavity growth under applied stress.....	99
4.17	Schematic diagram of the specimen clamp used to apply stress to the nickel specimens.....	100
4.18	Examples of strain measurements for the low, high and intermediate strain rates used in this experiment.....	102
5.1	Plot of mean bubble cross section vs annealing time at 500, 550 and 600°C.....	106
5.2	Histograms of the bubble cross sectional areas for series S specimens annealed at 500°C.	107
5.3	Histograms of bubble cross sectional areas for series T specimens annealed at 500°C.....	108
5.4	Histograms of series T specimens annealed at 550°C.....	109
5.5	Histograms of the bubble cross sectional area for series T specimens annealed at 600°C.....	110
5.6	Plot of the mean corss sectional area for the longest anneals at each temperature.....	111

LIST OF FIGURES CONTINUED

<u>Figure</u>		<u>Page</u>
5.7	Plot of the measured and calculated bubble cross sections as a function of $D8^b.t$ for all three temperatures.....	116
6.2	Grain boundary sliding evidence.....	124
a	.....	125
b	.....	126
6.3a	Comparison of cavity cross sectional areas in the stressed and unstressed portions of specimen R4-G.....	128
6.3b	Comparison of cavity cross sectional areas in the stressed and unstressed portions of specimen R4-B.....	129
6.4	Cavity growth rate vs initial stress.....	131
6.5	Cavity growth rate vs strain rate.....	132
6.6	Cavity growth vs the angle between the grain boundary surface normal and the applied stress axis.....	134
6.7	Mean cavity cross sectional area vs time for two stresses and temperatures.....	135
6.8a	Comparison of the calculated cavity growth rate and the measured cavity growth rate as a function of the applied, $\sigma_T/2$, at 500°C.....	138
6.8b	Comparison of the calculated cavity growth rate and the measured cavity growth rate as a function of the applied, $\sigma_T/2$, at 550°C.....	139
6.9a	Expected and measured cavity growth rates vs grain boundary angle for R4-B.....	140
6.9b	Expected and measured cavity growth rates vs grain boundary angle for R4-L.....	141
6.9c	Expected and measured cavity growth rates vs grain boundary angle for R4-G.....	142
6.10	Ratio of the observed to the expected cavity growth rates vs the strain rate.....	144

ST OF FIGURES CONTINUED

<u>Figure</u>		<u>Page</u>
A.1	Schematic diagram of the positions, vectors, and coordinates necessary to determine grain boundary orientation by stereography.....	155
A.2	Angular relationships used in stereo analysis..	157
A.3	Program to determine grain boundary orientation.....	159
A.4	Program to calculate bubble size from index numbers on template.....	162

GRAIN BOUNDARY CAVITY GROWTH UNDER APPLIED STRESS AND INTERNAL PRESSURE

James Frank Mancuso, Ph.D.
Cornell University 1977

ABSTRACT

The growth of grain boundary cavities under applied stress and internal gas pressure was investigated. Methane gas filled cavities were produced by the $\underline{\text{C}} + 4\underline{\text{H}} \rightleftharpoons \text{CH}_4$ reaction in the grain boundaries of type 270 nickel by hydrogen charging in an autoclave at 500°C with a hydrogen pressure of either 3.4 or 14.5 MPa. Intergranular fracture of nickel was achieved at a charging temperature of 300°C and 10.3 MPa hydrogen pressure. Cavities on the grain boundaries were observed in the scanning electron microscope after fracture. Photomicrographs of the cavities were produced in stereo pairs which were analyzed so as to correct for perspective distortion and also to determine the orientational dependence of cavity growth under an applied tensile stress.

Cavities that were produced by hydrogen charging at 14.5 MPa for ~1.5 hours grew during vacuum anneals performed after charging. The observed growth kinetics is consistent with the grain boundary diffusion model for cavity growth and the ideal gas law. The grain boundary diffusion constant was taken as $.07 \exp(-1.19/kT) \text{ cm}^2/\text{sec}$. An internal gas

pressure at ~ 5 MPa was determined from the growth measurement. The observation that cavities grow after the charge at 14.5 MPa hydrogen pressure and not after the 3.4 MPa charge support Shewmon's contention that cavity growth during charging can be limited by either vacancy diffusion to the cavity or methane production at the cavity surface.

For the case of cavity growth under an applied stress, the grain boundary cavity growth rate is also consistent with the vacancy diffusion model. Both the strain rate and orientation dependence of cavity growth suggest that the grain boundary normal stress is influenced by grain boundary sliding at low strain rates. The effect of grain boundary sliding on the cavity growth rate is in qualitative agreement with a model developed by Hart for the stress at the boundary between sliding grains during high temperature deformation.

INTRODUCTION

The economical and safe operation of systems for energy conversion depends on the ability of materials to withstand stresses at temperatures near one-half their absolute melting points for long periods of time. One phenomenon that limits the service life of many high-temperature materials is the occurrence of intergranular fissures. The origin of these cracks, which lead to sudden, brittle failure, has been associated with grain boundary cavitation.

Grain boundary cavitation is the process where holes nucleate and grow at the interfaces of adjacent grains in a polycrystalline solid. Cavities are created at elevated temperatures, during creep or as a result of insoluble gases collecting at the grain boundaries. These cavities are usually distributed over the entire grain boundary. The growth and linkage of cavities lead to fissuring and intergranular failure. At conditions typical to engineering applications, fissuring can occur at relatively small strains and causes a severe loss of total ductility.

Present day examples of this type of damage are found in high temperature gas turbine blades and steam generator tubes. Other examples include steam restorers in petroleum refineries and possibly fuel cladding in power reactors. Grain boundary cavitation is also expected to be a serious problem for components in the advanced energy conversion systems. These include the fast breeder fuel cladding and fusion reactor first wall. Moreover, cavitation has already

been identified as a cause of material failure in the piping of prototype coal-conversion plants.

Due to the high costs of plant shutdowns, the economic viability of present and future energy systems depends on accurate estimates of component life. The present empirical methods which are used to predict in-service cavitation failure are inadequate for this purpose. Furthermore, a fundamental understanding of the cavitation phenomenon is needed as a basis to develop the required capabilities in this area.

The main purpose of this dissertation is to investigate the driving force and the kinetics of cavity growth in the grain boundary. The existing models, which consider the controlling mechanism for cavity growth to be vacancy diffusion along the grain boundary, are adopted in the present work. However, a major deviation from the existing theories is made. It considers for the first time the possibility that the driving force for cavity growth, which is the grain boundary normal stress, is relaxed by grain boundary sliding. Experiments were performed in nickel to test the predictions of the model on the growth of cavities under internal gas pressure and external applied stress. The results of these experiments confirm the validity of the proposed model and provide a physical basis for the development of methods of failure prediction.

A new experimental technique was developed to produce grain boundary cavities for the growth experiments and to embrittle the grain boundaries so that they would fracture intergranularly for SEM examination. The basic procedure was

o charge the nickel specimens with hydrogen gas at high temperatures. Reaction of the hydrogen with dissolved carbon created methane gas at the boundaries resulting in cavitation and embrittlement. This is an example of the phenomenon called hydrogen attack. In as much as this process is used extensively in these experiments, the work performed here yields information on the phenomenon of hydrogen attack itself, and in its own right, may be important to engineering applications.

The plan of this dissertation is as follows:

Chapter 2 describes the reported work on the phenomenon of grain boundary cavitation.

Chapter 3 outlines the current models for cavity growth by vacancy diffusion. It also discusses the effect of irradiation and the deformation rate on cavity growth.

Chapter 4 presents a detailed description of the procedures used in the cavity growth experiments.

Chapters 5 and 6 report the experimental results of cavity growth under internal gas pressure and applied stress, respectively.

Chapter 7 is a discussion of the conclusions and implications of this work.

CHAPTER 2 - PREVIOUS WORK

Grain boundary cavitation in polycrystals has been observed at elevated temperatures under a variety of conditions:

1) Cavitation can occur during creep under an applied stress. (1,2,3,4,5,6,7,8,9,10) 2) Cavitation can proceed in a stress-free solid when large amounts of insoluble gases appear at the grain boundaries. (11,12,13) Finally, 3) a combined case can occur where both gases and applied stress contribute to cavitation. (14,15)

Cavitation during creep can be divided into two stages; a nucleation stage and a growth stage. Each has been investigated both experimentally and theoretically. (1,2,3,4,5,6,7,8,9,10) In the absence of gases, the generally accepted mechanism for cavity nucleation is the process whereby grains slide over obstacles or inhomogeneities and leave holes at the grain boundary. (16,17) However, two different mechanisms, 1) grain boundary sliding and 2) stress-induced vacancy diffusion to the cavities, (5,9,18) have been proposed to describe cavity growth. In the sliding mechanism, cavities grow as a result of the relative displacement of adjacent grains. The rate of growth will depend on the relative sliding velocity. On the other hand, diffusional growth requires that vacancies be absorbed at the surface of the growing cavity. The grain boundaries themselves are the source of the vacancies, which

are transported to the cavities by the process of grain boundary diffusion.

Low solubility gas atoms can be formed inside solids by either chemical or nuclear reactions. The chemical reaction of interest in this work is the process of hydrogen attack in which methane gas is formed at grain boundaries. The nuclear reactions considered are the (n,α) transmutation reactions that occur in a neutron radiation environment.

In the case where insoluble gases are present, grain boundary cavity nuclei are gas filled bubbles. If the cavities are under high internal pressure, cavity growth under an applied stress may also be enhanced, or in the absence of an applied stress, cavities can grow due to an internal pressure alone. The magnitude of the pressure is determined by either 1) the rate of gas evolution or transport to the cavity or 2) the rate at which the cavity grows to relieve the gas pressure, or 3) a combination of both. Cavity growth due to internal pressure is by a vacancy diffusion mechanism similar to the one proposed for the growth of cavities under an applied stress.

In this chapter the reported experimental and theoretical studies on cavitation are reviewed. First, the case of cavitation under an applied stress in the absence of insoluble gases is considered. Hydrogen attack and the growth of bubbles under both internal pressure and applied stress will also be studied. Finally, the effects of helium on grain boundary cavitation will be discussed.

2.1 Cavitation Without Insoluble Gases During Creep

This section reviews the work reported on the phenomenon of grain boundary cavitation under an applied stress.

In 1954 Greenwood showed that cavities form on the grain boundaries of copper, alpha brass, and magnesium during creep at one-half their melting points. (5,6) The cavities appeared as rounded holes (as can be seen in Figure 2.1) and are called "r" type cavities. Although "r" type cavities had been observed prior to his experiments (1,4) Greenwood was the first to realize that grain boundary cavities could account for the severe loss of ductility in materials in this temperature range. It should be noted that these cavities are distinguished from a different kind of cavity known as "w" type cavities or wedge cracks. (4,6) Wedge cracks form at grain boundary intersections, as shown in Figure 2.2. They constitute a damage phenomenon where mass transport by diffusion is less important and will not be considered further in this work.

Greenwood, in his initial investigation, (5,6) had suggested that cavities nucleate and grow by the condensation of vacancies at the grain boundaries. The vacancies were believed to be created by either thermal or deformation processes. Machlin and other workers (16,17) quickly showed that while growth may have been due to vacancies, unreasonably high vacancy supersaturations are necessary to produce the observed cavity nucleation rates by homogeneous nucleation. As a result

Figure 2.1: Example of r-type cavities at grain boundaries in Nimonic 80A tested at 750°C (reference 19)

Figure 2.2: Example of a w-type cavity at a grain boundary intersection (reference 19)

1 cavitation models since that time have assumed that the nucleation of cavities on the grain boundaries is heterogeneous.

Machlin introduced the generally accepted approach to cavity nucleation, which suggests that cavities form at ledges or precipitates at the grain boundary (20,21,22,23) during grain boundary sliding. The basic model, shown schematically in Figure 2.3, is in agreement with the general findings that cavity nucleation varies nearly linearly with the total amount of sliding displacement. (4,7,24,25) Typical nucleation data, shown in Figure 2.4, illustrate how the total number of cavities is approximately linearly proportional to the total amount of deformation. (28) At the present time, only the detailed processes at the obstacles themselves are in dispute. (4.7) A review of this controversy, which is beyond the scope of this work, is presented in a recent article by Perry. (4)

It was recognized very early in the study of grain boundary cavitation that Machlin's approach to nucleation could not be applied to growth because the obstacles are generally too small to account for the observed cavity size. (4) A tenable theory for cavity growth was advanced by Balluffi and Seigle. (18) They used Herring's formulation (26) of the thermodynamics of vacancies in a stressed solid to show that it is energetically favorable for cavities to grow by absorbing vacancies created at the grain boundary interfaces under an applied normal stress. This process is equivalent to the loss of atoms from the cavity surface and an addition of

Figure 2.3: Schematic diagram of grain boundary cavity nucleation on precipitates and grain boundary ledges

Figure 2.4: Nucleation data showing cavity number density as a function of strain at various strain rates in α iron at 700°C (taken from reference 32)

atoms to the grain boundary. This process is illustrated in Figure 2.5.

Hull and Rimmer (9), using the assumption that atom or vacancy transport is by diffusion along the grain boundaries, developed an analytic expression for growth based on Herring's theory. The details of their analysis is presented in Chapter 3. In brief, they showed that the driving force for cavity growth is the normal stress on the grain boundary. This stress is $(\sigma_T - P)$ for a boundary normal to an applied stress, where σ_T and P are the tensile and hydrostatic stresses respectively. The derived growth law is of the form

$$\frac{dr}{dt} = \frac{D^{gb} w}{2kT a r} \Omega \left(\sigma_T - P - \frac{2\gamma}{r} \right) \quad (2.1)$$

where dr/dt is the radial growth rate, D^{gb} is the self-diffusion coefficient, w is the grain boundary thickness, a is the cavity spacing, Ω is the atomic volume, kT is Boltzmann's factor, γ is the surface tension and r is the cavity radius. The relation defines a critical stress that is numerically equal to $2\gamma/r$, and that must be exceeded before growth occurs. Based on this model, when $(\sigma_T - P)$ is much larger than the critical stress, the cavity radius should be proportional to time with an exponent of $1/2$. Under uniaxial stress the maximum rate of cavity growth is expected to occur on grain boundaries lying perpendicular to the applied stress axis, since they are expected to have the highest normal stress. In as much as growth relies on diffusion along the grain boundary,

Figure 2.5: Schematic diagram of the mechanism for grain boundary cavity growth by diffusion. Atom diffusion is along the grain boundary and proceeds by a vacancy mechanism

the temperature dependence of the cavity growth rate is essentially that of the grain boundary diffusion coefficient.

Many aspects of the diffusion model were verified by experiment. (4,7) For example, experiments showed that cavities did not grow when the quantity $(\sigma_T - P)$ was less than $2\gamma/r$, regardless of the deformation rate in the material. (9,27) In addition, most investigators reported that cavities were found predominantly on boundaries perpendicular to the stress axis. (6,4) Experiments measuring the growth kinetics of cavities in a variety of materials revealed that the time and temperature dependence for growth followed the vacancy diffusion model. (28,29,30)

Nevertheless, some observations were not in agreement with the predictions of Hull and Rimmer's analysis. The most important one concerned the failure of the model to predict the stress dependence of cavity growth. In particular, Cane (28) found that the cavity radius was proportional to $\sigma^{3/2}$ (as shown in Figure 2.6) rather than $\sigma^{1/2}$ predicted by Equation 2.1. Another was the observation that, at high stresses and strain rates, cavities became amoeboid or disk shaped (Figure 2.7). These shapes do not follow from the local equilibrium assumptions implicit in the vacancy diffusion model (discussed in Chapter 3) but can be a result of growth kinetics controlled morphology. (31,32)

Another vacancy generation mechanism, in which vacancies are generated by dislocations climbing along the grain boundary, was advanced by Ishida and McLean. (34) However, the

Figure 2.6: Cavity growth in α iron at 700°C shows $W_m \propto \sigma^{3/2}$, where W_m is a measure^m of the cavity radius (reference 28)

Figure 2.7: An example of an amoeboid shaped cavity formed in α iron at 700°C under applied stress. (reference 32)

detailed kinetics of the process have not been analyzed.

Evans (33) proposed an alternate growth mechanism based on grain boundary sliding. In his approach, growth can only occur by grain boundary sliding, and sliding cannot occur without cavity growth. The growth rate will be such that the total free energy change of the system will be a minimum. The free energy calculation considered 1) the surface energy of the cavities, 2) the elastic energy of the cavities, 3) the work done by the normal stress in increasing the volume of the cavities and 4) the work done by the shear stress in producing the sliding displacement. The dimensional changes of the cavities occur in the plane of the grain boundary so that the cavities will appear to be flat as illustrated in Figure 2.8. The growth law has the form

$$\frac{d\ell}{dt} \propto \left\{ 1 - \frac{K\bar{\sigma}_n \ell}{\gamma} - \frac{\bar{\sigma}_n^2 h}{2\gamma} \right\}^{-1} (\tau/w) \quad (2.2)$$

where h , ℓ , and w are the cavity dimensions (shown in the figure), γ is the surface tension, $\bar{\sigma}_n$ is the normal stress at the grain boundary, τ is the shear stress and K is a constant relating the elastic energy to the cavity size and the normal stress.

Because the normal stress contributes to the free energy change, Evan's theory predicts that cavitation will be favored on grain boundaries nearly perpendicular to the stress axis. It also follows that cavity growth will be inhibited by hydrostatic pressure.

Figure 2.8: The cavity described in Evan's analysis σ_T is the tensile stress on the specimen, σ_n is the normal stress on the grain boundary and τ is the shear stress at the grain boundary

Evan's inclusion of the work done by the shear stress can be questioned. In addition, the model does not describe the round cavities found at low strain-rates. It does not predict the $(t)^{1/2}$ dependence on the cavity radius mentioned previously. Another serious deficiency of this approach is that it requires that the value of the surface tension, γ , be one or two orders of magnitude higher than values reported in the literature. (33)

While neither model completely accounts for all of the observed growth phenomena, the vacancy diffusion model is favored in the present work as the basic mechanism for growth in the low strain rate range. Modifications to Hull and Rimmer's model have been proposed (39,40,41,42) and will be described in the next chapter. These changes however, do not alter the fundamental concepts introduced by Hull and Rimmer.

Summarizing this section, the concepts of grain boundary sliding and vacancy diffusion are both introduced to describe cavitation. Cavity nucleation can be a result of grain boundary sliding, while cavity growth is most probably due to a vacancy diffusion mechanism at low strain rates. However the current vacancy diffusion model does not account for all of the observed behavior. The most important deficiency of the model is that it does not predict the observed stress dependence of the rate of cavity growth.

2.2 Cavitation in the Presence of Insoluble Gases

This section reviews the phenomena of cavitation resulting

from insoluble gases collecting at the grain boundaries. Specifically, it deals with 1) the nucleation and growth of methane bubbles during hydrogen attack and 2) the creation of helium bubbles in materials subjected to intense neutron irradiation.

2.2.1 Hydrogen Attack

Hydrogen attack is the process whereby methane formation can occur when materials that contain dissolved carbon are exposed at high temperatures to a high pressure hydrogen gas. It is believed that the CH_4 molecule is large and insoluble, and that the reaction is favored at imperfections where misfit provides space for the molecule to form. These imperfections can be found on grain boundaries and at dislocation tangles. The manifestations of attack are the creation of methane bubbles at the imperfections, (especially grain boundaries) and a severe loss of ductility as measured by the reduction in area before failure.

Well known examples of hydrogen attack are found in the structural steels used in petroleum refineries and prototype coal gasification plants. (11,12) Empirical representations for the kinetics of attack have been developed for a number of steels. These are known as Nelson Diagrams and relate the incubation time for loss of ductility (designated t_i) to the hydrogen pressure and temperature. (11,35) The typical curves, shown in Figure 2.9 define the temperature and pressure below which no significant loss in ductility occurs in 100, 1000, or 10,000 hours.

A very limited number of experiments have shown that,

Figure 2.9: Nelson Diagram for steel showing incubation times as a function of temperature and hydrogen pressure (reference 11)

in iron and steel, the incubation time, t_i , may also vary with 1) the carbon solute concentration, (36) 2) the grain size, (36) 3) the amount of cold-work (37) and 4) the density of inclusions at the grain boundary. (11)

Westphal and Worzala (38) have correlated the incubation time with the size of methane bubbles. They found that the incubation time for iron is determined by the time it takes for bubbles to reach a given size, which is independent of the pressure, temperature, or time of exposure. In addition they observed that for a range of moderate conditions ($900\text{psi} < P_{H_2} < 1500\text{psi}$, $400^\circ\text{C} < T < 500^\circ\text{C}$, $10 < t_i < 90\text{hr}$) the incubation times were primarily determined by bubble growth (11,38) and not by bubble nucleation which required times much shorter than t_i .

Shewmon analyzed the factors determining the growth of bubbles during hydrogen attack. He concluded that cavity growth is controlled by vacancy diffusion and that the driving force for growth is the internal pressure inside the bubble. Referring to Raj and Ashby's cavity growth rate equation (11,39) (discussed in Section 3.1) he obtained a growth rate:

$$\frac{dV}{dt} = \frac{2\pi D^g b w \Omega}{kT} (\bar{\sigma}_n - p - \frac{2\gamma}{r}) \left[\frac{(1-x^2)^2}{x^2(1-\frac{x^2}{4}) - \frac{3}{4}} - \ln x \right] \quad (2.3)$$

where dV/dt is the rate of cavity volume change, $\bar{\sigma}_n$ is the normal stress on the grain boundary, p is the internal pressure, x is the ratio $2r/a$. The symbols r , a , $D^g b$, w , γ ,

and kT are the same as for Hull and Rimmer's formula in Section 2.1. Shewmon estimated that under typical hydrogen pressures, the internal CH_4 pressure of the bubbles would be very high ($\sim 10^4$ MPa at 500°C and 10^6 MPa at 300°C), by assuming that equilibrium was maintained between the bulk hydrogen and carbon concentrations. Under these circumstances, cavity growth would be limited by the rate of vacancy diffusion.

On the other hand, it was proposed that, when bubbles are very closely spaced, the carbon in the vicinity of the boundary can be easily depleted. In this case methane formation will be slowed by carbon starvation and the methane pressure will be much smaller than the equilibrium value calculated from the bulk concentrations. Consequently, the growth rate will be decreased and, in the limiting case, growth will be controlled by the rate of carbon diffusion to the cavity. Both vacancy diffusion limited and carbon diffusion limited growth will be illustrated by the experiments which are performed in the present investigation and which are discussed in Chapters 4 and 5.

A significant feature of Shewmon's analysis is that it explains qualitatively, the apparent two stage behavior seen in the Nelson Diagrams. The flat region, in which t_i is insensitive to changes in hydrogen pressure, can be a result of carbon starvation which limits the amount of methane production and thus, the magnitude of the internal pressure. The region where t_i is sensitive to the hydrogen pressure may reflect the growth of cavities at near equilibrium pressures.

In this case a sufficient carbon supply is available. Increasing the hydrogen pressure will increase the driving force for vacancy diffusion controlled cavity growth.

The analysis also explains the change in position of the curves in the diagram with temperature. As the temperature increases, both the carbon diffusion and self-diffusion coefficients will increase. However, self-diffusion has a higher activation energy than carbon diffusion so that the rate of self-diffusion will increase faster than the rate of carbon diffusion. As a result, the steep part of the curve, which is controlled by self-diffusion coefficients, will be more sensitive to temperature changes than the carbon diffusion controlled region.

For the case of nucleation, Shewmon argued that during the initial stage of cavity formation, the equilibrium pressure could always be attained. Classical nucleation theory was applied to determine the density of bubbles on the grain boundaries. At the typical hydrogen pressures (~ 10 MPa) it was found that 1) at high temperatures $\geq 500^{\circ}\text{C}$, when the equilibrium CH_4 pressure is low, calculated homogeneous nucleation rates are lower than the nucleation rate estimate, which is based on the incubation time data but 2) at lower temperatures $\leq 350^{\circ}\text{C}$, when the CH_4 pressure is high, the calculated homogeneous nucleation rates are higher than those observed from the data.

Shewmon suggested therefore, that at high T , heterogeneous nucleation occurs at all times. At low temperatures, on the other hand, carbon starvation will quickly lower the methane

pressure in subcritical cavities, and lower the initially high rate of homogeneous nucleation and again, heterogeneous nucleation becomes dominant.

The hypothesis that cavities may nucleate heterogeneously is consistent with the observed effects of cold-work and inclusions in decreasing t_i . The effect of increasing the carbon concentration is to raise the equilibrium CH_4 pressure and the CH_4 production rate and consequently, to increase the nucleation rate of cavities.

The comparison between the predictions of Shewmon's analysis and the limited amount of experimental observations shows qualitative agreement. More work is required to support the quantitative aspects of the model. In particular, experiments are necessary to verify the nucleation and growth kinetics in different temperature regimes. Measurements of the internal methane pressure during hydrogen exposure would also be useful, because they can give direct evidence for carbon starvation. In the case of carbon starvation, the pressure inside the cavity should be equal to $2\gamma/r$.

In summary:

- 1) Hydrogen attack is characterized by the nucleation and growth of methane filled cavities on the grain boundaries, and eventually leads to a severe loss in ductility.

- 2) The nucleation of bubbles most probably is heterogeneous at high temperatures and may be homogeneous at low temperatures.

- 3) The growth of cavities is probably by a vacancy

diffusion mechanism driven by the internal gas pressure.

4) Both nucleation and growth can be slowed by carbon starvation at low temperatures.

2.2.2 Grain Boundary Cavity Growth in the Presence of Helium

This section discusses the production of helium in stainless steel during neutron irradiation. It considers the role that helium plays in grain boundary cavitation and the influence of irradiation produced defects.

Helium gas is created in most structural materials during neutron irradiation. The helium is formed by the so-called (n,α) transmutations of the components of the material. The rate of helium production in any given structural material will be determined by the neutron energy spectrum to which it is exposed. (43) The graph in Figure 2.10 shows the flux spectrum for some positions in the Experimental Breeder Reaction (EBR II), the High Flux Isotope Reactor (HFIR) and also the first wall of the proposed controlled thermonuclear fusion reactor (CTR). It is clear that the energy profile is different for each reactor type and also for various positions in the given reactor and, therefore, a wide range of helium production rates are possible. Table 2.1 shows some calculated helium production rates for stainless steel in the EBR II, the HFIR and the CTR. Helium bubbles are expected to form at high fluences as a result of helium production. Investigations of helium production and embrittlement in

Figure 2.10: CTR, EBR II and HFIR flux energy spectra (taken from reference 43)

Table 2.1

Damage Rates in Type 316 Stainless Steel

Reactor	Neutronic Wall Loading (MW/m^2)	dpa/yr	He (ppm)/yr
CTR, Princeton	1.87	30	460
CTR, Wisconsin	1.25	18	285
EBR-II	---	60	12
HFIR	---	60	1900

Austenitic stainless steels that have been performed for the fast breeder program have shown that helium bubbles can influence the fracture of stainless steel (44,45). Irradiation experiments have been done in material testing reactors (43, 44,45) in which the helium production rates are ~ 10 ppm/year at higher temperatures. In general, the effect of helium bubbles formed during irradiation is to reduce ductility as determined by the strain-to-failure in post-irradiation creep-to-rupture tests. The failure mode observed is intergranular.

In specimens irradiated in the HFIR, large numbers of helium bubbles were found throughout the bulk of the sample, but the largest bubbles were observed on the grain boundaries. A typical micrograph of stainless steel irradiated in the HFIR in the absence of an applied stress is shown in Figure 2.11. These bubbles are expected to grow under an applied stress and will eventually lead to intergranular failure. Measurements of the bubble sizes before and after a post-irradiation creep test showed bubble growth due to an applied stress. (14) An example of growth data in stainless steel is shown in Figure 2.12.

In the relatively low temperature EBR II irradiations performed so far, bubbles are rarely found at the grain boundaries. A typical micrograph of irradiated type 316 stainless steel is shown in Figure 2.13. In this irradiation in the EBR II, fluence similar to that experienced by the specimen irradiated in the HFIR was attained, but the temperature during

Figure 2.11: Helium bubbles formed in annealed type 316 stainless steel neutron irradiated to a fluence of $4.2 \times 10^{22} \text{ n/cm}^2$ in HFIR (reference 43)

Figure 2.12: Helium bubble size distributions before and after the application of an applied stress (reference 14)

- a) immediately after irradiation
- b) after irradiation and annealing at 750°C
- c) after radiation and the application of applied stress

Figure 2.13: Helium bubbles in type 316 stainless steel subjected to 1.9×10^{22} n/cm² in EBR II. Compared to the situation shown in Figure 2.11 at a similar fluence for the HFIR irradiation, few bubbles form at the grain boundaries.

Irradiation was lower than in the HFIR.

The lack of helium bubbles on the grain boundaries in the specimen irradiated in EBR II is, in part, due to the previously mentioned fact that the helium production rate is lower in the fast reactor. Moreover, the lack of bubbles can also be attributed to the irradiation temperatures. Irradiations in the EBR II are mostly carried out at temperatures between 400°C and 600°C where void formation occurs. The voids can act as sinks for helium and prevent the helium from ever reaching the grain boundaries. Of course, at lower temperatures, the helium mobility is also lower. Since in the EBR II experiment, helium bubbles were not usually found in the grain boundaries, the role of helium in embrittlement has not been clearly delineated.

In cases such as the inner wall of the fast reactor fuel cladding, temperatures can be too high for void formation. ($> 600^{\circ}\text{C}$) Under these conditions more helium may reach the grain boundary (46).

In the proposed CTR the helium production rate is expected to be between that in the HFIR, and that in the EBR II. At the present time there is no experimental information as to the bubble density and size distribution which will result from fusion reactor conditions. Li et al (47) estimated the expected bubble densities in stainless steel under CTR first wall conditions. They applied the GRASS Code, which was originally established for fission gas bubble behavior in

ceramic fuels, to find that densities of about $10^{11}/\text{cm}^3$ (spacing 10^{-3} cm.) can be expected for grain boundary bubbles that range from 10^{-6} to 10^{-4} cm. in radius. If their estimates are correct, it is likely that the helium in the CTR first wall will contribute to cavitation at the grain boundaries.

In all of the above cases, helium bubbles can be viewed as cavity nuclei. They are expected to grow by absorbing vacancies. The driving force for cavity growth can be the helium gas pressure as well as applied stress on the grain boundaries. Under irradiation vacancies can also be generated in the grain matrix as a result of irradiation produced displacements. (40,42) The kinetics of cavity growth under the simultaneous influence of stress and irradiation has been determined for two rate limiting cases, which are treated in detail in Chapter 3. (42)

In the first case, the absorption rate of irradiation produced defects to the grain boundaries and cavities is limited by bulk diffusion. In the other, this absorption is limited by the reaction (absorption) rates at the surfaces of these sinks.

In summary:

- 1) During neutron irradiation, helium bubbles can be produced on the grain boundary.

- 2) The density of bubbles will depend on the irradiation conditions, the total neutron fluence and the flux spectrum.

3) Bubbles are expected to form on grain boundaries in the CTR first wall and in the highest temperature regions of the fast reactor fuel cladding.

4) These bubbles at the grain boundary can be viewed as cavity nuclei and grow by a vacancy mechanism.

CHAPTER 3 - MODELS FOR GRAIN-BOUNDARY CAVITY GROWTH

As indicated in Chapter 2, vacancy absorption is the most likely mechanism for grain boundary cavity growth under internal gas pressure or under an applied stress at low strain rates. Vacancies are probably generated at the grain boundaries and diffuse along the boundaries to the cavity surface. Under irradiation vacancies can also be created within the bulk. It will be shown that the rate limiting process for vacancy absorption at the sinks determines whether irradiation produced defects influence the growth kinetics.

The driving force for cavity growth is the sum of the normal stress at the grain boundary and the internal gas pressure of the cavity. However, the normal stress at the grain boundary is not easily determined. It will be influenced by the relative importance of the deformation processes in a polycrystalline solid. These processes include grain matrix deformation and grain boundary sliding. In a given material the relative contributions of each mechanism depend on temperature, deformation history, and strain rate. (48,49,50) Under conditions in which grain boundary sliding is negligible, the material behaves essentially as a uniform solid, and the normal stress on the grain boundary can be found simply by geometrical decomposition of the applied stress. When grain

boundary sliding is important, the stresses at the boundaries will be relaxed. It will be shown in the present work that, in this case, the normal stress at the boundary will be less than that predicted by geometrical decomposition.

In this chapter, the work of Hull and Rimmer and others on the vacancy diffusion model for cavity growth in the absence of irradiation effects is presented in detail. The driving force for the cavity growth is taken as the internal pressure in the cavity and the normal stress at the grain-boundary. Cavity nucleation will also be considered. Next work performed by the author on the influence of irradiation on the kinetics of cavity growth will be discussed. Two cases will be considered. In the first, the rate limiting step is bulk diffusion, and in the second case, the surface reaction (absorption) rate at the sink is the rate limiting process for absorption.

The relaxation of the normal stress at the grain boundary due to grain boundary sliding is examined in light of Hart's model for the deformation of polycrystals. This discussion provides a qualitative explanation of the strain rate dependence of the grain boundary normal stress.

3.1 Models for Vacancy Diffusion Controlled Cavity Growth

This section considers, in detail, cavity growth by the absorption of vacancies at the cavity surface. The kinetics of cavity growth will be developed for an idealized array of identical cavities on a planar grain boundary. The controlling

process for growth is assumed to be the diffusion of vacancies along the grain boundary. The diffusional flow of vacancies is governed by a chemical potential gradient that is related to the normal stress at the boundary.

3.1.1 Development and Comparison of Models

The idea that vacancy absorption could account for cavity growth was first expressed by Greenwood. (5) Later Balluffi and Seigle suggested that grain boundaries themselves were the most likely sources of vacancies and they considered the thermodynamics of the transfer of vacancies from the grain boundary to the cavities. (18) In their treatment they assumed local equilibrium both at the cavity surface and at the grain boundary. As such, the free energy must be a minimum with respect to the transfer of atoms between any portion of these surfaces and the volume immediately beneath. This concept was first developed by Herring. (26)

At local equilibrium the chemical potential of a vacancy and an atom can be computed for a flat surface. The transfer of an atom to a surface necessarily means that a vacancy is created beneath the surface.

The free energy change associated with the filling of a vacancy beneath a surface is the difference between the chemical potentials of the vacancy formed and the atom it replaces. In local equilibrium this difference must equal the work (equal to $\sigma_n \Omega$) done in placing an atom on the stressed surface.

thus

$$\mu_a - \mu_o - \mu_v = - \sigma_n \Omega \quad (3.1)$$

where μ_a and μ_v are the chemical potentials of a atom and vacancy, respectively and μ_o is the reference chemical potential of the atom.

Computation of the free energy change in growth by moving an atom from a cavity surface to a stressed boundary yields

$$\Delta(\mu_a - \mu_v) = \left(\frac{2\gamma}{r} - \sigma_n \right) \Omega \quad (3.2)$$

Here γ is the surface tension and r is the cavity radius. The term $2\gamma/r$ is equal to the energy of curvature. It is clear that growth is an energetically favored process when $\sigma_n > 2\gamma/r$.

Hull and Rimmer (9) developed a formulation for the kinetics of cavity growth. In their analysis grain boundary diffusion was assumed to be much more important than lattice diffusion at temperatures of practical interest. This assumption can be supported by the following argument: The ratio of 1) the number of vacancies transferred from the boundary to the cavity by lattice diffusion, to 2) the number of vacancies transferred by grain boundary diffusion is given approximately by

$$\frac{D^B r}{D^{gb} w} \quad (3.3)$$

where D^B and D^{gb} are the bulk self-diffusion and grain boundary self-diffusion coefficient respectively; r is the cavity radius ($< 10^{-2}$ cm.) and w is the grain boundary

thickness ($\sim 10^{-7}$ cm.) The ratio is $\sim .01$ for most materials up to one-half the absolute melting point.

The vacancy flux along the boundary due to the gradient of the chemical potential difference, $\nabla(\mu_a - \mu_v)$ is

$$\bar{J}_v = \frac{D^{gb}}{kT\Omega} \nabla(\mu_a - \mu_v) \quad , \quad (3.4)$$

where kT is Boltzmann's factor, $\bar{J}_v$ is a vacancy current density and ∇ is a two dimensional gradient operator in the grain boundary plane. Since the grain boundary and cavity surfaces are assumed to be the only sources and sinks for vacancies, the divergence of $\bar{J}_v$ is related to the vacancy generation rate, $G(\bar{R})$, at each point $\bar{R}$ on the grain boundary by the equation:

$$\frac{dC_v(\bar{R})}{dt} = G(\bar{R}) - \nabla \cdot \bar{J}_v \quad . \quad (3.5)$$

Here $dC_v(\bar{R})/dt$ is the rate of change of the vacancy concentration at the point $\bar{R}$ on the grain boundary. The generation of vacancies at the grain boundary is equivalent to the deposition of atoms between the grain such that the specimen will elongate under an applied stress. In order to avoid misfit at the boundary or distortion of the specimens, the atoms should be deposited uniformly along the grain boundary. Therefore, G can have no $\bar{R}$ dependence. Under the quasi-steady-state assumption, Equation 3.5 becomes

$$0 = G - \nabla \cdot \bar{J}_v \quad . \quad (3.6)$$

With the substitution of the equations 3.4 and 3.1 into Equation 3.6 a quasi-steady-state mass balance equation is obtained for vacancy flow along the grain boundary:

$$\frac{-D^{gb}}{kT} v^2 \sigma_n (R) = G \quad (3.7)$$

At this point the analyses of the various investigators diverge.

Hull and Rimmer's original approach was to envision a square array of spherical cavities separated by a distance, a , apart. They solved the steady-state mass balance equation by using a fourier series solution and the following boundary conditions: 1) The value of σ_n at the grain boundary is $\frac{2\gamma}{r}$; 2) the solution has the periodicity of the square lattice and 3) the total load on a unit cell due to the applied normal stress, $\bar{\sigma}_n$, is equal to $\bar{\sigma}_n \cdot a^2$. In their solution the number of vacancies entering the cavity in a unit of time (dN/dt) is expressed by

$$\frac{dN}{dt} = - \int_0^{2\pi} j_v(\bar{r}) \cdot w \bar{r} d\theta \quad , \quad (3.8a)$$

where $\bar{r}$ is a point on the cavity surface and $w \bar{r} d\theta$ is an element of the cavity surface that intersects the grain boundary.

Radial symmetry is assumed at the cavity surface so that only the magnitudes of the current and the radius were necessary to compute dN/dt , and thus Equation 3.8a becomes

$$\frac{dN}{dt} = -j(r) (2\pi r w) \quad (3.8b)$$

Finally, the substitution of the fourier series solution yields

$$\frac{dN}{dt} = \frac{2(wD^{gb})}{kT} \frac{4\pi^2}{a} \left(\sigma - \frac{2\gamma}{r}\right) \cdot S \quad (3.9)$$

where

$$S = \sum_m \sum_n \frac{C_{mn}/B}{(m^2+n^2)^{1/2}} J_1 \left(\frac{2\pi r}{a} (m^2+n^2)^{1/2} \right) / \sum_m \sum_n \frac{C_{mn}}{B(m^2+n^2)} \quad (3.10a)$$

and

$$\frac{C_{mn}}{B} = - \frac{r}{a(m^2+n^2)^{1/2}} J_1 \left(\frac{2\pi r(m^2+n^2)^{1/2}}{a} \right) - \quad (3.10b)$$

$$\left(1 - \frac{\pi r^2}{a^2}\right) J_0 \left(\frac{2\pi r(m^2+n^2)^{1/2}}{a} \right)$$

Once dN/dt is known, the rate of cavity growth can be found by

$$\frac{dV}{dt} = \Omega \frac{dN}{dt} \quad (3.11)$$

Assuming the cavity remains spherical, a radial growth equation can be written as:

$$\frac{dr}{dt} = \left[\frac{2\pi\Omega(wD^{gb}) \left(\bar{\sigma}_n - \frac{2\gamma}{r}\right)}{kT\alpha r} \right] \cdot S \quad (3.12)$$

S is a function of r/a only. Calculations showed $S \approx 1$ for the cases which Hull and Rimmer considered.

Speight and Harris (41) suggested that the approximation for S is not accurate for large cavity spacings where Equation 3.12 predicts a vanishing growth rate. They attempted to avoid having to compute a new S for each new spacing and solved the quasi-steady-state mass balance Equation 3.7 in a different way. They considered the same square array of cavities, but treated each cell in isolation. This simplified the analysis because the solution, $\sigma_n(\bar{R})$, was then assumed to be radially symmetric about the cavity for $r/2a \ll 1$.

Their mass balance equation was equivalent to Equation 3.7, but was written for the case of radial symmetry such that

$$\frac{Dgb}{kT} \left[\frac{\partial^2 \sigma_n}{\partial^2 R} + \frac{1}{R} \frac{\partial \sigma_n}{\partial R} \right] - G = 0 \quad (3.13)$$

where R is the magnitude of $\bar{R}$ measured from the center of cavity. This equation has the general solution:

$$\sigma_n(R) = - \frac{GkTR^2}{4Dgb} + A \ln R + B \quad (3.14)$$

The boundary conditions for the solution are: 1) The value of σ_n at the cavity boundary intersection is $2\gamma/r$. 2) The flux of vacancies halfway between the cavities is zero. 3) The value of σ_n at $r=a/2$ is equal to the applied normal stress at the boundary. The first two conditions are equivalent to Hull and Rimmer's first two boundary conditions. The third, which is different from Hull and Rimmer's third boundary condition, underestimates the load on the boundary. (39,40,42)

The result of Speight and Harris' calculation is:

$$\frac{dr}{dt} = \frac{wD^{gb} \Omega (\bar{\sigma}_n - 2\gamma/r)}{2kTr \{ \ln(a/2r) - (a^2 - 4r^2)/2a^2 \}} \left[\frac{1}{r} - \frac{4r}{a^2} \right] \quad (3.15)$$

Recent investigators (39,40,42) have pointed out the error involved in Speight and Harris' third boundary condition and have replaced it with an expression that equates the load on the cell to $a^2 \bar{\sigma}_n / 4$, (39,42) that is:

$$\int_r^{a/2} \sigma_n(R) 2\pi R dR = \frac{\pi a^2}{4} \bar{\sigma}_n \quad (3.16)$$

The latter boundary condition gives the growth rate expression adopted in the present work as

$$\frac{dr}{dt} = \left(\frac{wD^{gb}}{kT\Omega} \right) \left(\frac{\Omega}{r} \right) \left[\left(\frac{2r}{a} \right)^2 - 1 \right] \frac{(\bar{\sigma}_n - \frac{2\gamma}{r}) \{ 1 - (\frac{2r}{a})^2 \}}{3/4 + 1/4 (\frac{2r}{a})^4 + \ln(\frac{2r}{a}) - (\frac{2r}{a})^2} \quad (3.17)$$

This expression was arrived at independently by both Raj and Ashby (39) and also Mancuso, Huang and Li (42). This expression is derived in Appendix B.

In the case where the internal gas pressure of the cavity is p , the chemical potential difference at the cavity surface becomes

$$\mu_a - \mu_v = p - \frac{2\gamma}{r} \quad (3.18)$$

and the term $(-2\gamma/r)$ in the growth equations becomes $(p - 2\gamma/r)$.

The various terms in the expression for the growth rate adopted in the present work (Equation 3.17) can be interpreted as follows:

1) The factor (Ω/r^2) relates the radial growth to the cavity volume change associated with the absorption of a vacancy.

2) $[\bar{\sigma}_n \Omega + p - (2 \gamma/r) \Omega]$ is the driving force of stress induced diffusion.

3) $(1 - 4r^2/a^2)$ is a stress enhancement factor, due to the fact that cavities reduce the load carrying area and thus increase the stress on a boundary.

4) The factor $[3/4 + 1/4(2r/a)^4 + \ln(2r/a) - (2r/a)^2]$ takes into account the fact that the grain boundary must be uniformly drained of vacancies. This term decreases as the cavity takes up more of this boundary, such that it contributes to the increase in the growth rate at large cavity radii.

The last two factors are considered in principle in Hull and Rimmer's analysis. However, in the approximation $S=1$, both effects disappear.

The calculated radial growth rates based on equations 3.12, 3.15 and 3.17 are plotted as a function of $(2r/a)$ in figure 3.1. From the graph it can be seen that Equation 3.17 and the Speight and Harris expression give the same results until the ratio $(2r/a)$ approaches unity. They both differ significantly from Hull and Rimmer's prediction for very small and very large values of $(2r/a)$.

3.1.2 The Significance of the Cavity Growth Model

According to the analysis described in the previous section, the radial growth rate is explicitly a function of a number of physical parameters. They are the self-diffusion coefficient and grain boundary thickness, the cavity spacing, the applied stress, the internal gas pressure and time. These parameters will, in turn, depend on other parameters such as the temperature, the cavity nucleation rate, etc.

First the temperature dependence of the growth rate will be examined. According to Equation 3.17 it is easy to see that the temperature dependence of the radial growth rate will be the same as the temperature dependence of the grain boundary self-diffusion coefficient, D^{gb} .

The cavity spacing, a , varies with the number density of cavities, such that the radial growth rate will be influenced indirectly by cavity nucleation. If continuous nucleation occurs, this dependence can be accounted for by up-dating the cavity spacing as a function of time.

In the absence of internal gas pressure, the stress dependence is clearly indicated by Equation 3.17, where the value dr/dt is essentially proportional to $(\bar{\sigma}_n - 2\gamma/r)$. The slopes of the graphs in Figure 3.1 show that, under an applied stress, all three growth formulae (Equations 3.12, 3.15, and 3.17) predict that $dr/dt \propto r^{-1}$. The cavity cross-section (πr^2) then has a nearly linear time dependence.

When cavities grow under an internal gas pressure alone,

Figure 3.1: The radial growth rate, as a function of $2r/a$, for cavities under an applied stress and no internal pressure. The curves are calculated from equations 3.12, 3.15, and 3.17.

the growth rate (dr/dt) is proportional to $(p - 2\gamma/r)$. If (as in the case discussed in Chapter 5) the amount of gas inside the cavity is fixed, the internal gas pressure will decrease as the cavity grows and the gas expands. The time dependence of the cross sectional area, for this case, is illustrated in Figure 3.2 (as calculated by Equation 3.17 and the ideal gas law). Cavities grow until the internal gas pressure equals $2\gamma/r$.

In the case where cavities, which have a fixed amount of gas with an initial gas pressure ($2\gamma/r$), are subjected to an applied stress, the radial growth rate is proportional to $(\sigma_n + p - 2\gamma/r)$. As shown in Figure 3.3, for cavity sizes of interest in this work, the cavity cross section also has a linear time dependence. This type of growth is discussed in Chapter 6.

3.1.3 Summary of Vacancy Diffusion Model

Grain boundary cavity growth by vacancy absorption at the cavity surface has been analyzed. The analysis can be summarized as follows:

- 1) Grain boundaries under an applied normal stress can be sources of vacancies that produce cavity growth.
- 2) Stress induced vacancy transport is along the grain boundary.
- 3) The growth of cavities can be described by the equation:

Figure 3.2: Example of the expected cavity cross-section as a function of time for a fixed amount of gas with an initial pressure $> 2\gamma/r$.

Figure 3.3: Cavity cross-section as a function of time under an applied stress for an initial gas pressure equal to $2\gamma/r$ and a spacing of $11 \times 10^{-4} \text{ cm}$. Points indicate results of a numerical integration of dr/dt .

$$\frac{dr}{dt} = \left[\frac{w_{Dgb}}{kT} \right] \left[\frac{\Omega}{r^2} \right] \left[\left[\frac{2r}{a} \right]^2 - 1 \right] \frac{\left\{ \bar{\sigma}_n - \frac{2}{r} \left[1 - \left(\frac{2r}{a} \right)^2 \right] \right\} \Omega}{3/4 + 1/4 \left(\frac{2r}{a} \right)^4 + \ln \left(\frac{2r}{a} \right) - \left(\frac{2r}{a} \right)^2}$$

4) The cross sectional area of a growing cavity varies nearly linearly with time and the normal stress on the grain boundaries.

5) The temperature dependence of growth is determined by the temperature dependence of the grain boundary diffusion coefficient.

3.2 Cavity Growth Under Applied Stress and Irradiation

This section discussed work previously published by the author on the influence of irradiation on cavity growth under an applied stress. (42) In this work a modification to the vacancy diffusion controlled cavity growth model was introduced.

3.2.1 Analysis

During irradiation both grain boundaries and grain boundary cavities will be sinks for the point defects created in the grain matrix. It is reasonable to expect that the flow of defects from the bulk will contribute to the growth of cavities and affect the mass transport along the grain boundary. (42,51)

In the following, the kinetics for cavity growth under irradiation will be developed for two limiting cases. The first is the case where defects are absorbed at the sinks, at a rate controlled by defect diffusion from the bulk. In the second case the rate of defect absorption is controlled

by the absorption or reaction rates at the sink. (42,51)

The mechanisms for mass transport by vacancies in the grain boundary are not well defined. If the condition of local equilibrium is maintained, the flow of vacancies is proportional to the gradient of a well defined vacancy chemical potential in the region of the grain boundary. If, on the other hand, local equilibrium does not apply, the total amount of atomic transport can be still expressed as the sum of the vacancy currents for each possible diffusion path or mechanism. In general, the rates of vacancy flow by each mechanism may be independent. If a condition of quasi-steady-state is assumed, however, the rate of diffusion from each path can be related to the gradient of the vacancy concentration at the grain boundary by a factor that takes into account all the other quasi-steady-state vacancy flows involved in the grain boundary region.

In the bulk diffusion controlled case, the defect concentration will have a profile given by the diffusion equation. A schematic diagram of this profile is shown in Figure 3.4a. Since local equilibrium is maintained at the sink, the chemical potential argument of the analysis given previously remains applicable, and the stress-induced growth rate will be the same with and without the influence of irradiation.

During irradiation, surface reaction rate controlled defect absorption will result in an entirely different concentration profile, which is schematically shown in Figure 3.4b.

Figure 3.4: Profiles of vacancy concentration by a surface during irradiation for a) diffusion controlled vacancy absorption and b) surface reaction rate controlled vacancy absorption.

Physically this profile represents the pile-up of vacancies at the sink because the absorption rate there is limiting. The condition of local equilibrium will no longer exist at the sink. It is possible to calculate the rate of defect flow under a quasi-steady-state assumption and by the use of mass balance considerations.

Under the assumption of a quasi-steady-state, mass balance also must be maintained between defect flow from the bulk and absorption at the grain boundary. Under the same assumption, the gradient of the vacancy concentration can be taken as the driving force for stress induced mass transport from the grain boundary to the cavity.

The vacancy flux from the bulk can be expressed as

$$\frac{D_v^b}{L} [C_v^b - C_v^{gb}] \quad , \quad (3.19)$$

where C_v^b is the vacancy concentration in the bulk; D_v^b is the bulk vacancy diffusion coefficient, which is independent of the vacancy concentration; L is a characteristic diffusion length; and C_v^{gb} is the vacancy concentration at the grain boundary. The vacancy absorption rate at the grain boundary is:

$$K[C_v^{gb} - C_v^e] \quad (3.20)$$

Solving for C_v^{gb} , equation 3.20 yields

$$C_v^{gb} = \frac{D_v^b C_v^b / L - K C_v^e}{D_v^b / L + K} \quad . \quad (3.21)$$

At the grain boundary the thermal equilibrium concentration of vacancies is related to the normal stress by:

$$C_v^e = C_0 \exp [\sigma_n \Omega / kT] \quad , \quad (3.22)$$

where C_0 is the equilibrium concentration at zero stress. The thermal equilibrium concentration of interstitials is negligible, and thus, will not be considered here. The mass flux of vacancies along the grain boundary, $\bar{J}_v$, due to the existence of a gradient in C_v^{gb} is

$$\bar{J}_v = - D_v^{gb} \nabla C_v^{gb} \quad . \quad (3.23)$$

Here D_v^{gb} is the grain boundary vacancy diffusion constant, (as opposed to the grain boundary self-diffusion constant, D^{gb}) which includes all the possible mechanisms for mass transport by vacancies along the grain boundary.

By relating C_v^{gb} to C_v^e and C_0 by Equation 3.21, $\bar{J}_v$ is found to be

$$\bar{J}_v = D_v^{gb} \left(\frac{C_v^e}{kT} \right) \left(\frac{K}{K + D_v^{gb}/L} \right) \nabla \sigma_n (\bar{R}) \quad . \quad (3.24)$$

The mass balance equation 3.6 still applies so that

$$\nabla \cdot \bar{J} = G \quad .$$

We obtain

$$D_v^{gb} \left(\frac{\Omega}{kT} \right) \left(\frac{K}{K + D_v^{gb}/L} \right) \nabla \cdot (C_v^e \nabla \sigma_n (\bar{R})) + G = 0 \quad . \quad (3.25)$$

the term $\nabla \cdot (C_v^e \nabla \sigma_n (\bar{R}))$ is equal to $C_0 \nabla^2 \sigma_n (\bar{R})$ to the

first order in $\sigma_n(\bar{R})$. Consequently, the mass balance equation becomes:

$$\left[\frac{(\Omega C_o D_v^{gb})}{kT} \right] \left[\frac{K}{K + D_v^b/L} \right] \nabla^2 \sigma_n(\bar{R}) + G = 0 \quad (3.26)$$

Equations 3.23 to 3.26 have been derived in reference 42 in terms of the atomic mobility, B , and the atom flux, j_a during irradiation (p. 1284 paragraph 2). In that work,

$$j_a = \left(\frac{\delta B k T}{\Omega C_v^{gb}} \right) \nabla C_v^{gb} ,$$

where δ is equivalent to w in this presentation. The factor $B k T / \Omega C_v^{gb}$ is equivalent to the grain boundary vacancy diffusion coefficient, D_v^{gb} , that is used in the present formulation.

As long as D_v^{gb} is independent of irradiation, the factor, $(\Omega C_o D_v^{gb})$ is identical to the grain boundary self-diffusion constant, D_v^{gb} , used in Equation 3.17. Consequently, Equation 3.26 becomes

$$D_v^{gb} \left[\frac{K}{K + D_v^b/L} \right] \nabla^2 \sigma_n(\bar{R}) + G = 0 \quad (3.27)$$

This equation has the same mathematical form as the mass balance equation without irradiation, except for the factor, $K/(K + D_v^b/L)$. In the reaction rate controlled case $K \ll D_v^b/L$. Thus, the factor $K/(K + D_v^b/L)$ should be much less than one in the case where the reaction rates at the sinks are controlling, and will effectively reduce the diffusion coefficient at the grain boundary. Equation 3.27 can be solved by the use of

the same boundary conditions as for Equation 3.14, except that Condition (1) has to be replaced by the condition that C_v^{gb} at the cavity-boundary intersection should equal the concentration at the cavity surface. If the absorption of defects at the cavity surface is also reaction rate controlled, and the constants K and L are the same as for the grain boundary, the radial growth rate during irradiation, dr_{irr}/dt then related to the out-of-pile growth rate, dr/dt by

$$\frac{dr_{irr}}{dt} = \left(\frac{K}{K + D_b/L} \right) \frac{dr}{dt} \quad (3.28)$$

Thus, for surface reaction rate controlled defect absorption, cavity growth under a given applied stress, can be reduced from that expected for the case without irradiation. In addition, dr_{irr}/dt approaches dr/dt in the case where K becomes large and bulk diffusion is limiting.

The result, that the stress-assisted diffusion mechanism for cavity growth is either unaffected or inhibited by irradiation, has significant implications to fuel element behavior. At first glance it suggests that for a given applied stress, the time-to-failure of a reactor component can be computed in the same way as for the out-of-pile case, except for the factor $K/(K + D_b/L)$ discussed above. However, it will be shown in the next section, that the hardness and flow behavior under the influence of irradiation, will also

affect the value of $\bar{\sigma}_n$ and consequently, the growth rate. Unfortunately, the latter effect of radiation is not known

quantitatively.

3.2.2 Summary

1) The rate controlling mechanism (either bulk diffusion or reaction rates at the sinks) for the absorption of irradiation produced defects determine the effects of radiation on the cavity growth rate.

2) For the bulk diffusion controlled case no effect on growth is expected.

3) Cavity growth may be inhibited when defect absorption is controlled by surface reaction rates at the sinks.

3.3 Normal Stress at the Grain Boundaries During Creep Deformation

The discussion in this section will show that the normal stress at the grain boundary depends on both the applied stress and the grain boundary sliding rate. This connection between grain sliding and the driving force for diffusion, $\bar{\sigma}_n$, was introduced in a work done previously. Grain boundary sliding will create stress concentrations at grain intersections and will relax the stresses at the boundary, such that the normal stress at the grain boundary will be much less than that predicted by geometrical decomposition of the applied stress. At high strain-rates, when grain boundary sliding is not important, the stress at the grain boundary will be as predicted by geometrical decomposition.

3.3.1 Analysis

In the cavity growth analysis given previously, the grain boundary normal stress, $\bar{\sigma}_n$, is the driving force for cavity growth and must be known in order to estimate the cavity growth rate. Previous investigators took the value of $\bar{\sigma}_n$ at a grain boundary to be that calculated by geometrical decomposition of the applied tensile stress. (4,8,9) Under this assumption

$$\bar{\sigma}_n = (\sigma_T \cos^2 \theta) \quad , \quad (3.29)$$

where θ is the angle between the boundary normal and the applied tensile stress axis. This procedure is justified if the specimen is deforming homogeneously. However, when a material is not deforming uniformly, as in the case where grain boundary sliding is important, $\bar{\sigma}_n$ will no longer be a simple function of the applied stress. For a material with a given grain size and texture, the value of $\bar{\sigma}_n$ will depend on the extent of the contribution of grain boundary sliding to deformation. This, in turn, is controlled by parameters such as temperature, hardness, and strain-rate.

The effects of grain boundary sliding on the stress distribution in a polycrystal under an applied stress were first considered by Zener for an elastic solid. (53) He concluded that when free sliding occurs, the stresses on grain boundaries are altered such that the elastic constants of a polycrystal should be less than those in a non-sliding polycrystal. Hart

extended this concept (48,49) to plastically deforming materials and developed a variation of the Voight model to describe the relationship between viscous sliding and power law matrix deformation.

According to Hart's model, grain matrix processes control the deformation rate at very high or very low stresses. At intermediate stresses the strain rate will be influenced by grain boundary sliding. An example of the stress-strain rate data in the region where grain boundary sliding is important, is shown in Figure 3.5 for type 316 stainless steel. (42) In Hart's model the high and low stress regions are represented by the upper and lower plateaus respectively. Physically, in the low stress region, the grain boundary is free to slide such that the deformation is controlled by grain matrix processes. On the other hand, at the high stress region, grain boundary sliding is more difficult. The transition region is influenced by the contributions of both grain boundary sliding and matrix flow to deformation.

In the intermediate and low strain-rate regimes, grain boundary sliding will have the effect of creating stress concentrations at obstacles (including grain boundary intersections) to sliding. The stresses at the grain boundaries have been estimated by Hart, (49) who computed the net unbalanced shear stress on a sliding boundary by idealizing it as a shear crack (Figure 3.6) and found:

$$\tau_c = \tau_{\text{applied}} - \tau_{\text{gb}} \quad (3.30)$$

Figure 3.5: Typical stress vs strain data for type 316 stainless steel at 600°C (reference 42)

Figure 3.6: Schematic diagram of the shear crack treated by Hart's analysis (reference 39)

where τ_c is the unbalanced shear stress that must be compensated for at the grain corners; τ_{applied} is the stress expected by geometrical decomposition of the applied stress; and τ_{gb} is the actual stress at the grain boundary. Hart estimated τ_c by computing the stress intensity at the crack tip for a given sliding velocity. He obtained:

$$\tau_c = Yd^{\mu-1/2} \tau_o \dot{\epsilon}_g^{\mu}$$

Y is a stress intensity factor; d is the crack length; and $\dot{\epsilon}_g$ is the contribution of grain boundary sliding to the total strain rate. The constants τ_o and μ are defined by the power law creep expression $\tau_{\text{applied}} = \tau_o \dot{\epsilon}_m^{\mu}$ where the subscript, m , denotes the grain matrix. Consequently, one obtains for the ratio of the stress on the grain boundary to the applied stress:

$$\frac{\tau_{gb}}{\tau_{\text{applied}}} = 1 - Yd^{\mu-1/2} \left(\frac{\dot{\epsilon}_g}{\dot{\epsilon}_m} \right)^{\mu} \quad (3.32)$$

According to the above equation the ratio $\dot{\epsilon}_g/\dot{\epsilon}_m$ will have a strain-rate dependence like that shown qualitatively in Figure 3.7. The value of $\tau_{gb}/\tau_{\text{applied}}$ can be used to estimate the ratio of $\bar{\sigma}_n$ to the value of the normal stress calculated by Equation 3.29. A consequence of the qualitative argument given above is that the normal stress will be smaller than that calculated by geometrical decomposition at low strain rates but it will approach the latter as the strain-rate is increased. An important objective of the present work is to

Figure 3.7: The qualitative behavior of $\dot{\epsilon}_g / \dot{\epsilon}_m$ as a function of the strain rate

demonstrate this possibility experimentally.

Crossman and Ashby (50) obtained a similar result by performing a finite element analysis of a regular array of grains undergoing both grain boundary sliding and power law creep. Their results are shown in Figure 3.8 in the form of strain-rate contours for various values of n ($n=1/\mu$). As the value of n increases, there is a decrease in both the strain rate in the grain boundary region and the shear stress at the grain boundary. These conclusions are consistent with Hart's results.

Since the normal stress at the grain boundary is the driving force for cavity growth, the argument made above can be used to rationalize the observed non-linear stress dependence of the observed cavity growth rate (28). It can be used also to rationalize the observation that the impurity level and cold-work (discussed in Chapter 2) influence the cavity growth rate. For example, impurities can introduce precipitates or inclusions at the grain boundary. These particles can be obstacles to grain boundary sliding and therefore alter the stress concentration discussed previously.

3.3.2 Summary

This section is summarized as follows:

- 1) During creep deformation the normal stress at the grain boundary cannot always be computed by simple geometrical decomposition of the applied stress.

Figure 3.8: Crossman and Ashby's normalized strain rate contours in hexagonal grains for various values of n for the case of free sliding. The upper left hand quadrant indicates divisions used for finite element calculation. High stress concentrations are predicted for the grain mid-plane and grain corners. (Reference 50) The contours are labeled by the ratio of the calculated strain rate to the average strain rate.

2) Grain boundary sliding will introduce stress concentrations at grain corners and relax the stresses at the grain boundary.

3) The relaxation of grain boundary stress during sliding can qualitatively account for the stress dependence of cavity growth.

CHAPTER 4 EXPERIMENT

The kinetics of grain boundary cavity growth in nickel was investigated by the experimental procedures described in this chapter. A method was established to measure the growth of cavities under an internal pressure, as well as under an applied stress. The effect of grain boundary orientation on cavity growth under an applied stress was also determined. During the growth kinetics measurement the ambiguities associated with cavity nucleation were avoided by introducing cavities of a known size distribution prior to the experiments, and by ensuring that further cavity nucleation was negligible during the experiment. The initial cavities were bubbles which were produced by exposing the nickel specimens to high pressure hydrogen at high temperatures. Cavities with a gas pressure equal to $2\gamma/r$ were used in the growth studies under an applied stress. Cavities with pressures higher than $2\gamma/r$ were used for measurements of cavity growth under an internal pressure.

A scanning electron microscope (SEM) was used to obtain photo-micrographs of the intergranularly fractured surfaces from which the cavity size distribution was determined. The photo-micrographs were taken in stereo pairs to correct for tilt distortion and, for experiments under an applied stress, to determine the grain boundary orientation relative

to the applied stress axis.

In Section 1, specimen preparation and the process for methane bubble production are presented. Fracture surface preparation and the stereo SEM techniques used are discussed in Section 2. Finally, Section 3 describes the apparatus and experimental procedures used for investigating cavity growth under an applied stress.

4.1 Specimen Examination and Cavity Size Distribution Determination

This section presents the principles and methods used for the measurement of the cavity size distribution. SEM techniques and the computational method are discussed.

4.1.1 Morphological Considerations

The growth analysis presented in the previous chapter describes the dimensional changes of spherical grain boundary cavities. Under this idealized condition the relationship between the chemical potentials and the dimensions of the cavity (including radius, cross-sectional area, and volume) are simply related. However, in reality cavities are rarely spherical. Their shape is determined by the crystallographic anisotropy and an equilibrium condition, which can reasonably be assumed to hold at the intersection of the cavity with the grain boundary. The geometry of the grain boundary-cavity intersection is shown in Figure 4.1. The angle β shown in the figure, is given by the relationship

Figure 4.1: Schematic diagram of expected grain boundary cavity shape. The angle β is determined by the equilibrium condition (Equation 4.1).

$$\beta = \cos^{-1} \left(\frac{\gamma_B}{2\gamma} \right) \quad (4.1)$$

where γ is the cavity surface tension and γ_B is the surface tension of the grain boundary. (39,54)

Johnson (55) has developed the thermodynamics for non-spherical cavities, and has shown that the volume, V , of a cavity with an equilibrium shape can be related to a single dimension L_0 by

$$V = KL_0^3,$$

where K is a shape factor. He generalized the Gibbs-Thomson equation in terms of the parameter L_0 such that

$$\mu_a - \mu_v = \frac{2\gamma}{L_0} \Omega \quad (4.2)$$

In this work it will be assumed that the equilibrium shape of the cavity is maintained. The shape factor, K , will be taken to be that for a sphere ($4/3 \pi$) and the relationship between the cavity cross-section, A , and the volume will be given by

$$V = \frac{4\pi}{3} \left(\frac{A}{\pi} \right)^{3/2} \quad (4.3)$$

The cavity size in the present work is measured experimentally by its cross-sectional area. The approximations made will lead to a systematic error (of order unity) in the absolute values of V and L . These errors will not affect the time and

stress dependence that is determined for cavity growth. The errors will introduce, however, an uncertainty in the value

of the measured rate constant for growth. Since most of the parameters in equation 3.17 are not known precisely, this uncertainty is not important for the purpose of the present work.

4.1.2 The Stereo SEM Technique

Cavity size was measured by use of SEM photo-micrographs of intergranularly fractured surfaces such as those shown in Figure 4.2. The orientation of the grain boundary plane relative to the applied stress axis was determined by the use of stereo images of the fractured surfaces. The stereo techniques also allow for the correction of tilt distortion.

The SEM used in this work was manufactured by Advanced Metals Research Corporation (Model 900). Fractured surfaces were viewed and focused through a display cathode ray tube. Another cathode ray tube was used to record the image on Type 52 Polaroid film.

The SEM was operated such that a beam of electrons accelerated by 21 kV. was focused and scanned along the specimen surface. The beam scanning pattern, called a raster, was in two perpendicular directions along the surface. Images were formed by 1) detecting electrons coming off the surface and 2) converting the electrical signal from the detector to the CRT beam of corresponding intensity, which moved in synchronization with the electron beam.

The total magnification of the sample was known to $\pm .5\%$.

Figure 4.2: Typical fracture surface examined in SEM

Local changes in magnification ($< \pm .5\%$) occurred due to CRT distortion. In this work sizes were measured usually at 2000x or 5000x magnification.

SEM specimens were mounted on the standard AMR specimen holder with a hole of .317 cm. diameter drilled parallel to the holder axis. (shown schematically in Figure 4.3) The base of the specimens was machined by using a lathe to obtain a diameter which gives a tight fit in the hole of the holder. This procedure assured that the longitudinal axis of the specimen would be parallel to the axis of the holder.

The orientation of the grain boundary plane is defined by the angle δ between the surface normal and the specimen axis as shown in Figure 4.4. The orientation can be determined by observing the surface from two different angles to obtain a stereoscopic view of the sample. This was done by changing the tilt angle (ϕ) of the specimen stage which is also shown in Figure 4.4. The value of ϕ was changed by 5° or 10° between views.

The process of changing the tilt angle (ϕ) also translated the surface away from the raster. This translation is shown schematically in Figure 4.5. Thus, it was necessary to translate the specimen back to the raster by the x, y, and z stage controls, so that the specimen is moved back to the focal plane of the beam to maintain a constant magnification.

In this work the procedure used to obtain the second

Figure 4.3: Schematic diagram of specimen position in holder

Figure 4.4: Relationships between the angles determined in the stereographic analysis

Figure 4.5: Two dimensional diagram of the translation expected after a tilt change

view of the stereo pair is described as follows:

- 1) The tilt angle was varied by 5° or 10° .
- 2) The second image on the display CRT was compared to the first micrograph and the x and y translation controls were used to make the region observed by the second image coincide with those of the first. This procedure eliminated most of the error due to the non-linearity of the cathode ray tube image, which is discussed by References 56 and 57.
- 3) The z control was applied to focus the surface at 2000x.
- 4) Fine focusing was performed at 10,000x with the third magnetic lens to allow an error in magnification of less than .1%.
- 5) The image was recorded on the polaroid film.

The photographs were analyzed by a triangulation routine developed by G. S. Lane. (56) In this procedure the (x, y and z) coordinates of three points on the surface are determined by the stereographic analysis. Two surface vectors can be determined from these points. The cross-products of the vectors gives the surface normal. The calculation method is described in detail in appendix A.1.

Two tests were performed to estimate the accuracy of the orientation measurement. In one of the relative orientation of the cleaved faces of a cubic salt crystal was determined. In another the orientation of a flat focusing grid was measured. For both tests the measured angle was within 3° of the known

gle.

4.1.3 Cavity Size Determination

The cavity cross-sectional area, determined by comparison of the cavity image to indexed circles in a standard drawing template, was used as a measure of cavity size. The cross-sectional areas were calculated by using a computer routine that correlated the index numbers to the area in cm^2 . This computer routine also corrected any distortion due to perspective. The nature of the perspective error can be seen schematically by Figure 4.6. In the figure the angle α , which is the angle between the surface normal and the electron beam, determines the projection designated by L made from the specimen designated by $\overline{AB}$. The details of the computational method are described in Appendix A.2.

The cavity size distribution in each sample was represented by a histogram in terms of cavity size. It was necessary to examine ~ 100 cavities before a reproducible mean area ($\pm 5\%$) could be obtained for a fractured surface. Depending on the choice of specimen, for the same experimental conditions up to a 25% variation in mean area could be found for samples originating from widely separated regions of the recrystallized nickel bar from which specimens were made. An example of the variation is shown in Figure 4.7.

It is suspected that this variation in mean cavity size caused by changes in the carbon concentration along the

Figure 4.6: Demonstration of the origin of perspective error. $\overline{AB}$ and $\overline{A'B'}$ represent specimen surfaces exposed to the electron beam. L_{AB} and $L_{A'B'}$ are the projections of $\overline{AB}$ and $\overline{A'B'}$ respectively.

Figure 4.7: Example of the variation in cavity size due to suspected carbon concentration variation.

nickel bar. To minimize this effect, for a given experimental sequence, the fractured surfaces were obtained from regions in the nickel bar less than 6 cm. apart.

4.2 Specimen Preparation

This section describes the procedures used for producing grain boundary cavities in the form of methane bubbles in nickel by hydrogen charging. First, the fabrication of specimens is outlined. Next, the hydrogen charging procedure and the effect of the charging conditions on bubble size and number density are presented. Finally, the behavior of the bubbles during high temperature anneals performed after hydrogen charging is discussed.

4.2.1 Materials

In this section the material used in the experiments is described. The test specimens were fabricated from nickel bar (Type 270), which was purchased from International Nickel Co. with a nominal diameter of 2.4 cm. Its composition, as determined by the manufacturer, is given in Table 4.1. The bars were first hot swaged (courtesy of G.T.B. Sylvannia at Towanda, Pennsylvania) to 1.4 cm. The final diameter of 0.36 cm. was obtained by subsequent cold swaging in eight passes from 1.4 to 0.36 cm. The rods were vacuum annealed to produce the desired grain structure by recrystallization. A variety of annealing times and temperatures

TABLE 4.1

Chemical Analysis of Specimen (Ni 270)

<u>Composition</u>	<u>Percent</u>
Ni	99.98
C	0.01
Mn	<0.001
Fe	<0.003
S	<0.001
Si	<0.001
Cu	<0.001
Cr	<0.001
Ti	<0.001
Co	<0.001

were used which produced different grain structures as shown in Figure 4.8. The various heat treatment conditions are listed below.

- 1) Type A- a 1000°C anneal for one hour followed by a 600°C anneal for 124 hours;
- 2) Type B- an 800°C anneal for one hour;
- 3) Type C- a 650°C anneal for one hour followed by a 750°C anneal for one hour.

The average grain size resulting from these treatments (as determined by the line intercept method) was $90\text{ }\mu\text{m}$, $40\text{ }\mu\text{m}$ and $46\text{ }\mu\text{m}$ for conditions A, B, and C respectively.

4.2.2 Hydrogen Charging and Production of Bubbles

This subsection describes the procedures for hydrogen charging and the phenomenon of methane bubble formation in nickel.

The hydrogen charging procedure consisted of loading the specimens in an autoclave, which was originally designed by Allen et al. (58) The schematic diagram of the autoclave is shown in figure 4.9. For hydrogen charging the vessel was first evacuated to 10^{-3} torr, brought to the desired temperature in a split furnace and finally loaded with hydrogen gas to a prescribed pressure. The hydrogen pressure was read from the gauge on the regulator at the end of the hydrogen gas cylinder. Charging times ranged from 15 minutes to 24 hours. To remove the specimen, the autoclave was lifted from the furnace and cooled under running water. Then the

(a)

(b)

(c)

Figure 4.8: Examples of grain structure for the various heat treatments; a) treatment A, b) treatment B, c) treatment C

Figure 4.9: Schematic diagram of the autoclave used for hydrogen charging (Reference 58)

hydrogen gas was released and the specimen was removed.

Limiting (minimum) exposure conditions of the time, the hydrogen pressure and the temperature for hydrogen charging were found experimentally. With charging conditions more severe than these limiting conditions, it was possible to fracture the specimens intergranularly. For charging times close to the limiting condition, few bubbles were observed at 5000x magnification. For longer times, well identifiable bubbles were found on most grain boundaries. (see Figure 4.10a.) Charging for extremely long times at high temperatures and hydrogen pressure led to dense bubble formations and honeycombing. (Figure 4.10b)

Carbon and sulfur are the only two measureable impurities that can react with hydrogen to form a gas. They can combine with hydrogen to form methane (CH_4) and hydrogen sulfide (H_2S) respectively. In Chapter 5 it will be shown that the amount of gas formed, as estimated from the total volume of the cavities observed, is greater than the amount of H_2S that can be produced from the concentration of sulfur in the material. There is, however, a sufficient amount of carbon for the bubbles to be filled with methane. Consequently, it will be assumed in this work that the dominant reaction for gas bubble formation is $4\text{H} + \text{C} = \text{CH}_4$.

In this work two types of bubbles were prepared by hydrogen charging. The first kind, which were used to measure cavity growth kinetics under an internal pressure, contained

(a)

(b)

Figure 4.10: Examples of bubbles after charging at 500°C for a) in 3.4 MPa hydrogen for 3 hours and b) in 10.3 MPa hydrogen for 24 hours.

a gas pressure for which the quantity $p - 2\gamma/r$ is greater than zero. These bubbles will grow during high temperature anneals in the absence of hydrogen. The test specimens for these experiments were prepared by charging Type-B specimens in 14.5 MPa of hydrogen at 500°C for either 1.5 or 1.75 hours. An example of bubbles produced is shown in Figure 4.11.

The second type of bubble was used in the investigation of cavity growth under an applied stress. For this purpose, the internal gas pressure of the bubble was such that $p - 2\gamma/r = 0$ and no growth was expected during stress free anneals in the absence of hydrogen. The test specimen for the latter experiments were prepared by an hydrogen charge of Type-A specimens at 3.4 MPa and at 500°C for 4 hours. The stability of the bubbles produced was tested by a 600°C vacuum anneal for 56 hours. The test results, shown in Figure 4.12 indicate that no measureable change in the cavity size distribution occurred during the anneal.

In summary:

- 1) The initial cavities for the growth experiments can be obtained by hydrogen charging.
- 2) The cavities of the present work most likely contain methane gas.
- 3) The number density, size and internal gas pressure of these cavities could be controlled by varying the charging conditions.

(a)

(b)

Figure 4.11: Examples of bubbles given a hydrogen charge of 14.5 MPa at 500°C for 1.5 hour a) before and b) after a 124 hour 500°C vacuum anneal

Figure 4.12: Comparison of bubble size distributions for specimens charged at 3.4 MPa for 4 hours at 500°C a) immediately after charging and b) after a subsequent 56 hour 600°C vacuum anneal

4) For experiments measuring the growth of cavities under an internal pressure, Type-B specimens were used. The charging conditions were: 1.5 or 1.75 hours of 14.5 MPa hydrogen at 500°C.

5) For measurement of cavity growth under an applied stress, Type A specimens were used. The charging conditions were 4 hours at 3.4 MPa hydrogen at 500°C.

4.2.3 Cavity Size Measurement

The cavity size in this work was measured by using photo-micrographs of the exposed grain boundaries on the intergranularly fractured surfaces. As was stated in Section 4.2.1, hydrogen charging can embrittle nickel such that it will fracture intergranularly. However, if charged specimens are subjected to the elevated temperatures typical to those involved in the cavity growth experiments, they regain ductility and the percent of intergranularly fractured grain boundaries decreases significantly. The decreased probability of intergranular fracture occurs whether or not cavities exist on the grain boundary. An example of the fracture surface showing the transgranular mode is shown in Figure 4.13. The specimen used was known to contain cavities on the grain boundary. A technique to embrittle the specimens intergranularly, by an additional hydrogen charging after the growth experiment, was developed to avoid the difficulty mentioned above.

Figure 4.13: Example of transgranular fracture typical of a sample annealed at 500°C after hydrogen charging

One essential requirement of the recharging procedure was that it could not influence the number and the size of the cavities at the grain boundaries. A number of charging conditions were tried on annealed samples with and without existing cavities on the grain boundary to determine the optimum procedure for embrittlement.

For the case of samples without existing cavities, series of chargings were performed at a hydrogen pressure of 2.8 MPa and at temperatures ranging from 250°C to 500°C. After the hydrogen charge the specimens were notched, cooled in liquid nitrogen and fractured in tension. The fracture surfaces were examined visually. When necessary the SEM was used to determine whether or not the fracture was predominantly intergranular or transgranular. The results of these tests are shown in Figure 4.14. These data suggest that the length of exposure time, which produces the transition between transgranular and intergranular fracture, follows a systematic temperature dependence. It was also noted that for charging conditions in the transition region few cavities were formed.

For specimens with existing grain boundary cavities, higher hydrogen pressures were required to cause intergranular fracture at a given charging time and temperature. The required hydrogen pressure was dependent on the extent of existing cavitation. For the specimens used in the cavity growth experiments, a 12 hour recharge at 10.3 MPa and at

Figure 4.14: Plot of hydrogen charging time of nickel versus temperature at a hydrogen pressure of 2.8 MPa

300°C was sufficient to cause nearly 100% intergranular fracture. These recharging conditions were used for all the samples in the cavity growth experiments. The temperature of the recharging was sufficiently low, such that further growth was not expected during this treatment.

To ensure that there is no change in cavity size during the recharge, the specimens were recharged at a hydrogen pressure of 10.3 MPa and at 300°C for 12 hours, after an initial charge at 500°C and 3.4 MPa for 4 hours. Cavity size measurements were made before and after the second charge and the results are shown in Figure 4.15. No significant change in the mean cavity area or size distribution could be measured.

A possible explanation for the intergranular embrittlement caused by the recharge is that cavities, too small to be resolved by the SEM, form during the second charge and weaken the grain boundaries. Another possibility is that embrittlement of the grain boundaries is a result of a monolayer of methane molecules formed there.

The section can be summarized as follows:

- 1) Hydrogen charging could produce intergranular fracture of nickel specimens.
- 2) Annealing after charging caused ductility to be restored.
- 3) A second charge was necessary to ensure intergranular fracture of the specimens for the cavity growth experiments.

Figure 4.15: Comparison of cavity sizes before and after a recharge at 300°C and 3.4 MPa for 12 hours

4) The recharge conditions used here were 300°C at 10.3 MPa for 12 hours.

4.3 Apparatus for Cavity Growth Experiments Under an Applied Stress

The equipment used to produce cavity growth under an applied stress is shown schematically in Figure 4.16. This equipment was designed for constant load experiments at elevated temperatures with strain measurement capabilities.

The temperature of the experiment was controlled to within $\pm 2^{\circ}\text{C}$ by a Speedomax H Temperature controller (Leeds and Northrop) with a chromel-alumel thermocouple. A Marshall electric furnace (12" long, 7" O. D., 2.5" I. D.) was used for specimen heating. Two additional thermocouples were placed 3 cm. above and below the specimen to monitor the temperature gradient. A gradient of less than $1^{\circ}/\text{cm.}$ was observed.

Loads were applied by using slotted lead (Pb) weights. The load train was fabricated from type 316 stainless steel. The pullrods (1.9 cm. diameter) were threaded to the specimen holders. The upper rod was attached to a universal joint and the lower rod was connected to the weight pan. The test specimens for the cavity growth experiment were cylindrical rods with a diameter of 0.36 cm. with a gauge length of 3.14 cm. The specimen holder used is shown schematically in Figure 4.17.

Figure 4.16: Schematic diagram of equipment used to produce cavity growth under an applied stress

Figure 4.17: Schematic diagram of the specimen clamp used to apply stress to the nickel specimens

The applied stress reported was based on the initial cross sectional area of the specimen. The initial stress may differ from the final stress at the highest strain rate by less than 5% due to changes in the specimen dimensions.

Strain was measured at fixed time intervals from the extension of the load train by using a Hewlett Packard direct current linear transducer (Model #7 DCDT) mounted below the lead weights. Its output was measured by a millivolt potentiometer and the calibration was 0.325 cm./volt. The accuracy of the strain rate measurement was of the order of 10%. Examples of the extension versus time data are shown for the highest, the lowest and an intermediate strain rate S in Figure 4.18.

Figure 4.18: Examples of the voltage reading for the strain measurements for the low, high and intermediate strain rates used in this experiment.

CHAPTER 5 CAVITY GROWTH UNDER INTERNAL PRESSURE

The investigation of the kinetics of cavity growth at the grain boundary under internal pressure is reported in this chapter. The vacancy diffusion model for cavity growth described previously by Equation (3.17) predicts that gas-filled cavities will expand until the difference between the internal pressure (p) and the term $(2\gamma/r)$ becomes zero. According to the model, the rate of growth is given by:

$$\frac{dr}{dt} = \left(\frac{wD^{gb}}{kT}\right) \left(\frac{\Omega}{r^2}\right) \left[\left(\frac{2r}{a}\right)^2 - 1\right] \frac{\left[p - \frac{2\gamma}{r}\right] \left[1 - \left(\frac{2r}{a}\right)^2\right]}{3/4 + 1/4 \left(\frac{2r}{a}\right)^4 + \ln\left(\frac{2r}{a}\right) - \left(\frac{2r}{a}\right)^2} \quad (5.1)$$

In the experiment described in this chapter, methane-filled cavities with internal temperatures and the growth kinetics was observed. These experiments served three purposes:

- 1) to verify the vacancy diffusion model for grain boundary cavity growth;
  - 2) to determine a value for the rate constant, wD^{gb} , which can be used to predict cavity growth under applied stress;
  - 3) to estimate the magnitude of the internal pressure.
- This third aspect provided information about the methane bubble formation during hydrogen exposure.

The chapter is organized as follows: first, the cavity

growth data is presented. Next, the experimental results are compared to the predictions by Equation 5.1. From this comparison a value for the product wD^{gb} is estimated. Finally, the value of the internal methane pressure obtained is compared to that calculated, based on the hydrogen reactions discussed in Chapter 2.

5.1 Experimental Data and Observations

Cavities in the form of gas-filled bubbles were first formed by charging B-type nickel specimens at a temperature of 500°C and a hydrogen pressure 14.4 MPa for 1.5 hours (S-series) or 1.75 hours (T-series). The samples that were charged for 1.5 hours came from a 6 cm. long bar. Portions of the bar (~1.5 cm. long) were annealed at 500°C for 0, 12, 50 or 124 hours. The specimens charged for 1.75 hours were from an 18 cm. long bar that was cut into three 6 cm. segments. Portions of one segment were annealed at 500°C for 0, 5, 10, 47 or 296 hours; portions of the second were annealed at 550°C for 0, 16, 55 or 98 hours and portions of the third were annealed at 600°C for 3, 17, or 53 hours. All anneals were in a quartz glass tube at a vacuum of $<10^{-5}$ torr. The temperatures reported are accurate to within $\pm 2^{\circ}\text{C}$.

After the anneals the specimens were embrittled and fractured in the manner described in Section 4.2.3. The fractured surfaces were examined in stereo at 5000x magnification in the SEM and the mean cavity cross sectional area was

etermined for each fractured surface by the procedure presented in Appendix A. The mean areas plotted in Figure 5.1 demonstrate that growth occurs during the anneals. In addition, the histograms in Figures 5.2, 5.3, 5.4 and 5.5 indicate that the distribution of cavity sizes does not appear to change due to coalescence of the bubbles. Cavity morphology remains unchanged throughout the anneals.

The cavities appear to reach a limiting mean size. At each temperature this size can be estimated by using the mean area of the bubbles subjected to the longest anneal. In Figure 5.6 the limit is shown to vary linearly with the annealing temperature.

5.2 Discussion of the Growth Data

In this section the vacancy diffusion model and the ideal gas law are used to describe the kinetics of cavity growth. The discussion includes an estimation of the gas pressure, which is the driving force for growth, as well as the rate constant for diffusion controlled growth.

According to the vacancy diffusion model, the driving force for bubble growth is proportional to the quantity $(p - 2\gamma/r)$. The ideal gas law is obeyed, such that

$$p = \frac{nRT}{V} \quad , \quad (5.2)$$

where n , R , and T represent the number of moles of gas in the bubble, the gas constant, and the absolute temperature

Figure 5.1: Plot of the mean bubble cross section vs annealing time at 500, 550, and 600°C

Figure 5.2: Histograms of the bubbles cross-sectional areas for series S specimens annealed at 500 °C

Figure 5.3: Histograms of the bubble cross-sectional areas for series T specimens annealed at 500°C

Figure 5.4: Histograms of the bubble cross-sectional areas for series T specimens annealed at 550°C

Figure 5.5: Histograms of bubble cross-sectional areas for series T specimens annealed at 600°C

Figure 5.6: Plot of the mean cross-sectional areas for the longest anneals at each temperature (T-series)

respectively. In this experiment a constant amount of gas was assumed to be contained in the bubbles and the pressure varies with only T and V . This is equivalent to the assumption that negligible methane decomposition occurs during the anneals.

From Equation 4.1 we can write

$$p - \frac{2\gamma}{r} = \frac{1}{r^3} \left[\frac{3nRT}{4\pi} - 2\gamma r^2 \right] \quad (5.3)$$

Since r^2 is proportional to the bubble cross sectional area, this equation also gives the temperature dependence of the limiting cross section, A_{equi} , as

$$A_{\text{equi}} = \frac{3nRT}{8\gamma} \quad (5.4)$$

This equation is consistent with the observation (discussed in the previous section) that the limiting bubble cross sectional area increased linearly with temperature. This agreement also supports the assumption of the ideal gas law.

The ideal gas law can be used to compute the initial bubble pressure, p_i , by the relationship:

$$p_i = p_{\text{equi}} (A_{\text{equi}}/A_i)^{3/2} \quad (5.5)$$

where A_{equi} and A_i are the initial and final mean bubble cross sections. Table 5.1 gives the calculated values of p_i and p_{equi} for the four sets of data reported. From the

able it can be seen that the pressure in the initial bubble is about 20% higher than the pressure after the long anneal.

The observed kinetics of cavity growth can be accounted for in terms of the vacancy diffusion model and the ideal gas law as discussed in Chapter 3. According to Equation 5.1 the rate of growth is given by:

$$\frac{dr}{dt} = \left(\frac{wD^{gb}}{kT} \right) \left(\frac{1}{r^3} \left[\frac{3nRT}{4} - 2\gamma r^2 \right] \right)^{\frac{1}{2}} \frac{\left[p - \frac{2\gamma}{r} \right] \left[1 - \left(\frac{2r}{a} \right)^2 \right]}{3/4 + 1/4 \left(\frac{2r}{a} \right)^4 + \ln \left(\frac{2r}{a} \right) - \left(\frac{2r}{a} \right)^2} \quad (5.7)$$

At a given temperature this equation can be integrated numerically to give the variation of the cross sectional area as a function of time, provided the following parameters are known:

- 1) the rate constant
- 2) the surface tension, γ
- 3) the cavity spacing, a
- 4) the number of moles of gas in the bubble, n .

The estimates of both γ and wD^{gb} were based on values found in the literature. For the present work, the value of γ was taken as 1900 erg/cm. (59) and was assumed to be temperature independent. The rate constant, wD^{gb} , which was taken from a range of values reported in the literature, (60,61) was equal to $3.5 \times 10^{-9} \exp(-1.19/kT) \text{ cm.}^3/\text{sec.}$

The values for a and n were determined experimentally by the charging conditions. A typical value of the cavity spacing was 4 μm . The values of n which were calculated for each

test series were based on the values of p_{equi} listed in Table 5.1.

If grain boundary diffusion of vacancies controls growth, Equation 5.7 applied and $D^{gb} \cdot t$ determines the change in cavity area in a given time. In Figure 5.7 the calculated and experimentally determined mean cavity areas are plotted against $D^{gb} \cdot t$ for all three temperatures. It is seen from the figure that the calculated curves are in rough agreement with the experimental data. This suggests that the temperature dependence and the time dependence of the rate of cavity growth are consistent with the predictions based on Equation 5.7 and the values of the required parameters used. These experimental results support the validity of the vacancy diffusion controlled growth model adopted in this work.

The results in Figure 5.7 yield an estimation of the value of wD^{gb} that can be used in the investigation of cavity growth under an applied stress. The uncertainty in the value of this rate parameter is related to the uncertainties of the values of the three other parameters in Equation 5.7, namely γ , a , and n . The uncertainty involved in all these parameters can be of the order of 50%, and as a result, the value of wD^{gb} cannot be expected to be known by better than a factor of two.

In conclusion the investigation of cavity growth under an internal gas pressure shows that:

- 1) Cavity growth kinetics are controlled by vacancy diffusion along the grain boundary.

Table 5.1

Estimated Initial and Final Pressure in T-Series Bubbles

<u>Ann. Temp. (°C)</u>	<u>Time (hr)</u>	<u>p_i (MPa)</u>	<u>p_{equi} (MPa)</u>
500	298	6.8	5.0
550	98	6.0	4.9
600	53	6.5	4.6

Figure 5.7: Plot of the measured and calculated bubble cross-sections as a function of Dt for all three temperatures

2) The internal pressure in the bubble can be determined as a function of bubble size and temperature from the ideal gas law.

3) The rate constant for diffusion can be obtained from the cavity growth data and is estimated as:

$$wD^{gb} = 3.5 \times 10^{-9} [\pm 1.7 \times 10^{-9}] \exp \left(- \frac{1.19 [\pm .02] \text{ev}}{kT} \right) \text{ cm.}^3/\text{sec.}$$

5.3 Bubble Growth During Hydrogen Charging

The results of the previous section also yield information on bubble growth in nickel during hydrogen charging. Both the $2\text{H} + \text{S} = \text{H}_2\text{S}$ and the $4\text{H} + \text{C} = \text{CH}_4$ reactions are considered.

According to the analysis for methane formation presented in Chapter 3, the rate limiting mechanisms for bubble growth could be determined from knowledge of the internal gas pressure in the bubbles. Two cases were considered. In the first the methane production rate is slow relative to the growth rate and the methane gas pressure is equal to $2\gamma/r$ during cavity growth. A possible cause of this situation is so-called carbon starvation suggested by Shewmon. In the second case the methane is produced at a much faster rate than the cavity can grow to maintain a balance between the internal pressure and $2\gamma/r$. The pressure in the most extreme limit can be equal to the thermo-equilibrium methane pressure calculated from the $4\text{H} + \text{C} = \text{CH}_4$ reaction.

The initial pressure in the bubbles has been shown to be approximately 20% higher than the value of $2\gamma/r$ (Table 4.1). This result suggests that under the charging conditions described in Section 5.1 for sample preparation, vacancy diffusion is controlling the growth process. It should be noted that the observed pressure is much less than the thermo-equilibrium pressure calculated for either CH_4 or H_2S based on the charging conditions and the bulk carbon and sulfur concentration respectively. The details of the calculation are given in Appendix C. In both cases the thermo-equilibrium gas pressure is found to be orders of magnitude higher than the observed pressure. This result suggests that the activity coefficient of dissolved carbon or sulfur was much less than one, and/or the situation of carbon starvation existed.

In contrast, the bubbles in the specimens used in the cavity growth experiments under an applied stress did not show growth during anneals after charging. Under the charging conditions for these specimens, the pressure must balance the $2\gamma/r$ term at the end of the charging process. It is likely, therefore, that carbon or sulfur diffusion is the rate controlling process for the latter case.

In order to test whether the bubbles contain CH_4 or H_2S , the total amount of gas formed in the bubble is estimated and compared to that available from CH_4 and H_2S production at the bubble surface.

The number of gas molecules in a bubble of average size

n be obtained from:

$$n = \frac{PV}{RT} \quad (5.8)$$

The average bubble volume is $\sim 2 \times 10^{-2} \text{ cm}^3$. For a bubble pressure of 5 MPa at 500°C one finds that

$$n \sim 10^{-15} \text{ moles}$$

The amount of gas formed at the surface can be no greater than the total amount of carbon or sulfur that can reach the surface during the hydrogen charge. This is roughly equal to the amount of impurity (carbon or sulfur) within a sphere of radius $(D_{\text{IMP}} t)^{1/2}$. Here D_{IMP} is the diffusion coefficient of the impurity and t is the charging time. For carbon, D_{IMP} is $1 \times 10^{-11} \text{ cm}^2/\text{sec}$. (62). The carbon concentration is approximately $7.4 \times 10^{-5} \text{ moles-C/cm}^3$, so that the total amount of carbon available to the bubble in one hour is $\sim 1 \times 10^{-15}$ moles. For the case of sulfur, the diffusion coefficient is expected to be at least an order of magnitude smaller than for carbon. (63) The concentration of sulfur in nickel is less than $3 \times 10^{-6} \text{ moles/cm}^3$. It can be concluded that the amount of sulfur reaching the cavities is much less than the observed amount of gas. The above calculations show that most of the gas in the bubbles is likely to be methane and that cavity growth, depending on the charging conditions, can be limited by the rate of methane formation during charging.

5.4 Summary

Bubbles formed during hydrogen charging were found to grow when subjected to high temperature anneals in the absence of hydrogen. The measurement of the growth rate demonstrated that:

- 1) The driving force for cavity growth was the quantity $p - 2\gamma/r$.

- 2) The growth kinetics could be described by the vacancy diffusion model.

The experiment also yielded information on the process of bubble formation during hydrogen charging. Both the H_2S and CH_4 reactions were considered. It was shown that:

- 1) The sulfur concentration was too low for H_2S formation to be significant to cavity growth.

- 2) A sufficient amount of carbon was available to produce bubbles by methane formation.

- 3) Evidence of both vacancy diffusion controlled growth and methane formation controlled growth during the hydrogen charging could be found.

According to the analysis given in Chapter 3, the normal stress, $\bar{\sigma}_n$, on a grain boundary is the driving force for cavity growth rate was given in Equation 3.17. It was suggested in Section 3.3 that $\bar{\sigma}_n$, in a non-uniform solid, is not a simple function of the applied stress along the specimen axis or of the orientation of the grain boundary plane with respect to the stress axis. Rather, the normal stress at the grain boundary is expected to vary with the state of hardness of the material and the strain rate, as well as the applied stress. In a given material the most important aspect of the variation of the ratio of the grain boundary normal stress to the applied stress is its dependence on the relative contribution of grain boundary sliding to deformation.

In this chapter the growth of grain boundary cavities under an applied stress is measured for a range of applied stresses in which grain boundary sliding contributes significantly to the total deformation. The measured growth data are compared to the predictions of the cavity growth models discussed in Chapter 3. Since an estimate of the rate constant for cavity growth obtained in the previous chapter, it is possible to determine how the absolute value of the average normal stress at the grain boundary varies with the deformation conditions (applied stress and strain rate).

The results of the data analysis suggest that the normal stress varies in a way that is in qualitative agreement with the concept that grain boundary sliding relaxes the normal stress at the grain boundary.

6.1 Experimental Data and Observations

The experiment consisted of a series of constant load creep tests performed at 500 and 550°C, with specimens containing bubbles produced by hydrogen charging. The preparation and hydrogen charging conditions of the specimens are described in Sections 4.2.1 and 4.2.2. The initial cavities were widely spaced with a ratio (a/r) approximately equal to 20.

The measured steady-state-strain rate is plotted against the initial applied stress in Figure 6.1. Under the conditions of the experiment, detectable recrystallization in the specimens was found to be negligible. These data show a stress dependence of the strain rate, which indicates a varied stress exponent with values between 2 and 4.

Previous creep studies in nickel in this range of temperatures and stresses have shown that grain boundary sliding is an important deformation process. These studies have also indicated that the contribution of sliding to the total strain increases with decreasing strain rates. (64,65)

For the present work direct evidence of grain boundary sliding is given in Figure 6.2, where surface steps formed

Figure 6.1: Measured strain rate vs initial applied stress for this experiment

Figure 6.2 a, b: Grain boundary sliding evidence.

Specimen surface found after creep at a strain rate of 3.1×10^{-5} sec⁻¹ for 55 hours (on the right hand side) is compared to surface without creep deformation (on the left hand side). Figure 6.2a is at 90 times magnification and Figure 6.2b is at 360 times magnification

(a)

(b)

...ring deformation are shown. Since these observations were made on specimens deformed at the highest strain rate of the test series, it can be safely assumed that the sliding occurred at all the strain rates included in this experiment.

In the cavity growth measurement it was assumed that the portion of the specimen in the upper half of the specimen clamp was under negligible stress. The amount of cavity growth under an applied stress was determined as the difference in mean cavity cross-sectional area for the stressed and unstressed parts of the sample. The fractured surfaces were produced and examined in the manner described in Chapter 4. Figure 6.3 shows the cavity size distribution and SEM micrographs for the highest and lowest strain rates in the experiment. These data show clearly stress induced cavity growth. The shapes of the distributions, on the other hand, did not change, suggesting the absence of the nucleation of new cavities and also a negligible amount of cavity coalescence. Cavity morphology appeared to be unaffected by growth. Appendix D lists the data for each run in tabular form.

Table 6.1 lists the mean cavity sizes, the initial applied stress, the steady-state creep rate, the run time, and the temperature for each run. This data is presented in Figures 6.4 and 6.5 in which the growth rate for each run is plotted as a function of initial stress and the steady-state-strain rate, respectively. The data in Figure 6.4

show clearly that the cavity growth rate is not a linear

Figure 6.3a: Comparison of cavity cross sectional areas in the stressed and unstressed portions of specimen R4-G

Figure 6.3b: Comparison of cavity cross sectional areas in the stressed and unstressed portions of specimen R4-B

Table 6.1

Data for Cavity Growth Under an Applied Stress

Run	Temp.	Initial Tensile Stress (MPa)	Strain Rate (sec ⁻¹)	Time (hrs)	Mean Area (Stressed) (10 ⁻⁸ cm ²)	Mean Area (Unstressed) (10 ⁻⁸ cm ²)
R4-B1	550	35	3.1 x 10 ⁻⁷	68	6.8	1.9
R4-B2	550	35		25	4.4	2.6
R4-B3	550	35		45	5.7	1.7
R4-F	550	9.3	9.8 x 10 ⁻⁹	68	1.8	1.4
R4-G1	500	9.3	1.2 x 10 ⁻⁹	616	1.9	1.5
R4-G2	500	9.3		332	1.7	1.5
R4-H	500	52	3.0 x 10 ⁻⁷	100	6.6	1.8
R4-I	500	28	1.2 x 10 ⁻⁸	100	2.4	1.3
R4-K	550	21	3.4 x 10 ⁻⁸	66	2.7	1.6
R4-L	550	27	5 x 10 ⁻⁸	64	4.0	2.3

Figure 6.4: Cavity growth rate (as measured by the mean cross sectional area) vs initial stress

Figure 6.5: Cavity growth rate (as measured by the mean cross sectional areas) vs strain rate

nction of either the applied stress or the strain rate.

The angular dependence of the cavity growth rate is shown for three different strain rates at both 500 and 550°C in Figure 6.6. The graphs show stronger angular dependence at high strain rates.

The time dependence of cavity growth as measured by the cavity cross sectional area for two different strain rates is shown in Figure 6.7. Both sets of data show that the cross sectional area varies linearly with time.

The experimental data and observations can be summarized as follows:

- 1) Cavity growth was observed at all stresses.
- 2) Cavity nucleation and coalescence were not found during the experiment.
- 3) The rate of cavity growth shows non-linear dependence in the applied stress and in the strain rate.
- 4) The angular dependence of the cavity growth rate was observed to decrease with decreasing strain rate.
- 5) The cross sectional area at cavities under an applied stress varies linearly with time.

6.2 Discussion

In this section the predictions of the vacancy diffusion model, as well as the expected effects of grain boundary sliding, are compared with the results of the experiment.

Figure 6.6: Cavity growth (as measured by the mean cross sectional area) vs the angle between the grain boundary surface normal and the applied stress axis

Figure 6.7: Mean cavity cross sectional area vs time for two stresses and temperatures

6.2.1 Cavity Growth by Grain Boundary Sliding

The data in Figure 6.5 suggest that the cavity growth rate decreases monotonically with decreasing strain rate and does not appear to be sensitive to temperature. Based on these results one may suspect that the observed cavity growth may be caused by shearing due to grain boundary sliding. The maximum sliding rate, v_{gb} , may be estimated as:

$$v_{gb} \approx \dot{\epsilon} \cdot d,$$

where $\dot{\epsilon}$ is the total strain rate and d is the grain diameter. Computed in this way, the v_{gb} varies from 10^{-8} to 10^{-6} cm/hr, and is of the same order as the observed rate of change in the linear dimension of the cavities.

The possibility of cavity growth by grain boundary displacement can be ruled out, however, by the data shown in Figure 6.6 in which the cavity growth rate is found to be insensitive to the angle between the grain boundary plane and the applied stress axis.

6.2.2 Vacancy Diffusion Controlled Growth

In this subsection the vacancy diffusion model for cavity growth is compared to the experimental data. All calculations of the cavity growth rate will use the value of the rate constant, wD^{gb} , estimated in Chapter 5.

It is readily seen from Figure 6.7 that the time dependence of cavity growth is consistent with the predictions

the diffusion model for cavity growth. (Equation 3.17)

The dependence of cavity growth on the applied stress and strain rate will now be considered. In the absence of grain boundary sliding, the normal stress at the grain boundaries can be found by geometrical decomposition of the applied stress such that, by Equation 3.29

$$\bar{\sigma}_n = \sigma_T \cos^2 \theta$$

By this expression the value of $\bar{\sigma}_n$, computed for boundaries typical to this experiment, will be close to $\sigma_T/2$.

The expected average growth rate was computed by Equation 6.1 for an average applied stress of $\sigma_T/2$. In this calculation the cavity spacing is taken as 10^{-3} cm and the initial cavity cross sectional area is taken to be the mean cavity area at the clamped end of the specimen. The results of this calculation are shown in Figure 6.8. Included for comparison, are the measured growth rates as a function of the applied stress. The angular dependence, computed by the same equations as above is given in Figure 6.9. In both figures the agreement, which is shown between the predictions of the diffusional model and the experimental data, is good at high strain rates and very poor at low strain rates.

These results are consistent with the concept suggested in Section 3.3, that grain boundary sliding can relax the normal stress at the grain boundary. According to the arguments given there, the relaxation of the normal stress at the

Figure 6.8a: Comparison of the calculated cavity growth rate and the measured cavity growth rate as a function of the applied stress, $\sigma_T/2$, at 500°C

Figure 6.8b: Comparison of the calculated cavity growth rate and the measured cavity growth rate as a function of the applied stress, σ/T , at 550°C

Figure 6.9a: Expected and measured cavity growth rates
(as determined by mean cross sectional area)
vs grain boundary angle for R4-B

Figure 6.9b: Expected and measured growth rates (as determined by mean cross sectional area) vs grain boundary angle for R4-L

Figure 6.9c: Expected and measured cavity growth rates
(as determined by mean cross sectional area)
vs grain boundary angle for R4-G

grain boundary is expected to increase as the strain rate decreases. At high strain rates where the contribution of grain boundary sliding is less important and the polycrystalline solid behaves as a nearly uniform solid, the agreement is expected between the predictions of Equations 3.29 and 3.17 and the experimental data.

The extent of the relaxation of the normal stress at the grain boundary can be illustrated in another way by plotting the ratio of the observed growth rate to the rate calculated from Equations 3.17 and 3.29 versus the strain rate. This is shown in Figure 6.10. Since the growth rate is proportional to the normal stress at the boundary, these graphs essentially demonstrate how the ratio $\bar{\sigma}_n/(\sigma_T/2)$ varies with the strain rate. The latter ratio is given on the vertical axis on the right hand side of the graphs. At high strain rates ($>10^{-7} \text{ sec}^{-1}$) the ratio of $\bar{\sigma}_n/(\sigma_T/2)$ should approach a value of one. The ratio drops to less than one-half for strain rates of $\sim 10^{-8} \text{ sec}^{-1}$ and is expected to become strain rate insensitive at very low strain rates.

In conclusion, the vacancy diffusion model is found to be consistent with the observed cavity growth kinetics at the temperatures and strain rates involved in this work. The driving force for cavity growth, $\bar{\sigma}_n$, can be computed by geometrical decomposition of the applied stress at high strain rates (above 10^{-7} sec^{-1}). At strain rates below 10^{-7} sec^{-1}

normal stress based on geometrical decomposition cannot be

Figure 6.10: Ratio of the observed ($\dot{A}_{\text{OBS}}$) to the expected ($\dot{A}_{\text{EXP}}$) cavity growth rates (as measured in terms of cavity cross sectional area) vs the strain rate. The ratio $\bar{\sigma}_n / \sigma_r / 2$ is given at the vertical axis on the right hand side.

ed to account for the magnitude of the cavity growth rate or its dependence on orientation. At low strain rates the observed growth rates reflect the relaxation of the driving force due to grain boundary sliding.

6.3 Summary

The measurement of the growth of cavities on grain boundaries under stress has shown:

1) Grain boundary cavities grow under an applied stress at high temperatures.

2) The cavity growth rate increases with increasing stress, temperature and strain rate.

3) The grain boundary displacement mechanism cannot be used to account for the observed cavity growth.

4) The observed growth kinetics are consistent with the predictions of the vacancy diffusion model.

5) At high strain rates the mean cavity growth rate and its dependence on the grain boundary orientation, is consistent with the calculated results based on

$$\bar{\sigma}_n = \sigma_T \cos^2 \theta \quad .$$

6) At low strain rates $\bar{\sigma}_n$ becomes less than $\sigma_T \cos^2 \theta$. This is consistent with the concept that grain boundary sliding will lead to stress relaxation at the grain boundary.

CHAPTER 7 DISCUSSION

7.1 Summary of Results

The experimental results reported in this work support the vacancy diffusion model for grain boundary cavity growth. They demonstrate that both internal gas pressure and applied tensile stress can provide the driving force for growth. It is also shown that the kinetics of mass transport to the cavities can be described by vacancy diffusion along the grain boundary.

The measurement of the cavity growth under an applied stress suggests that the stress distribution in a polycrystalline solid varies with the contribution of grain boundary sliding relative to other deformation processes. At high strain rates, the stress distribution approaches that of a uniform solid and geometrical decomposition of the applied tensile gives the normal stress on the grain boundary. At low strain rates, the normal stress on the grain boundaries could not be obtained from geometrical decomposition. Finally, it was shown that the average normal stress on the boundaries varied non-linearly with the applied tensile stress.

The latter finding is in qualitative agreement with Cane's observation that the radial growth rate varied as $\sigma_T^{3/2}$ rather than $\sigma_T^{1/2}$ as predicted by Equation 3.17 and simple

ometrical decomposition of the applied stress. In this case grain boundary sliding provides a significant contribution to the total strain rate and the mechanism of grain boundary relaxation presented in this work applies.

The hydrogen charging process was also investigated in the present work. Methane formation was shown to be the cause of bubble formation. Evidence for two rate limiting cases for bubble growth during charging was shown. The first was vacancy diffusion controlled growth which was demonstrated by the fact that the cavities continued to grow during anneals at 500, 550 and 600°C after charging. The second rate limiting process observed was methane formation controlled growth. The latter possibility was demonstrated by bubbles that did not grow upon annealing at 600°C after charging.

7.2 Practical Implications and Suggestions for Further Work

The practical importance of this work is that it points out a number of parameters that must be considered in formulating damage equations used for high temperature structures. In particular it shows that:

- 1) Both the stress and the grain boundary sliding rate must be taken into account in any estimation of cavity growth.
- 2) In the case of hydrogen attack, the rate limiting mechanism for growth can be found by determining whether growth of the cavities occurs during anneals performed after charging.

3) The temperature dependence of the rate constant for cavity growth under applied stress or internal pressure is the same as for grain boundary self-diffusion.

4) The cavity cross sectional area increases approximately linearly in time under a given driving force.

7.3 Suggestions for Further Work

This work can be extended in a number of directions. First, the investigation of cavity growth under an applied stress should be extended to cover other materials. The effect of impurities and precipitates on cavity growth can lead to added information as to the mechanisms that determine the stress distribution in materials. It would also be useful to extend the range of deformation rates during cavity growth. This type of work also can add to the understanding of deformation.

In-pile experiments can be devised to determine the simultaneous effect of stress and irradiation damage on the growth of grain boundary cavities. The possibility that irradiation produced defects can influence the cavity growth kinetics is discussed in Section 3.2. It is also likely that the extent of grain boundary relaxation will be influenced by irradiation. The study of the combined effect would be useful to the prediction of creep cavitation failure in both the fusion and fission reactors.

The approach developed for determining the rate limiting process for methane bubble growth during hydrogen

attack can be applied to other materials, notably commercial alloys. In addition, the experimental conditions can be extended to include the case where cavities grow in response to both an internal gas pressure and an applied stress.

REFERENCES

1. C. H. M. Jenkins, E. H. Bucknall and E. A. Jenkinson, J. Inst. Met., 1944, 70, p. 57.
2. M. E. Whitaker, E. Voce and A. R. Bailey, Metallurgica, 1948, 39, p. 21.
3. J. Herenguel and M. Schniedecker, Rev. Met., 1951, 48, p. 574.
4. A. J. Perry, J. of Mat. Sci., 1974, 9, p. 1016.
5. J. N. Greenwood, J. Iron and Steel Inst., 1954, 176, p. 268.
6. J. N. Greenwood, P. R. Miller and J. W. Suiter, Acta Met., 1954, 2, p. 250.
7. F. Garafalo, Fundamentals of Creep and Creep Rupture in Metals, p. 210, MacMillan Co., N. Y., 1965.
8. A. Gittins and H. D. Williams, Phil. Mag., 1967, 16, p. 849.
9. D. Hull and D. E. Rimmer, Phil. Mag., 1959, 4, p. 673.
10. R. C. Grifkins, Fracture, p. 44, Butterworth and Co., London, 1963.
11. P. G. Shewmon, Met. Trans., 1976, 7A, p. 279.
12. J. P. Hirth and H. H. Johnson, Corrosion, 1976, 32, p. 3.
13. D. A. Woodford, J. P. Smith and J. Moteff, J. Nucl. Mat., 1967, 24, p. 118.
14. A. F. Rowcliffe, J. Nucl. Mat., 1966, 18, p. 60.
15. A. F. Rowcliffe, G. J. C. Carpenter, H. F. Merrick and R. B. Nicholson, Effects of Radiation on Structural Metals, ASTM STP 426, 1967.
16. R. W. Balluffi and L. L. Seigle, Acta Met., 1955, 3, p. 170.
17. N. J. Grant, Fracture, p. 562, John Wiley, New York, 1959

- . R. W. Balluffi and L. L. Seigle, Acta Met., 1957, 5, p. 449.
19. C. W. Weaver, J. Institute of Met., 1959-1960, 88, p. 296.
20. C. W. Chen and E. S. Machlin, Acta Met., 1956, 4, p. 655.
21. C. W. Chen, Trans. Met. Soc. AIME 206, 1956, p. 1416.
22. D. McLean, Rep. Prog. Phys., 1966, 29, p. 1.
23. B. J. Reid, and J. N. Greenwood, Trans. Met. Soc. AIME 212, 1958, p. 503.
24. J. Intrater and E. S. Machlin, Acta Met., 1959, 7, p. 140.
25. E. S. Machlin, Fracture, p. 45, John Wiley, New York, 1959.
26. C. Herring, J. A. Phys. 1950, 21, p. 437.
27. R. T. Ratcliffe and G. W. Greenwood, Phil Mag., 1965, 12, p. 59.
28. B. J. Cane, and J. N. Greenwood, Met. Sci., 1975, 9, p. 55.
29. A. F. Sirenko, Phys. Met. Met., 1971, 31, p. 172.
30. V. M. Rozenberg, A. V. Shalimova and T. S. Zvereva, Phys. Met. Met., 1968, 25, p. 134.
31. W. W. Mullens and R. R. Seckerka, J. Of App. Phys., 1963, 34, p. 323.
32. A. L. Wingrove and D. M. R. Taplin, Jour. of Mat. Sci., 1969, 4, p. 789.
33. H. E. Evans, Phil. Mag., 1971, 23, p. 1101.
34. Y. Ishida and D. McLean, Met. Sci. J., 1967, 1, p. 171.
35. "Steel for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants", API Publ. 941, July 1970.
36. L. C. Wiener, Corrosion, 1961, 17, p. 137.
37. H. H. Johnson, Private Communication, 1977.
- D. A. Westphal and F. J. Worzala, Hydrogen in Metals, Ed. I. M. Bernstein and A. W. Thompson, ASM 1974, p. 79.

39. R. Raj and M. F. Ashby, *Acta Met.*, 1975, 23, p. 653.
40. J. Weertman, *Met. Trans.*, 1974, 5, p. 1743.
41. M. V. Speight and J. E. Harris, *Met. Sce. J.*, 1967.
42. J. F. Mancuso, F. H. Huang and Che-Yu Li, *Fundamental Aspects of Rad. Dam. In Metals*, 2, M. T. Robinson and F. W. Youngs Ed., Oct. 1975, p. 1279.
43. F. W. Wiffin and E. E. Bloom, *Nucl. Tech.*, 1975, 25, p. 113.
44. D. A. Woodford, J. P. Smith and J. Moteff, *J. of Nuc. Mat.*, 1969, 29, p. 103.
45. R. S. Barnes, *Nature*, 1965, 206, p. 1307.
46. V. Z. Jankus and R. W. Weeks, *Nuc. Eng. and Design*, 1972, 18, p. 83.
47. Che-Yu Li, J. Rest, S. Danyluk and R. B. Poeppel, "Grass-Code Calculation for the Behavior of Helium in Austenitic Stainless Steels", presented at the 2nd ANS Topical Meeting on Sept. 1976. To be published in the proceedings of that topical meeting.
48. E. W. Hart, *Acta Met.*, 1970, 18, p. 599.
49. E. W. Hart, *Acta Met.*, 1967, 15, p. 1545.
50. F. W. Crossman and M. F. Ashby, *Acta Met.*, 1975, 23, p. 425.
51. J. F. Mancuso, Che-Yu Li and J. L. Straalsand, *J. of Nuc. Mat.*, 1976, 59, p. 327.
52. L. K. Mansur, P. R. Okamoto, A. Taylor and Che-Yu Li, "Surface Reaction Limited Void Growth", *Proc. of the 7th ASTM Symp. on Rad. Eff. in Str. Mat. in Gatlinburg, Tenn.*, 1974.
53. C. Zener, *Phys. Rev.*, 1941, 60, p. 906.
54. P. J. Clemm and J. C. Fisher, *Acta Met.*, 1962, 10, p. 765.
55. C. A. Johnson, *Surface Science*, 1965, 3, p. 429, 444.
56. G. S. Lane, *J. Phy. E.*, 1969, 2, p. 545.
57. A. Boyde, *J. Microscopy*, 1973, 98, p. 452.

- R. E. Allen, R. J. Jansen, P. C. Rosenthal, and F. H. Vitovec, Proc. API 1962, 42, p. 452.
59. J. M. Blakely, Introduction to the Properties of Crystal Surfaces, p. 64, Pergamon Press, 1973.
60. G. Martin and B. Perrailon, J. Physique, 1975, 36, p. 165.
61. A. R. Wazan, J. Appl. Phys., 1965, 36, p. 3596.
62. J. J. Lander, H. E. Kern and A. L. Beach, J. Appl. Phys., 1952, 23, p. 1305.
63. Handbook of Material Science, V. 1, p. 133, CRC Press.
64. Shyun-Jing Chao, Thesis (M.S.), Cornell University, May 1976.
65. P. W. Davies, J. P. Dennison, R. W. Evans, J. Inst. of Metals, 1964-1965, 93, p. 25.
66. JANAF Thermochemical Tables 2nd Edition, NSRDS-NBS 37, 1971.
67. L. C. Isett, Mat. Sci. Center Report #2340, Cornell University, 1975.
68. P. Cotterill, Prog. Mat. Sci., 1961, 9, p. 205.
69. S. J. Rosenberg, Nickel and Its Alloys, p. 49, NBS 106, 1968.

APPENDIX A PROCEDURE FOR DETERMINING GRAIN BOUNDARY ORIENTATION AND CAVITY AREA

A.1 Stereomicroscopy and Determination of Grain Boundary Orientation

Grain boundary orientation was determined by the analysis of stereo photo-micrographs produced by the SEM. This procedure involved essentially:

- 1) The determination of the direction in space of two non-parallel vectors lying in the grain boundary plane, and
- 2) the computation of a vector cross product which yielded another vector normal to the plane.

Once the surface normal was obtained, the orientation of the grain boundary with respect to either the specimen axis or incident electron beam axis could be determined.

Two vectors were selected by identifying three or four points or features common to both photographs of different tilts. The coordinates of the points were measured with respect to the rectangular coordinates where the x axis was in the same direction as the tilt axis. The positions, vectors and coordinate system are shown schematically in Figure A.1. The position and tilts were put into a computer routine written in BASIC that calculated the orientation of the vectors in space. The formulae used were developed by Lane (56) and are given below.

$$h_o = (y_a - y_b) \frac{\sin\phi}{2\sin\Delta\phi} + (y_a + y_b) \frac{\cos\phi}{2\cos\Delta\phi} \quad (A.1a)$$

Figure A.1: Schematic diagram of the positions, vectors and coordinates necessary to determine grain boundary orientation by stereography. The coordinates (x_1, y_1) and (x'_1, y'_1) etc. represent identical features on the two pictures.

$$k = (y_a - y_b) \frac{\cos \phi}{2 \sin \Delta \phi} - (y_a - y_b) \frac{\sin \phi}{2 \cos \Delta \phi} \quad (\text{A.1b})$$

$$(\text{A.1c})$$

$$\theta_{(a \text{ or } b)} = \tan^{-1} \left(\tan \psi_{(a \text{ or } b)} \cos (\phi_{(a \text{ or } b)} - \tan^{-1} k/h_o) \right)$$

$$h = \{(h_o^2 + k^2) \cos^2 \theta - k^2\}^{1/2} \quad (\text{A.1d})$$

$$y_a = y_1 - y_3 \quad (\text{A.1e})$$

$$y_b = y_2 - y_4 \quad (\text{A.1f})$$

$$\phi = (\phi_1 + \phi_2)/2 \quad (\text{A.1g})$$

$$\Delta \phi = (\phi_2 - \phi_1)/2 \quad (\text{A.1h})$$

$$\tan \psi_a = X_a/Y_a \quad (\text{A.1i})$$

$$\tan \psi_b = X_b/Y_b \quad (\text{A.1j})$$

where h is the component of the vector, $\overline{PQ}$, in the plane perpendicular to the specimen axis and k is the component of $\overline{PQ}$ along the specimen axis. h_o is the projection of h on the plane perpendicular to the tilt axis and θ is the angle between the $\overline{PQ}$ and its projection on the same plane. These relationships are shown in Figure A.2. The computed value of

Figure A.2: Angular relationships used in the stereo analysis. $PQ'P$ is the plane perpendicular to the specimen axis and PQ is the vector being determined.

angles θ_a and θ_b should be the same if no error is made in the measurement.

The components of the vector in the x, y, and z direction of the specimen are now x (as measured), h_0 , and k respectively. The surface normal, $\hat{n}$, is a unit vector defined by the cross product of the two vectors $\overline{AB}$ and $\overline{CD}$.

$$\hat{n} = \frac{\overline{AB} \times \overline{CD}}{|\overline{AB} \times \overline{CD}|},$$

and the angle between $\hat{n}$ and the specimen z axis is δ and is given by

$$\delta = \cos^{-1} (\hat{z} \cdot \hat{n}),$$

where $\hat{z}$ is a unit vector in the z direction. If (x_1, h_{01}, k_1) and (x_2, h_{02}, k_2) represent the two vectors, then

$$\hat{z} \cdot \hat{n} = \frac{(x_1 \cdot h_{0,2} - x_2 \cdot h_{0,1})}{[(x_1 \cdot h_{0,2} - x_2 \cdot h_{0,1})^2 + (h_{0,1} \cdot k_2 - h_{0,2} \cdot k_1)^2 + (k_1 \cdot x_2 - k_2 \cdot x_1)^2]^{1/2}}$$

The angle that the surface normal makes with the electron beam (α) can also be computed. $\cos(\alpha)$ is a correction factor for the error in the measurement of cavity area, since the grain boundary plane is not perpendicular to the electron beam axis. As can be seen from Figure 4.5 the correction factor is $\cos(\alpha)$. The program also computes the angle α and a correction factor for the cavity area measurement which is simply equal to

```

0015 REM      DIMENSIONS CAN BE READ DIRECTLY OFF ANY ARBITRARY
              LINEAR SCALE
0016 REM      THE COORDINATE AXIS IS DEFINED BY LANE'S CONVENTION
              SHOWN THE APPENDIX
0020 DIM A(3),B(3),C(3),K(3),H(3),D(3),U(3),V(3)
0021 REM ***  TILT ANGLES ARE IN DEGREES FROM BEAM AXIS.
0025 INPUT "TILT ONE = ",T1,"  TILT TWO = ",T2
0026 LET T=(T1+T2)*3.1416/360
0027 LET D1=(T2-T1)/360*3.1416
0029 INPUT " ***** ---***** <<COMMET>> ",V$
0031 FOR I=1 TO 2
0033   LET J=J+1
0040   REM ***  VECTOR LENGTHS ARE CALCULATED BY SUBTRACTING END POINTS
              OF
              VECTORS
0042   INPUT "FOR TILT ON X1,Y1,X3,Y3ARE ",X1,Y1,X3,Y3
0043   INPUT "FOR TILT TWO                ",X2,Y2,X4,Y4
0044   LET Y1=Y1-Y3
0045   LET Y2=Y2-Y4
0046   LET X1=X1-X3
0047   LET X2=X2-X4
0049   LET T2=X2/Y2
0050   LET T1=X1/Y1
0051   REM ***  PARALLAX IS COMPARED TO THE ACCURACY OF THE MEASMENT
0052   LET H3=(Y1-Y2)/.02
0053   PRINT " RELATIVE PARALLAX = "H3
0054   IF I=2 THEN GOTO 0057
0056   PRINT " SECOND VECTOR"
0057   PRINT
0058   REM ***  STATEMENTS 60 THRU 75 FOLLOW DIRECTLY FROM THE EQUATIONS
              QUOTED IN THE APPENDIX
0060   LET H0=(Y1-Y2)*SIN(T)/2/SIN(D1)
0061   LET H0=H0+(Y1+Y2)*COS(T)/COS(D1)/2
0062   LET K(1)=(Y1-Y2)*COS(T)/SIN(D1)/2
0063   LET K(1)=K(1)-(Y1+Y2)*SIN(T)/COS(D1)/2

```

Figure A.3: Program to determine grain boundary orientation.


```

0070 LET Q=ATN(KC11/H0)
0072 LET A(1)=ATN(T1*COS(T-D1+Q))
0073 LET B(1)=ATN(T2*COS(T+D1+Q))
0075 LET C(1)=(A(1)+B(1))/2
0078 LET U(1)=X1
0079 LET D(1)=H0
0080 NEXT I
0081 REM *** THE SURFACE NORMAL IS CALCULATED FROM THE CROSS PRODUCT
      OF THE TWO VECTORS
0082 REM *** D2,E,AND F ARE THE X,Y,AND Z COMPONENTS OF THE NORMAL
0090 LET D2=D(1)*K(2)-K(1)*D(2)
0092 LET E=K(1)*U(2)-U(1)*K(2)
0094 LET F=U(1)*D(2)-D(1)*U(2)
0096 LET G=(D2*2+E*2+F*2)/F*2
0098 LET G1=ATN(SQR(G-1))*180/3.1416
0099 REM *** G1 IS THE ANGLE THE SURFACE NORMAL MAKE WITH THE SPECIMEN
      AXIS
0103 LET C(1)=C(1)*180/3.1416
0104 LET C(2)=C(2)*180/3.1416
0105 LET E5=A(1)-B(1)
0106 LET E6=A(2)-B(2)
0107 LET E5=E5*180/3.1416
0108 LET E6=E6*180/3.1416
0110 PRINT " ANGLE IS ";G1
0112 PRINT " C1=";C(1); " ERR-1 =" ;E5; " C2 =" ;C(2); " ERR-2=" ;E6
0113 PRINT
0114 LET H4=COS(T)*F+SIN(T)*E
0115 LET H4=(D2*2+E*2+F*2)/H4*2
0116 LET H4=ATN(SQR(H4-1))*180/3.1416
0117 LET H5=1/COS(H4*3.1416/180)
0120 PRINT "BEAM ANGLE = ";H4," COR FACTOR = ";H5
0122 PRINT
0123 REM *** H4 IS THE ANGLE BETWEEN THE SURFACE NORMAL AND THE
      ELECTRON BEAM

```

Figure A.3 Continued

$$\cos (\alpha) = [\hat{x} \cdot \hat{n} \cos \phi + \hat{y} \cdot \hat{n} \sin \phi] \quad .$$

The computer program used also tests the consistency of the data as mentioned previously. It computes θ_a and θ_b for each vector and prints the difference between them as an indication of the error. The difference should be less than 2° for acceptable measurements.

A.2 Measurement of the Bubble Area

Cavities were measured on the picture by comparing their cross sections with the size of the holes in the template for mechanical drawing. The holes ranged from 9/128 inch diameter to one inch, and were labeled such that the index number could be used in a computer program. (Each integer increase corresponded to a 1/64 inch diameter change.)

The program did the following:

- 1) It computed an area for each index number in cm^2 .
- 2) It computed the true cross sectional area by dividing by the magnification and multiplying by the correction factor $\cos (\alpha)$ introduced in the previous section.
- 3) It calculated the mean value of the cavity area for each grain boundary being considered.

After the grain boundary had been analyzed, the overall mean cavity area was obtained.

The program was written in BASIC and is listed in Figure

```
0001 REM      CAVITY SIZE EVALUATOR
0002 REM VALUES FOR MAG. AND COR. FACTOR FROM ANGLE MEAS.
0003 REM      FOR CALCULATION
0010 DIM A(50)
0020 DIM V$(2)
0039 REM      STATEMENT 40 IDENTIFIES THE RUN
0040 INPUT "DESCRIPTION ** ",V$
0041 INPUT " MAG. = ",Z1
0042 INPUT " COR. FAC. = ",Z2
0043 PRINT "NOW INPUT INDEX NUMBERS"
0250 LET T=0
0251 LET T2=0
0252 LET T3=0
0260 ON ESC THEN GOTO 0390
0300 INPUT A(N)
0301 REM TEMPLATE CONVERSION
0305 LET A(N)=(((2*A(N)+11)/128)+2)*3.1416/4
0309 REM METRIC CONVERSION
0310 LET A(N)=A(N)*2.54*2.54
0311 LET A(N)=A(N)*Z2/Z1/Z1
0315 LET T=T+A(N)
0325 LET N=N+1
0350 GOTO 0300
0390 PRINT
0395 PRINT
0398 ON ESC THEN STOP
0399 PRINT " AREA IN CM2  "
0402 FOR I=1 TO N-1
0410   PRINT A(I)*1E+8
0420 NEXT I
0430 PRINT "MEAN = ";T/(N-1);"   TOTAL = ";T;"   FOR ";N-1
0500 STOP
```

Figure A.4: Program to calculate bubble size from index numbers on template.

APPENDIX B SOLUTION OF THE MASS BALANCE EQUATION

For the case of radial symmetry the mass balance Equation 3.13 has the form

$$\frac{Dg^b}{kT} \frac{1}{R} \frac{\delta}{\delta R} R \left(-\frac{\delta}{\delta R} \sigma_n(R) \right) = -G \quad (B.1a)$$

The equation can be rearranged such that

$$\frac{\delta}{\delta R} R \left[\frac{\delta}{\delta R} \sigma_n(R) \right] = \frac{-GkT}{Dg^b} R \quad (B.1b)$$

Since $\sigma(R)$ is dependent on R only the distinction between the partial and full derivatives can be ignored and (B.1a) can be integrated with respect to R as

$$\int R \frac{\delta}{\delta R} \sigma(R) dR = \int -\frac{GkT}{Dg^b} R dR \quad (B.2a)$$

or

$$\frac{\delta}{\delta R} \sigma(R) = -\frac{GkT}{2Dg^b} R + A/R \quad (B.2b)$$

where A is a constant to be determined by the boundary conditions. This expression can also be integrated to yield

$$\sigma(R) = -\frac{GkT}{4Dg^b} R^2 + A \ln R + B \quad (B.3)$$

where B is another constant to be determined by the boundary conditions.

Applying boundary condition 1 ($\sigma_n(r) = 2\gamma/r$) yields

$$B = \frac{GkT}{4Dgb} r^2 - A \ln R + \frac{2\gamma}{r} \quad (B.4)$$

Then boundary condition 2 gives

$$A = \frac{GkT}{2Dgb} \left(\frac{a}{2}\right)^2 \quad (B.5)$$

$\sigma_n(R)$ can be expressed in terms of A and B by substitution of B.4 and B.5 into B.3 such that

$$\sigma_n(R) = - \frac{GkT}{4Dgb} \left[r^2 - R^2 + 2 \left(\frac{a}{2}\right)^2 \ln (R/r) \right] + \frac{2\gamma}{r} \quad (B.6)$$

The last boundary condition, that

$$\int_r^{a/2} \sigma_n(R) 2\pi R dR = \bar{\sigma}_n \pi \left(\frac{a}{2}\right)^2$$

can be used to show that

(B.7)

$$\bar{\sigma}_n = \frac{GkT}{2Dgb} \left\{ r^2 - 1/4 r^2 \left(\frac{2r}{a}\right)^2 - \frac{3}{4} \left(\frac{a}{2}\right)^2 - \left(\frac{a}{2}\right) \ln\left(\frac{2r}{a}\right) + \frac{2\gamma}{r} \left[1 - \left(\frac{2r}{a}\right)^2\right] \right\}$$

Solving for G we find

$$G = \frac{2Dgb}{kT} \left(\frac{a}{2}\right)^2 \frac{\bar{\sigma}_n - \frac{2\gamma}{r} \left[1 - \left(\frac{2r}{a}\right)^2\right]}{\left(2r/a\right)^2 - 1/4 \left(\frac{2r}{a}\right)^4 - 3/4 - \ln(2r/a)} \quad (B.8)$$

Substitution of (B.7) into B.5 yields

$$\sigma(R) = \frac{1}{2} \left(\frac{a}{2}\right)^2 \left\{ \frac{\bar{\sigma}_n - \frac{2\gamma}{r} \left[1 - \left(\frac{2r}{a}\right)^2\right]}{\left(2r/a\right)^2 - 1/4 \left(\frac{2r}{a}\right)^4 - 3/4 - \ln\left(\frac{2r}{a}\right)} \right\} \quad (B.9)$$

$$\bullet \{ [r^2 - R^2 + 2 \left(\frac{a}{2}\right)^2 \ln (R/r)] \} + \frac{2\gamma}{r}$$

Using the relationships in Equations 3.1, 3.4, 3.8 and 3.11, the final growth Equation 3.17 can be found.

APPENDIX C EQUILIBRIUM PRESSURES FOR GAS BUBBLES DURING CHARGING

C.1 Thermo-Chemical Equilibrium of Methane

The thermo-equilibrium constant for CH_4 formation was computed by consideration of the following reactions at 500°C . (66,67)

where C_g is graphite (the standard state for carbon at these temperatures and pressures) and, $\underline{\text{C}}$ and $\underline{\text{H}}$ represent the atomic concentration in nickel of carbon and hydrogen respectively. The standard state of the gases is at 1 atm (≈ 0.1 MPa) pressure. For the case of high temperature charging, the hydrogen mobility is high (68) and equilibrium between the bulk concentration of hydrogen $\underline{\text{H}}$ and the external hydrogen pressure p_{H_2} is quickly reached.

In this case, detailed balance arguments apply and the methane pressure can be determined by either

For this analysis the former reaction is used. The equilibrium constant for this reaction in terms of the activities (a) is

$$K_{eq} = \frac{a_{CH_4}}{a_{H_2}^2 \cdot a_S} = 3 \times 10^6$$

For the maximum carbon concentration shown in Table 4.1 (5×10^{-4} mole C/mole) and a H_2 pressure of 10 MPa

$$a_{CH_4} = 16 \times 10^6$$

where the hydrogen fugacity is approximated by the hydrogen pressure and the activity coefficient of carbon is assumed to be unity. The fugacity of methane under these conditions can be expected to be ~5 times the pressure (11) so that

$$P_{CH_4} \sim 10^5 \text{ MPa}$$

C.2 Thermo-Chemical Equilibrium of Hydrogen Sulfide

The thermo-chemical equilibrium constant for H_2S formation was computed by consideration of the following reactions at 500°C . (66)

- 1) $2 H_{2(g)} + S_{2(g)} \rightleftharpoons 2 H_2 S_{(g)}$
- 2) $2 S \rightleftharpoons S_{2(g)}$
- 3) $H_2 + S \rightleftharpoons H_2 S_{(g)}$

The standard state of sulfur at this temperature and pressure is $S_{2(g)}$.

By the same arguments for the equilibrium between H_2 and H used in C.1, the equilibrium of H_2S can be computed in terms the reaction

In this case

$$K_{\text{eq}} = \frac{a_{\text{H}_2\text{S}}}{a_{\text{H}_2} \cdot a_{\underline{\text{S}}}} = 4.2 \times 10^5$$

The maximum sulfur concentration by Table 4.1 is 2×10^{-5} $\left[\frac{\text{moles S}}{\text{mole}}\right]$ and the charging conditions are 10 MPa H_2 pressure at 500°C . If the activity coefficient for S is assumed to be unity and the H_2 fugacity is approximated by the H_2 pressure,

$$a_{\text{H}_2\text{S}} \approx 800$$

If the fugacity in this activity range is approximately equal to the H_2S pressure so that

$$p_{\text{H}_2\text{S}} \approx 80 \text{ MPa}$$