FAILURE BY CREEP CRACKING AND CREEP FATIGUE INTERACTION
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FAILURE BY CREEP CRACKING AND CREEP FATIGUE INTERACTION
IN NICKEL BASE SUPERALLOYS

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SUMMARY

Most high temperature structural materials exhibit a minimum in ductility near one half of their melting point. The embrittlement occurs by the nucleation and growth of cavities in the grain boundaries. The objective of this investigation was to study the phenomenon of cavitation under conditions of creep-fatigue interaction and under creep crack growth. The first involved identifying and modeling the mechanisms by which cavitation may interact with the classical stage I and stage II crack growth in low cycle fatigue. Creep crack growth involved the growth of cavities in the local stress and strain field of a crack tip.

In the creep-fatigue work, experiments were carried out on model materials to identify various mechanisms of failure. At least five were found. The dominant one depended on the cycle shape, the frequency, temperature and the microstructure of the material. Cavitation was found to accelerate the initiation and propagation of fatigue cracks; these were the cases where creep damage interacted with the cracks which are normally produced under condition of low cycle fatigue. In other instances cyclic loading served to enhance cavitation damage; in this case failure occurred by the gradual accumulation of cavitation damage throughout the specimen rather than by the initiation and growth of a fatigue crack. The cavitation mode of failure was theoretically analyzed.

The accepted mechanism of creep crack growth is the nucleation and growth of cavities in the local stress field of the crack tip. Experiments were carried out on the nickel base superalloy MERL 76, to study the influence of loading rate on creep crack growth in compact tension specimens. We found that a slower loading rate decreased the fracture toughness. The result was explained in terms of the relative magnitude of plastic flow and the growth of
cavitation damage in front of the crack tip. It was argued that if the loading conditions favored damage rather than plastic flow, then the toughness will be lowered. Local plastic strain and damage strain near the crack tip were measured by the distortion of a lattice of markers etched on the specimen surface (using photo-lithography techniques). The lower fracture toughness was found to be associated with a higher value of damage strain relative to the plastic strain. A theoretical model was developed to describe the results. The model is general and may be used to predict creep crack growth behavior.

The grant provided whole or primary support for one post-doctoral associate, two Ph.D. students and one M.S. student. Eight papers have been published in Metallurgical Transactions, Acta Metallurgica and Metal Science, and one more has been accepted for publication in Acta Metallurgica.
INTRODUCTION

Grain boundaries have been recognized as planes of weakness in structural materials developed for high temperature applications. The embrittlement occurs at about the temperatures used in service. With the development of superalloys which have outstanding creep strength, fracture rather than creep behavior has become the more important consideration in design.

The mechanism of failure at elevated temperatures has been recognized to be the nucleation and growth of sub-micron cavities in grain interfaces. The cavities prefer to form at second phase particles such as the carbides and sometimes the gamma-prime precipitates [1,2]. The spacing of the cavities, therefore, is of the same order as the spacing of the precipitates. The closer this spacing the smaller is the ductility of the material. The ease of cavity nucleation also plays an important role in the determination of time to failure. It has been hypothesized that the environmental sensitivity of nickel base superalloys may be tied to the nucleation of cavities. One idea is that oxygen diffuses from the surface along the grain boundaries, reacts with the carbides to produce molecules of CO gas which promote the nucleation of cavities [3]. The oxidation of the carbide-matrix interface also weakens the boundary since oxides are generally less securely bonded to the matrix than the carbides [4].

The objective of this investigation was to study the mechanisms of failure under conditions of creep-fatigue interaction, and creep-crack-growth. The approach was to identify the mechanisms and then develop models for describing failure in terms of the loading variables and the microstructure. In the following sections, the results from each topic are summarized. Further details of the work are available in publications.
In addition to the work related directly to creep-fatigue and creep-crack growth, additional papers on cavitation were also published in the course of this investigation, notably on intergranular fracture under aggressive environments and on the description of damage under multiaxial loading. These papers will not be discussed in this report, but are attached in the Appendix.
CREEP CRACK GROWTH

The principal difference between stress-rupture, in smooth specimens, and creep-crack-growth, in notched specimens is that in notched specimens the nucleation and growth of cavities is limited to the crack-tip region. In fact the crack grows because the cavities coalesce ahead of the crack tip. A picture of such a mechanism is shown in Fig. 1. The modeling of such a process is complicated by the following factors:

(a) The stress field near the crack-tip is non-uniform, multiaxial, and time dependent.
(b) The nucleation and growth of cavities is time dependent even under a constant stress. Since the stress also varies with time the cavitation behavior can be analyzed only after making simplifying assumptions.
(c) Growth of cavities produces dilation in the material. This can alter the stress in the crack-tip region.
(d) Since the cavities form near the surface, environmental effects may play an important role in creep crack growth.

In the present research program we have completed three tasks. First a simple model for creep crack growth has been analyzed. In the model we have assumed that the cavities grow by diffusion and that the stress field in front of the crack is determined by the coupling between elastic deformation and time dependent cavity growth. In the second task we have examined the influence of the rate of loading on fracture toughness in MERL'76 at 1000K (1340°F). We have found that fracture toughness increases with increasing rate of loading. The result was explained in terms of the relative magnitude of plastic-strain and (cavitation) damage-strain near the crack-tip. It was argued that plastic flow and cavitation compete for dominance near the crack-tip. At slower
loading-rates, cavitation is dominant and the fracture toughness is low. Thirdly, we have developed a simple numerical model for creep crack growth where plastic flow as well as cavitation contribute to strain in the crack-tip region. The results of the model are in good agreement with experiments on MERL'76. The results from each of these tasks are now described.

Crack Growth Model - I

The growth of cavities in grain boundaries stressed in uniform tension, has been examined in detail in the literature [5-8]. The physical mechanism of cavity growth is illustrated in Fig. 2. Cavities grow by the transfer of atoms from cavity surfaces to the grain interface. As a result the cavities grow in size and the matter "plated" onto the grain boundary is accommodated by rigid body displacement of the two half crystals. If the cavities are assumed to have an equilibrium shape, then the grain boundary damage, $A_r$, defined as the separated fraction of the boundary area, the normal displacement of the crystals, $u$, and the average cavity spacing, $\lambda$, are related to each other by geometry. The detailed expressions are given in Ref. 9. If we normalize $u$ with respect to $\lambda$, so that:

$$\ddot{u} = \frac{u}{\lambda} \quad (1)$$

then the rate of growth of cavities (expressed in terms of $u$) can be related to the (normalized) applied stress, $\ddot{\sigma}_o$ by:

$$\frac{d\ddot{u}}{d\ddot{\tau}} = (\ddot{\sigma}_o - \ddot{\sigma}^*) \quad (2)$$

In (2), $\ddot{\sigma}^*$ is the threshold stress for the nucleation of cavities and $\ddot{\tau}$ is a normalized unit of time which depends on temperature through the boundary diffusion coefficient. The stress in equation (2) has been normalized with respect to the Young's Modulus. Equation (2) is the simple rather than the
exact version of the growth equation. The latter is discussed in Ref. 9. Recalling that the damage, $A_r$, is related to $\tilde{u}$ through geometry, the fracture condition, defined as the point where neighbor cavities grow to touch each other, can be defined in terms of $\tilde{u}$. It may be shown that this critical displacement, $u_c = 0.4$.

The stress field near a crack-tip is non-uniform and the displacement required to accommodate cavity growth will generate elastic back stresses, which will tend to relax the stress field at the crack-tip. That is the problem which we have analyzed in detail. One set of results are shown in Figure 3. Growth of cavities, which is characterized by the displacement $u$, relaxes the stress field. When $u = u_c$ at the crack-tip, the crack advances by one unit spacing. The calculation leads to the following interesting results:

(i) Crack velocity reaches a steady state after a readjustment of the stress field near the crack-tip.

(ii) For a crack moving in the steady state, the stress field remains constant.

(iii) The steady state crack-velocity, $\dot{a}$, is proportional to $K_I^2$, where $K_I$ is the applied stress-intensity factor.

(iv) A characteristic damage zone, of size $Z_A$, develops in front of the crack-tip. $Z_A$ also depends on $K_I$.

(v) Crack will not propagate if $K_I < K_{th}$. The threshold is related to the threshold stress for cavity nucleation.

The equations for the above properties of the model are given below:

$$K_{th} = (0.4 \lambda E\sigma^*)^{1/2}$$  \hspace{1cm} (3)
\[ \dot{a} = 7 \times 10^5 \frac{K^2_1 \omega}{E kT} \frac{\delta D_p}{\lambda^3} \quad \text{when } K_1 > K_{th} \quad (4a) \]

\[ \dot{a} = 0 \quad \text{when } K_1 < K_{th} \quad (4b) \]

In equations (3) and (4), E is the Young\'s modulus and \( \omega \) is the atomic volume. Although the equations agree quite with experiment in threshold behavior and \( K^2_1 \) dependence of crack-velocity, the measured crack velocities [10,11] appear to be about two to three orders of magnitude slower than those calculated. The discrepancy may arise from (i) the assumption that the crack moves in a flat plane rather than in a zig-zag manner as would be the case for an intergranular path in a polycrystal and, (ii) the influence of plastic flow, which has been disregarded in the model, on the crack-tip stress field. A comparison between theory and experiment is given in Ref. 9.

**Experiments to Measure Fracture Toughness of MERL\'76 at 1000K**

We have measured fracture toughness as the work of fracture required to initiate and propagate an intergranular crack from a notch in compact-tension-specimens. The concept underlying the experiments is illustrated in Fig. 4(a) and (b). Deformation near the crack-tip has two components: plastic flow, and grain boundary cavitation damage. Plasticity concentrates along the shear lobes where the shear stress is maximum. Cavitation, on the other hand would localize immediate ahead of the crack-tip since it responds to the maximum tensile stress. Whereas plastic flow will blunt the crack-tip, cavitation will move the crack forward and keep it sharp. Our view was that the relative magnitude of plastic strain and damage strain would influence the measured fracture toughness of the material. Their relative magnitude could be changed through the loading rate. We expected that the slower loading rates would enhance the relative significance of damage and, therefore, lower the fracture toughness.
The experimental results shown in Fig. 4(d) are in agreement with the above hypothesis. In order to confirm the hypothesis, the damage strain and the plastic strain were measured directly. The technique was to etch markers on the surface at a spacing of 6μm. Plastic strain was defined as the deformation of the grains, and was measured as the distortion of the etched grid on the scale of one grain size. Cavitation strain was defined, and measured, as the average separation of the grain interfaces per unit distance. A picture of a situation where the damage strain is significant but the plastic strain is negligible is shown in Fig. 4(c). A plot of the ratio of the plastic strain to damage strain is given in Fig. 4(d); note that the increase in the fracture toughness is directly correlated to this ratio.

An approximate computer analysis was developed to describe the results by a quantitative model. The model has been described quantitatively in Ref.12. The details of the model will not be discussed here. The results of the model were in good agreement with experiment as illustrated in Fig. 4(d).
CREEP-FATIGUE INTERACTION

Experiments

Creep-fracture is characterized by the nucleation and growth of cavities at grain boundaries, while low-cycle-fatigue is characterized by the Stage I crack initiation and Stage II propagation of a transgranular crack. Separately both failure processes are well understood but the interactions between them appear to be complex. A linear damage rule which assumes that the fatigue portion (defined by the number of cycles) and creep portion (defined as the time spent at maximum stress) add to cause failure has proved to be too simplistic. The data when plotted by this rule show a very large scatter suggesting that the interaction mechanisms are non-linear and that more than one type of interactions may be possible.

Our approach to the above dilemma was to carry out systematic experiments to characterize the mechanisms of creep-fatigue interactions. Aluminum-five percent magnesium alloy was chosen for the study because it has been shown to be very resistant to intergranular creep-fracture under monotonic loading. Experiments were done on smooth specimens with a uniform gage section (as opposed to hour-glass shaped specimens) and in ultra-high-vacuum to reduce the effects of the environment to a minimum. The temperature and the cycle shape were varied, but the plastic strain size and the frequency were held constant. It was felt that frequency and temperature are complementary parameters which may be normalized with respect to each other.

The results of the experiments are shown in Fig. 5b. The cycle shapes which were used are drawn in Fig. 5a. Metallography and fractography revealed at least five different failure mechanisms of creep fatigue interaction. They are designated by (a) thru (e) in Fig. 5b. Each one is described below. Further details and the micrographs are contained in Ref. 13.
(a) This was the classical low-cycle-fatigue mode of failure which is produced by the transgranular initiation of a Stage I crack and propagation of a Stage II transgranular crack. The propagation is characterized by striations on the fracture surface. The spacing of the striations is believed to be related to the crack-tip-opening-displacement [14].

(b) This failure mode occurred for all three cycle shapes at 423K, and at 473K for the equal ramp cycle shape. It differed from (a) in that crack-initiation changed transgranular to intergranular. But propagation remained transgranular and was marked by striations.

(c) This failure mode dominated at higher temperatures when the cycle shape contained a tensile hold-time. In this case the failure mode was totally different. Instead of crack initiation and propagation, intergranular creep damage was spread throughout the specimen. Interrupted tests under the same conditions revealed that the damage accumulated gradually with fatigue cycles. The damage was of 'r' type of cavities as shown schematically in Fig. 6.

(d) In this case, as in (c), failure was caused by cumulative creep damage, the difference being that 'wedge' type of grain boundary cracks were formed. The difference between 'r' and 'wedge' cavities is illustrated in Fig. 6. The cumulative nature of the damage, which was spread throughout the specimen, was confirmed through interrupted tests.

(e) Here a macroscopic instability and flow localization developed in the gage length of the specimen. It is possible that the instability was caused by microstructural degradation of magnesium-aluminide precipitates at 573K.

Theory

The cumulative damage mechanism of creep-fatigue interaction for the 'wedge' type of intergranular cavities was formulated and analyzed in detail.
This is the type (d) failure described in the previous section. The physical basis of the analysis and the cogent results are described here. The details are given in Ref. 15.

The crucial role of grain boundary sliding in the growth of wedge cracks may be appreciated from the schematic in Fig. 6(a). The basis of the model then is to correlate the applied strain to the local sliding at grain boundaries, and the sliding to the wedge crack damage. First, wedge damage, $A_w$, is defined by the equation:

$$A_w = \frac{w}{L}$$  \hspace{1cm} (5)

where $w$ is the length of the wedge crack and $L$ is the grain size. The sliding displacement, $v$, at the triple junction where the wedge crack initiates is also normalized with respect to the grain size, so that at:

$$v = \frac{v_{sliding}}{L}$$  \hspace{1cm} (6)

Then a simplifying assumption is made that $A_w$ and $v$ are linearly related through a material parameter, $\alpha$:

$$\frac{dA_w}{dv} = \alpha$$  \hspace{1cm} (7)

The connection between the applied strain $\varepsilon_e$ and the sliding strain, $v$, is complex but has been extensively studied experimentally and theoretically. Defining a quality $\beta$ such that:

$$\beta = \frac{v}{\varepsilon_e}$$  \hspace{1cm} (8)

it may be shown that $\beta$ varies sigmoidally with strain-rate as shown in Fig. 7. At slow strain rates $\beta$ approaches 0.5. As the strain-rate increases there is a transition until sliding becomes zero at very high strain-rate. The important
parameter is the strain-rate at which the transition is felt. It, \( \dot{\varepsilon}_W^* \), is a material parameter and has been found to depend on the microstructure of the grain boundary by the following equation:

\[
\dot{\varepsilon}_W^* = \frac{0.27Y\Omega}{6\sigma_b} \frac{6\sigma_b}{kT} f_b p^2 L
\]

Here \( Y \) is the yield stress, \( p \) is the size of the particles in the boundary and \( f_b \) is the area fraction of the particles in the boundary. In cases where these parameters cannot be characterized we have shown that \( \dot{\varepsilon}_W^* \) may be experimentally measured with the use of internal friction measurements of grain boundary sliding rate. These details are discussed in Refs. 13 and 17.

Equations (7) and (8), when combined give the result that:

\[
\frac{dA_W}{d\varepsilon_e} = \alpha
\]

where \( \beta = \beta(\varepsilon_e/\dot{\varepsilon}_W^*) \).

For a slow-fast cycle shape, the value of \( \beta \) in the tensile half of the cycle will be greater than in the compressive half of the cycle, because the tensile strain-rate is slower. If the tension strain-rate is \( \dot{\varepsilon}_t \), and the compression strain-rate is \( \dot{\varepsilon}_c \), then the damage per cycle will be given by:

\[
\frac{A_p}{\Delta \varepsilon_p} = \alpha \beta(\varepsilon_t) - \gamma \alpha \beta(\varepsilon_c)
\]

The first term in (11) is the positive damage caused by the tensile portion of the cycle. The second term is negative because compression would tend to heal the damage produced in tension. The coefficient \( \gamma \) has been asserted to account for the hysteresis in the recovery of damage. The cycles to failure, \( N_f = 1/\lambda_{p} \), which leads to the result:

\[
\Delta \varepsilon_p N_f = \frac{1}{\alpha(\beta(\dot{\varepsilon}_t) - \beta(\dot{\varepsilon}_e))}
\]
The result in (12) shows that $N_f = 1/\Delta\varepsilon_p$ when cumulative creep damage is the mechanism of failure (in low-cycle-fatigue, Coffin-Manson equation predicts a parabolic power-law-dependence). Equation (12) does contain two adjustable parameters $\alpha$ and $\gamma$ which can be fixed by simple experiments.

The application of the above result to our own measurements on aluminum and to published data for austentitic stainless steels has been discussed in Ref. 15. The agreement is quite good. The application of the analysis to nickel base superalloys has been less successful suggesting that cumulative creep damage may not be the primary failure mode in superalloys at temperatures encountered by disks in gas-turbine engines. We believe that the intergranular crack initiation mechanism (described by (b) in Fig. 5b) is more relevant in nickel-base superalloys. The sensitivity of superalloys to oxygen environments could also complicate the prediction of life by the simple analysis as described in this report.
REFERENCES

FIGURE CAPTIONS

1. Cavities forming ahead of a crack-tip of an advancing creep crack in MERL'76 at 1000K.

2. The diffusional transport mechanism of cavity growth. Atoms are removed from the cavity surface and inserted into the grain boundary adjacent to the cavities.

3. Numerical results from Ref. 9, showing the relaxation of stress just ahead of the crack tip with the growth of cavities. U is a measure of cavity growth. Eventually the crack moves at a steady state.

4. Model, theory and experiment for the fracture toughness of MERL'76 at 1000K. Details given on page 8.

5. (a) The cycle shapes employed in experiments to identify the mechanisms of creep-fatigue-interaction. (b) The influence of cycle-shape and temperature on fatigue life and on the failure mechanism; five failure mechanisms were identified. Taken from Ref. 13.

6. A schematic of two types of creep damage.

7. Variation of the ratio, $\beta$, of strain due to sliding to the applied strain as a function of the applied strain-rate $\varepsilon_e$ [16].
1. Cavities forming ahead of a crack-tip of an advancing creep crack in MERL '76 at 1000K.
2. The diffusional transport mechanism of cavity growth. Atoms are removed from the cavity surface and inserted into the grain boundary adjacent to the cavities.
3. Numerical results from Ref. 9, showing the relaxation of stress just ahead of the crack tip with the growth of cavities. $U$ is a measure of cavity growth. Eventually the crack moves at a steady state.
MODELING OF THE CREEP CRACK GROWTH PROCESS

(a) HIGH TOUGHNESS

(b) LOW TOUGHNESS

(c) DAMAGE DOMINATED DEFORMATION

(d) INFLUENCE OF LOADING RATE ON DAMAGE

4. Model, theory and experiment for the fracture toughness of MERL'76 at 1000K. Details given on page 8.
5. (a) The cycle shapes employed in experiments to identify the mechanisms of creep-fatigue-interaction. (b) The influence of cycle-shape and temperature on fatigue life and on the failure mechanism; five failure mechanisms were identified. Taken from Ref. 13.
6. A schematic of two types of creep damage.
7. Variation of the ratio, $\beta$, of strain due to sliding to the applied strain as a function of the applied strain rate $\dot{\varepsilon}$ [16].
PERSONNEL

Y.-M. Beissier (M.S. Thesis) "Influence of Loading Rate on Deformation and Fracture Near Crack-Tips at Elevated Temperature"

S. Baik (Ph.D. Thesis) "Mechanisms of Creep Fatigue Interaction"

C. Gandhi Post-Doctoral Associate

S. Baik Post-Doctoral Associate (partial)

L.C. Lim Ph.D. Candidate

PUBLICATIONS


APPENDIX

The following two papers discuss the environmental effects on cavitation and cavitation under multiaxial loading. They are included here because they have not been discussed in the text. Both papers are particularly relevant to nickel base alloys because (a) they are known to be environment sensitive and (b) they exhibit creep crack growth which involves the growth of cavities in a multiaxial stress field ahead of the crack tip.
CORRELATIONS BETWEEN CAVITATION, CREEP AND DILATION FOR MULTIAXIAL LOADING

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Abstract—Intergranular cavitation produces dilation in the specimen. It can also enhance the rate of creep as demonstrated convincingly by experiments of Needham and Greenwood [1]. Metals Sci. 9, 258 (1975). Expressions for cavitation enhanced creep, and for cavitation induced dilation are derived. The latter depends only on geometry, but the first is a consequence of the constrained cavity growth mechanism. That mechanism involves redistribution of stress from regions which have cavities to those which do not: as a result the stress on the constraining regions is increased leading to an increase in the measured creep-rate. A comparison of compressive vs tensile tests is suggested as a means of distinguishing the enhancement in creep-rate.

Résumé—La cavitation intergranulaire produit des dilatations dans l’échantillon. Elle peut également augmenter la vitesse de fluage comme l’ont démontré de manière convaincante les expériences de Needham et Greenwood [1]. Nous avons obtenu des expressions pour le fluage induit par cavitation et pour la dilatation induite par cavitation. Cette dernière ne dépend que de la géométrie, mais la première est une conséquence du mécanisme de croissance forcé des cavités. Ce mécanisme implique une redistribution de la contrainte des régions présentant des cavités vers celles qui n’en ont pas; il en résulte une augmentation de la contrainte dans les régions contraintes provoquant une augmentation de la vitesse de fluage expérimentale. Nous suggérons une comparaison des essais de compression et de traction afin de mettre en évidence l’augmentation de la vitesse de fluage.


INTRODUCTION

Deformation of a cavitating solid can be described by two scalar quantities: an effective strain \( \varepsilon_e \), which is a measure of the change in shape without a change in volume, and a cavitation strain \( \varepsilon_c \), which is the fractional increase in volume due to internal cavities. Intuition suggests that in multiaxial loading the mean stress, or pressure, should influence \( \varepsilon_c \) but not \( \varepsilon_e \), yet Needham and Greenwood [1], and Dyson et al. [2] have found that the effective strain-rate does not depend merely on the effective stress, as found in plastic flow of metals, but also on the state of the applied stress. They found that when creep tests were done on copper in a variable hydrostatic pressure, then the rate of creep was influenced by the pressure, even when the effective stress was kept constant. The pressures were too small to influence the self diffusion coefficient. Furthermore, the change in the creep-rate with pressure appeared to be unrelated to the extent of cavitation (as measured by the change in density).

Dyson et al., in their work with stainless steel, found a difference in the creep-rate between a tension test and a torsion test, for the same effective stress; but the difference appeared only when cavitation was present. In combination, the two sets of results imply that cavitation is a necessary condition for this effect, although the magnitude of the effect is not related to the extent of cavitation. This means the constitutive equation for cavitation enhanced creep should depend on the stress-state but may not necessarily include a state variable related to cavitation, such as \( \varepsilon_c \).

Dyson et al. proposed that the above phenomenon can be explained in terms of the constrained cavity growth mechanism [3-5]. Their concept is illustrated in Fig. 1. If cavities form preferentially on grain facets aligned nearly perpendicular to the maximum positive principal stress and if the cavities grow by diffusion then grains such as A and B must move apart from each other to accommodate the volume of material which is displaced by cavity growth. They will be constrained from doing so if the creep-rate in the neigh-
boring grains is slower than the displacement rate required to accommodate cavity growth. The displacement rate then becomes limited by the rate of creep in adjacent regions, such as M. (It must be remembered that there are different regimes of behavior depending upon the stress, temperature and microstructure. In general, low stress, high temperature, small cavity spacing, and a long time-to-failure favors the constrained growth mechanism [3-5]). This mechanism gives a qualitative explanation of why cavitation, but not the size of the cavities, may influence the creep-rate. In Fig. 1, for example, the load on boundary AB would be transferred to region M leading to an increase in the rate of creep. Yet, the magnitude of the effect will not depend on cavity size. The only condition for load transfer is that if an equal tensile stress were to be applied to region AB and region M, isolated from each other, then AB would elongate at a much faster-rate than M. It has been shown [6, 7] that the displacement rate of AB depends more strongly on cavity spacing than on cavity size.

When cavities form, then one of the conditions for pure plastic flow, that deformation should occur at constant volume, is no longer satisfied. In long term fracture experiments, done under conditions which approach the service conditions, the volumetric strain, in fact, can become the dominant strain [8, 9]. Thus it becomes necessary to distinguish between the shape-change component and the volumetric component of the total strain, before the usual multiaxial stress/strain-rate equations for power-law-creep [2] can be applied.

This paper consists of four parts. First a procedure for separating the creep or the effective strain and the cavitation strain is presented. Next, equations are developed for describing the cavitation-strain in terms of the geometry and the distribution of cavities in the grain boundaries. Third, a power-law constitutive equation, in the presence of growing cavities, is described. Finally, a possible form for the Monkman-Grant equation for use under multiaxial straining is given. The second and the third items are not new in concept. Harris et al. [8] have also considered the creep strain arising from the growth of cavities. Although the basic premise of their, and our approach is similar, there are important differences. Their formulation begins from the equations by Hull and Rimmer [10] and Speight and Harris [11] for diffusional cavity growth. It now appears that the constrained cavity growth mechanism is more relevant to long-term creep fracture experiments. In this mechanism, the rate of cavity growth is related to tensile strain, rather than to time as dictated in the Hull and Rimmer approach. Also, in the present work the dependence of the rate growth of cavitation strain on the following parameters: cavity, spacing, grain-size and the di-hedral angle, is explicitly defined.

The third problem, which pertains to the prescription of a constitutive equation for cavitation enhanced effective strain-rate has recently been considered by Dyson et al. [2]. The major difference between their results and the equations derived here lies in their assumption that deformation occurs at constant volume; the use of equation (2) in their paper is contingent upon this assumption. While the assumption may be reasonably valid when fracture occurs at large ductilities, it is misleading in long term experiments when the cavitation strain can become a significant fraction of the total strain [9]. The analysis given here distinguishes between creep strain, which is defined for deformation at constant volume, and the cavitation strain.

THE STRAIN-STATE

Any strain state can be described by the three principal strains, $\epsilon_1$, $\epsilon_2$ and $\epsilon_3$, and by the orientation of the axes along which these strains are prescribed. In general then

$$[\epsilon] = \begin{bmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_2 & 0 \\ 0 & 0 & \epsilon_3 \end{bmatrix}$$

(1)

The strain due to change in volume, $\epsilon_v$, and that due to change in shape $\epsilon_s$, can be separated as follows:

$$\epsilon_s = \epsilon_1 + \epsilon_2 + \epsilon_3$$

(2)

and

$$\epsilon_v = \frac{1}{2} \left[ (\epsilon_1 - \epsilon_2)^2 + (\epsilon_2 - \epsilon_3)^2 + (\epsilon_3 - \epsilon_1)^2 \right]$$

The strain $\epsilon_v$ is related to the change in density by
where the approximate form holds for small volumetric strain. Here \( \Delta \rho / \rho \) is the fractional change in density.

A comparison of equations (2) and (3) shows that \( \epsilon_\nu \) and \( \epsilon_s \) are independent of each other and, therefore, measure different effects of deformation. This also means that if both \( \epsilon_\nu \) and \( \epsilon_s \) are non-zero then at least two principal strains must be measured in order to distinguish between them. As an illustration, consider a uniaxial test. Here we must measure either the transverse strain, \( \epsilon_\nu \), or the change in density, in addition to the axial strain, \( \epsilon_s \), in order to distinguish between \( \epsilon_\nu \) and \( \epsilon_s \). Recognizing that two of the principal strains in a uniaxial test are equal, i.e. the transverse strains, we can derive the following expressions

\[
\epsilon_s = \frac{3}{2} \epsilon_\nu - \epsilon_\nu = \epsilon_s + \frac{1}{3} \frac{\Delta \rho}{\rho}
\]

\( \epsilon_s = -\Delta \rho / \rho = \epsilon_s + 2 \epsilon_\nu. \)

If \( \Delta \rho / \rho = 0 \) then \( \epsilon_s = \epsilon_\nu \), i.e. the axial strain becomes equal to the effective strain.

Measurements of \( \Delta \rho / \rho \) in creep experiments show that it usually lies in the range of \( 10^{-3} \) to \( 10^{-2} \) [1]. Thus in ductile materials the correction from \( \Delta \rho / \rho \) in the estimate of \( \epsilon_\nu \) in equation (5) is likely to be small. In long term creep-fracture experiments with structural materials, however, the apparent tensile strain at fracture can be small as \( 10^{-5} \). In that instance the correction becomes large and it should be implemented.

Since the cavitation strain measures the total volume of all the cavities, it can be estimated theoretically. The task becomes particularly simple if the following assumptions are made: (a) that the shape of the grain boundary cavities is lenticular, and (b) that the number of cavities remains fixed. The first assumption omits the fact that cavities can propagate like cracks under certain conditions [12], and the second that cavities usually increase in number as well as in volume with time [13]. Both factors can be taken into account by increasing the complexity of the calculation.

We assume, as illustrated in Fig. 1, that cavities form only those boundaries which are approximately normal to the applied tensile stress that their average spacing in a grain facet is \( l \), and that their shape is described by two parameters \( r \) and \( \theta \). From this geometry a relationship between \( \epsilon_a \) and \( A \), the area fraction of cavities in a grain facet can be found, using the expressions in Refs [6, 7]

\[
\epsilon_a = \pi^{1/2} A^{1/2} \theta
\]

where

\[
F_r = \frac{2\pi}{3} (2 - 3 \cos \theta + \cos^3 \theta)
\]

\[
F_b = \pi \sin^2 \theta.
\]

and where \( \zeta \) is the grain size.

In the constrained cavity growth mechanism, the rate of growth of cavities becomes controlled by matrix creep. Thus, even though cavities on a grain facet, such as AB in Fig. 1, grow by diffusion, they do so under a tensile stress which is much smaller than the applied tensile stress. If we assume this local stress to be \( \sigma \), then the following equation can be written for the rate of growth of damage \( A \)

\[
\frac{dA}{dt} = (1 - A) \left( \frac{1}{2} \ln \frac{1}{A} - \frac{3}{4} + A \left( \frac{1 - A}{4} \right) \right)
\]

where \( \zeta \) is a normalized unit of time, defined as

\[
\zeta = \left( \frac{3\sqrt{\pi} F_b kT}{32 \delta_0 \Omega \delta D_b} \right)^{1/3}
\]

where \( t \) is real time, \( \Omega \) is the atomic volume and \( \delta D_b \) is the boundary width times the grain boundary diffusivity.

Equation (10) is a constitutive equation for describing the rate of accumulation of damage with time. Interestingly, it is universal. The influence of the microstructural parameters, such as \( \lambda \), and the material parameters, e.g. \( \delta D_b \) and the stress, have been conveniently normalized with respect to time in \( \zeta \) defined in equation (11). The plot of \( A \) vs \( \zeta \) is given in Fig. 2. If we represent this master curve as function of \( \zeta \) such that

\[
A = g(\zeta)
\]

and substitute for \( A \) in equation (7), we obtain the following equation

![Graph](image-url)
such growth model [3, 4] the local stress on a grain facet may be lower than the applied stress, its magnitude depending on the micromechanics of stress redistribution on the scale of the grain-size. In the present paper this effect is accounted for by using a normalized function of time. The second difference is that a master curve has been derived for the change in relative density with time (Fig. 3). Convincing evidence is presented for the validity of the master curve. Several other experimental studies and a phenomenological formulation of life prediction using $\varepsilon_\text{p}$ as the critical parameter [14] have been reported in the literature. A review of these results is not attempted here.

Before closing this section, one feature of equation (7) is worth emphasizing. It explains how the change in density in the specimen at the time of fracture is related to microstructural parameters $\theta$, $\lambda$, and $\sigma'$. The relationship between $\varepsilon_\text{p}$ for different values of $\theta$ is plotted in Fig. 5. Note that for a given damage, say $A = 0.5$, the change in density increases as $\theta$ increases. Also, the change in density is proportional to $\sigma'$. The validit y of the universal curve in Fig. 3 is nicely demonstrated from the data of Needham and Greenwood [1]. They have obtained plots for $\log \varepsilon_\text{p}$ vs log $t$ for various levels of maximum principal stress in tensile tests done with a superimposed hydrostatic pressure. When the data in Ref. [1] are plotted with appropriate shift factors then excellent agreement with the master curve is obtained as shown in Fig. 4.

The analysis by Harris et al. [8] differs from the one given here in two respects: First, their analysis is based upon the Hull and Rimmer [10, 11] derivation in which the applied tensile stress acts directly on a transverse grain boundary, whereas in the constrained

EQUATIONS FOR FLOW

The next step is to consider the constitutive equations for flow in a cavitating solid. In particular we wish to explain how cavity growth can enhance the deviatoric component of the strain-rate, $\dot{\varepsilon}_d$. Dyson et al. [2] have suggested that the constrained cavity growth mechanism can explain this effect. Although similar in concept, our analysis differs from theirs in that the deformation is separated into two scalar parameters, $\varepsilon_\text{p}$ which is merely the fractional change in volume and $\varepsilon_\text{p}$ which accounts for the shape change at constant volume. Thus equation (13) can be used to compare analysis with the measurement of the change in density, $\varepsilon_\text{p}$, with time. If plotted on a log-log scale, all data should overlap on a single master curve if the shift factors $C$ and $\zeta/t$ are adjusted. Both factors depend on material, microstructural, and loading parameters. $C$ depends on $\theta$, $\lambda$, and, as given in equation (14) and $\zeta/t$ on $\theta$, $\lambda$, $\sigma'$, and $\delta D_0$ as described by equation (11). The master curve, which is exactly defined when $C = 0$, is shown in Fig. 3.

The next step is to consider the constitutive equations for flow in a cavitating solid. In particular we wish to explain how cavity growth can enhance the deviatoric component of the strain-rate, $\dot{\varepsilon}_d$. Dyson et al. [2] have suggested that the constrained cavity growth mechanism can explain this effect. Although similar in concept, our analysis differs from theirs in that the deformation is separated into two scalar parameters, $\varepsilon_\text{p}$ which is merely the fractional change in volume and $\varepsilon_\text{p}$ which accounts for the shape change at constant volume. Since the measured principal strain-rates contain a component of volume change, the Levy–Mises constitutive equations of plasticity [15], which apply only when deformation occurs at constant volume, may not be used [2, equation (2)]. The

![Diagram](image-url)
The present analysis is restricted to the description of \( \dot{\varepsilon}_e \) in terms of the principal stresses.

The formulation of creep enhancement is done through a new description of the deviatoric stress. Normal power law creep is represented by the following equation

\[
\dot{\varepsilon}_e = k_e \sigma^*_e \tag{15}
\]

where \( \sigma_e \), the von-Mises deviatoric stress has the form

\[
\sigma_e = \sqrt{\frac{1}{2}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]} \tag{16}
\]

In extending equation (15) to the situation of cavitation enhanced creep-rate, some features of the physical mechanism which is responsible for the enhancement must be accounted for. For example in Fig. 1, the strain-rate in direction 1 caused by a compressive principal stress \( \sigma_2 \) remains unchanged because cavity growth in interface AB depends only on \( \sigma_1 \). Also for the same reason a compressive \( \sigma_1 \) will not produce an enhancement in the rate of creep. Creep is enhanced through cavitation only when the principal stress components are tensile. Recognizing the need for distinguishing between a tensile and a compressive principal stress we define a vector \( \delta \) such that

\[
\delta_i = +1 \quad \text{if} \quad \sigma_i > 0 \\
\delta_i = -1 \quad \text{if} \quad \sigma_i < 0 \tag{17}
\]

where \( \sigma_i \) are the principal stresses defined by the stress tensor

\[
[\sigma] = \begin{bmatrix}
\sigma_1 & 0 & 0 \\
0 & \sigma_2 & 0 \\
0 & 0 & \sigma_3
\end{bmatrix}
\]

We still define the effective stress by the von-Mises expression but replace \( \sigma_e \), etc. in that expression by 

\[
[1 + \frac{1}{2}x(1 + \delta_1)]\sigma_e \tag{15}\]

Thus if \( \delta_1 = -1 \) then we recover the simple von-Mises form but if \( \delta_1 = +1 \), then a stress concentration factor of \( (1 + x) \) is obtained. Substituting these into the von-Mises equation gives an expression for the deviatoric stress, \( q_e \), which may be used for describing cavitation enhanced creep

\[
q_e = \sqrt{\frac{1}{2}[(1 + \frac{1}{2}x)(\sigma_1 - \sigma_2) + \frac{1}{2}x(\sigma_1 \delta_1 - \sigma_2 \delta_2)]^2} \\
+ \frac{1}{2}x(\sigma_2 \delta_2 - \sigma_3 \delta_3)]^2} \\
+ \frac{1}{2}x(\sigma_3 \delta_3 - \sigma_1 \delta_1)]^2}
\]

\[
(18)
\]

Note that setting \( x = 0 \), recovers the pure von-Mises form.

A few specific applications of equations (18) are interesting. First we consider the example of a tensile test superimposed with a hydrostatic pressure \( p \). Let \( \sigma_e \) be the tensile stress applied to the specimen inside the pressure vessel. If \( (\sigma_1 - p) > 0 \), then \( \sigma_e = \sigma_1 - p \). \( \sigma_2 = \sigma_3 = -p \) and \( \delta_1 = 1 \) and \( \delta_2 = \delta_3 = -1 \). If, however, \( (\sigma_1 - p) > 0 \), then \( \delta_1 = -1 \). Substituting these in equation (18) we obtain

\[
q_e = \sigma_e + x(\sigma_1 - p) \quad \text{if} \quad \sigma_1 - p > 0
\]

and

\[
q_e = \sigma_1 \quad \text{if} \quad \sigma_1 - p \leq 0. \tag{19}
\]

In a torsion test \( \sigma_1 = \sigma_2 \) and \( \sigma_2 = -\sigma_1 \) while \( \sigma_3 = 0 \). Therefore \( \delta_1 = +1 \), \( \delta_2 = -1 \) and we obtain that

\[
q_e = \sigma_1 \sqrt{3(1 + \frac{1}{2}(x + 2))^{1/2}} \approx \sigma_1 \sqrt{3(1 + \frac{1}{2}x)} \tag{20}
\]

where the approximate result neglects second and higher order terms in \( x \). Equations (19) and (20) provide a means of comparing the effective stress in a tensile and a torsion test. If \( p = 0 \), then the stress concentration factor in a tensile test is \( (1 + x) \). In a torsion test is \( (1 + 1/3x) \).

The cavitation enhanced effective strain-rate is calculated by substituting \( q_e \) instead of \( \sigma_e \) in equation (15).

For the purpose of comparing theory and experiment, the parameter \( x \) can be regarded as an adjustable parameter. The equivalent parameter in Dyson et al.'s analysis is \( A_1 \); and they are related through the equation \( (1 + x) = 1/(1 - A_1) \). Upon applying their own analysis to their tension torsion experiments, Dyson et al. found that \( A_1 = 0.33 \) gave satisfactory correlation with data. Applying it to the superimposed hydrostatic pressure creep experiments by Needham and Greenwood, a value \( A_1 = 0.5 \) was
 needed to give good fit with the data. The application of the present analysis to the same sets of data shows that using $\lambda = 0.42$ (or $A_1 = 0.3$) gives good correlation with the tension/torsion data and $\lambda = 1.5$ (or $A_1 = 0.6$) gives satisfactory correlation with Needham and Greenwood's data. The difference, although numerically small is a result of the different approach used in calculating the effective strain-rate from the effective stress$^\dagger$.

An extension of equation (18) when the loading is cyclic is given in the Appendix.

**MONKMAN--GRANT DUCTILITY**

In a simple uniaxial test, when $p = 0$, the minimum creep rate, $\dot{\varepsilon}_c$, and time-to-fracture, $t_f$, are often related by $\dot{\varepsilon}_c, t_f = \epsilon_{mp}$, a constant in long term fracture tests. The constrained cavity growth model successfully explains this result [3, 4].

If the tensile test is done in a superimposed hydrostatic pressure then the time-to-fracture should correlate with the maximum principal stress, $\sigma_1$, since, in the constrained cavity growth model, the fundamental mechanism of cavity growth is diffusion. The Monkman Grant equation should then take the form

$$k_p \sigma_1^n t_f = \epsilon_{mp}$$

(21)

In tests with superimposed hydrostatic pressure, $\sigma_1 = \sigma_a - p$. Needham and Greenwood did in fact find that $(\sigma_a - p)$ and $t_f$ are related through a power-law equation. It would also be interesting to consider if the growth in cavitation strain, $\epsilon_{ac}$, with time also follows a similar rule. A logarithmic plot of $\epsilon_{ac}$ normalized with respect to $(\sigma_a - p)^n$, against time is shown in Fig. 6. The results correlate quite well but they separate into two groups, one for $p = 0.1$ MPa and 3.5 MPa, and the other for $p = 6.5$ MPa, 10.4 MPa and 13.8 MPa. A possible explanation is that the cavity spacing for these two groups of results was different. Possibly, the material contained two types of nucleation sites, one requiring a greater threshold stress than the other. Presumably at the high tensile stresses ($p = 0.1$ and 3.5 MPa) both types nucleated leading to a smaller cavity spacing than at the lower stresses ($p \geq 6.5$ MPa) when only one type nucleated.

Whereas the form of equation (21) has a physical basis when tests are done in uniaxial loading under a superimposed hydrostatic pressure, caution must be exerted if it is to be extended to triaxial tensile loading of an isotropic material. The Monkman Grant equation arises from the fact that cavities form inhomogeneously in the material, and, therefore, their growth becomes limited by compatibility constraints. If the material properties were ideally isotropic, i.e. the grain-size were uniform and equiaxed with all boundaries having the similar density and types of nucleation sites, then under equi-triaxial loading the compatibility constraint should become unimportant, and the simple Hull and Rimmer analysis [7, 10, 11] should apply. In the author's view [4] any realistic situation is likely to depart considerably from the ideal conditions, and equation (21) should continue to hold even in a general multiaxial stress state.

**DISCUSSION**

Three inter-related topics have been discussed in this paper. First, the need for separating the cavitation strain and the creep strain is emphasized. Second, it is shown that the growth of cavitation strain with time can be represented on a master curve provided that the strain and the time are normalized with respect to the microstructural and the material parameters such as $\theta$, $\lambda$, $\sigma_a$ and $\bar{D}_b$. The master curve can be used to predict the residual life of a specimen after it has suffered some cavitation damage, if the normalization parameters $C$, in equations (13) and (14), and $\xi/t$, in equation (11), can be calculated. The parameters can be determined experimentally from the knowledge of $\epsilon_{ac}$, i.e. the volumetric strain at fracture, and the time-to-fracture, $t_f$. Substituting $A_1 = 1$ in equation (13) will give $C = \log_{10}\epsilon_{ac}$, while the ratio $\xi/t$ may be determined from the knowledge that $\xi/t = 0.011$ (see Fig. 2) and by using $\xi = \tilde{\xi} \cdot t_f$. Once the shift factors are established the master curve can be used to predict the evolution of damage with time.

The other topic in the paper deals with cavitation enhanced deviatoric creep. The peculiarities of the underlying mechanism for this phenomenon are rather novel in that grain facets which contain growing cavities behave as if they do not support much.
normal traction, even though the grain boundary has not physically separated. As a result the strain-rate, in a uniaxial test, is enhanced by a factor \((1 + \gamma \sigma^n)\) where \(\gamma\) is a factor of order one, and where \(n\) is the power-law stress exponent. The strain-rate, therefore, may be enhanced by almost a factor of 10. The parameter \(\gamma\) has been left as an adjustable parameter in the present analysis. Physically it is a measure of the extent to which the normal stress is transferred from the grain facets on which cavities are growing to the adjacent surrounding regions.

Factors which enhance the strain rate arising solely from the growth of cavities, relative to the rate of creep in the grain matrix, are likely to increase the value of \(\gamma\). Since cavities must grow by diffusion to produce this effect, while the grain matrix is assumed to deform by power-law creep, the following factors are likely to increase the value of \(\gamma\): smaller \(\gamma\) because that leads to faster cavity growth by reducing the diffusion distance; smaller applied stress because diffusional cavity growth varies linearly with stress while creep varies as stress to a power of 4 to 5; and intermediate temperatures because diffusional growth is usually dominated by grain boundary diffusion while power-law creep is controlled by lattice diffusion. The enhancement in the creep-rate would also depend upon the spatial redistribution of the load which is shed by the grain facets and transferred to the surrounding grain matrix. In a material with high strain rate sensitivity the load will quickly spread across the load bearing regions and, therefore, lead to a greater increase in the measured creep-rate.

Another interesting point about the above mechanism is that the creep-rate is insensitive to the size of the cavities, the only necessary condition is that cavities should have nucleated and should be growing. This result was confirmed by Needham and Greenwood who found the creep-rate did not depend on the extent of prior damage, and by Dyson et al. who found that the effect occurred only if the cavities have been pre-nucleated. This raises an interesting application of the phenomenon. Often in engineering materials, there is a need to determine when the cavities nucleate in a stress-rupture test. If an alternate compressive and tensile load were applied to the specimen, then the compressive creep-rate and the tensile creep rate should remain equal until the cavities nucleate. Thereafter, the tensile creep-rate will become significantly faster than the compressive creep-rate.

**SUMMARY**

1. In long term experiments with structural materials, when the fracture strain is small, the strain due to cavitation (change in volume) and the strain due to creep (shape change only) must be separated. The cavitation strain, \(\epsilon_c\), defined in equations (2) and (4) and the creep strain, \(\epsilon_c\), in equation (3), are independent quantities in any strain-state.

2. The constitutive flow equation for \(\dot{\epsilon}_c\), however, may be coupled to and enhanced by cavitation if the cavities are growing by the constrained cavity growth mechanism. Then the effective stress and \(\dot{\epsilon}_c\) are still related through the usual flow equation, but the effective stress, \(\sigma_{eff}\), is no-longer described by the customary von-Mises equation.

3. A possible new definition for the deviatoric stress, \(\sigma_{dev}\), is given in equation (18). It depends not only on the principal stresses but also on the sign of the principal stresses, since a tensile stress is required to grow cavities by diffusion. The expression contains an adjustable parameter \(\lambda\).

4. \(\lambda\) can be determined by comparing the flow behavior in simple tension and simple compression.

5. The relative rates of flow in tension and compression may also be used to evaluate cavity nucleation, since creep enhancement in tension is possible only after the cavities have nucleated.

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**REFERENCES**


**APPENDIX**

In a fatigue experiment where compressive deformation is imposed after allowing the cavities to grow in tension, some enhancement in the compressive creep-rate may also be expected because the cavities sinter in compression which will lead to a displacement rate of A and B toward each other (see Fig. 1). The enhancement factor in compression is likely to be smaller than in tension. Let the corresponding value of \(\lambda\) in compression be \(\lambda_c\). Then the principal stress in the von-Mises equation should be written as 

\[1 + \frac{\sigma}{2(1 + \lambda_c)} + \frac{\sigma}{2(1 - \lambda_c)}] \sigma_{eff},\]  

etc. Note that they
reduce to \([1 + \frac{1}{2}(1 + \delta_1)]\sigma_1\), and so on, for tension and
\([1 + \frac{1}{2}(1 - \delta_1)]\sigma_1\) for compression. With these substitu-
tions the expression for von-Mises effective stress becomes:

\[
\sigma_e = \sqrt{\left\{(1 + \frac{1}{2}x + \frac{1}{2}y)(\sigma_1 - \sigma_2) + \frac{1}{2}(x - y)(\delta_1\sigma_2 - \delta_2\sigma_1)\right\}^2 + \left\{(1 + \frac{1}{2}x + \frac{1}{2}y)(\sigma_3 - \sigma_4) + \frac{1}{2}(x - y)(\delta_3\sigma_4 - \delta_4\sigma_3)\right\}^2 + \left\{(1 + \frac{1}{2}x + \frac{1}{2}y)(\sigma_5 - \sigma_6) + \frac{1}{2}(x - y)(\delta_5\sigma_6 - \delta_6\sigma_5)\right\}^2}.
\]
INTERGRANULAR CREEP FRACTURE IN AGGRESSIVE ENVIRONMENTS

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Abstract Gaseous species can diffuse along a boundary and oxidize impurities or precipitates. In nickel alloys $\text{O}_2$ can attack $\text{C}$ or carbides to produce $\text{CO}$ at high virtual pressures. This provides a driving force for cavity nucleation and growth at particle interfaces, which acts in addition to the applied stress in forcing fracture. In this paper it is shown that the oxidation pressure can become comparable to, or even larger than, the stresses normally applied in stress-rupture tests. The dependence of this pressure on temperature and oxygen pressure is derived for various oxidation reactions. Since oxide-dispersion-strengthened alloys are known to be more susceptible to cavitation than precipitate strengthened alloys, it is also possible that internal oxidation enhances cavitation by producing oxide particles from elemental impurities, or by converting metal carbide and metal-intermetallic interfaces to metal-oxide interfaces. The kinetic steps which may become rate limiting when cavity nucleation and growth is induced by oxidation, are discussed.

Résumé Les gaz peuvent diffuser le long d'un joint de grains et oxyder des impuretés ou des précipités. Dans les alliages de nickel, l'oxygène $\text{O}_2$ peut attaquer le carbone ou les carbures et former de l'oxyde de carbone $\text{CO}$ sous fortes pressions virtuelles. Ceci induit une force motrice pour la germination et la croissance des cavités aux interfaces avec les particules, force mortice qui s'ajoute à la contrainte appliquée pour provoquer la rupture. Dans cet article, nous montrons que la pression d'oxydation peut devenir comparable ou même supérieure aux contraintes appliquées normalement au cours d'essais de rupture sous contrainte. Nous avons obtenu la variation de cette pression en fonction de la température et de la pression d'oxygène pour diverses réactions d'oxydation. Les alliages renforcés par une dispersion d'oxyde présentant plus fréquemment le phénomène de cavitation que les alliages renforcés par des précipités, il est également possible que l'oxydation interne favorise la cavitation en transformant des impuretés sous forme d'éléments en particules d'oxyde, ou en transformant les interfaces métal-carbure et métal composé intermetal, en interfaces métal oxyde. Nous discutons les étapes de la cinétique susceptibles de limiter la vitesse lorsque la germination et la croissance des cavités proviennent de l'oxydation.


1. INTRODUCTION

Nearly always, engineering materials face aggressive environments during service, which is why a fundamental understanding of phenomena such as hydrogen and liquid metal embrittlement and stress-corrosion cracking is so important. At high temperature, the sensitivity of Ni alloys to air-environment has been reported by Sadananda et al. [1, 2, 3]. Recent experiments by Woodford and Bricknell [4, 5, 6] have established beyond doubt that oxygen is an aggressive species in the creep-fracture behavior of nickel base alloys. They have shown [5] that cavities can be induced in Ni even when it contains small amounts of C ($\sim 100$ ppm), and at oxygen pressures which are low enough to be reducing with respect to NiO. They propose that the cavities are bubbles of CO. This reinforces this author's belief that oxygen attack in alloys of Ni does not involve a new mechanism of creep fracture, but that it accentuates the usual creep-
fracture mechanism, i.e., cavity nucleation and growth, which occurs even in an inert environment when a tensile stress is applied. This intuition is based on the study of phenomenological data which compares fracture in ‘vacuum’ and air environments, e.g., Ref. [7] In general, one observes (a) that although fracture occurs sooner in air than in vacuum, cavitation is still the principal feature of fracture surfaces, and (b) that strong nickel base alloys are often more notch sensitive in air than in vacuum although, again, cavitation is the cause of fracture. The second point can be rationalized as being due to enhanced cavitation by the diffusion of oxygen from the surface.

In this paper, therefore, the earlier work on nucleation and growth of cavities under stress [8, 9, 10], is extended to include the additional thermodynamic driving force for cavitation due to the gas produced by the reaction between O and C (and its compounds). Like the tensile stress across the boundary, the gas pressure attempts to pry the boundary apart. Consider a cavity in a grain boundary. A normal tensile stress is applied. This will involve the work done by \( \sigma \), by \( \sigma \), and by the ‘sintering pressure’, \( \gamma \), where \( \gamma \) is the surface energy and \( r \) is the radius of curvature (assuming that both radii of curvature in the surface are equal). Thus

\[
\delta W = \int \delta x \left( p - \frac{2\gamma}{r} \right) dS - \sigma, \delta V
\]

where \( \delta x \) is the small normal surface displacement, and the integral represents integration over the surface S. If \( p \geq \frac{2\gamma}{r} \) or if the cavity is of an equilibrium shape so that \( r \) is uniform at all parts of the cavity surface then \( p \) becomes constant and (3) reduces to

\[
\delta W = \left( p - \frac{2\gamma}{r} + \sigma \right) \delta V.
\]

It follows that in calculations of cavity nucleation and growth \( \sigma \) may be replaced by \( (\sigma + p - 2\gamma/r) \) provided that the cavity has a near equilibrium shape or if \( \sigma + p \geq 2\gamma/r \). Earlier, this author has proposed a diffusive model for cavity nucleation [10] where a cavity grows by clustering of vacancies until the cavity becomes super-critical. For sub-critical voids, the surface-energy factor is dominant and the cavity grows slowly; in this instance equation (7) should apply because the cavity is small and slow growing so that it would retain its equilibrium shape. When the cavity is much larger than the critical size then the \( 2\gamma/r \) term should become relatively small and again equation (7) should apply, provided that \( \delta x \) is independent of S. Caution is needed when the cavity is just a bit bigger than its critical size.

\[
2C + O_2 = 2CO
\]
In equation (7), \( p \) is the mechanical pressure of the gas. If the gas is produced by chemical reactions (R1 thru R5), then the virtual pressure, also \( p \), will be given by:

\[
f = f' p
\]

where \( f \) is the activity, or the fugacity, and \( f' \) is the activity coefficient, \( f \), thus, is determined through the free-energy of the reaction in question, and becomes the 'chemical' driving force for cavity nucleation. We now discuss the magnitudes for \( f \) and \( p \).

2.2 \( \kappa \) Produced by reactions between C, carbides and \( O_2 \)

The fugacity of \( CO \) for reactions (R1 to R5) is calculated in this section. The standard free energy of formation of the different carbides of \( Cr \), CO and \( CO_2 \), and \( Cr_2O_3 \), are listed in Table 1. The values for the carbides have been taken from Ref. [12] because they were obtained by seeking equilibrium with CO gas and because they are in agreement with other measurements where equilibrium with CO was also used to obtain thermodynamic data [14]. These numbers differ slightly from those given in Ref. [13] (by less than 3\( \times \)10\(^{-4}\) for \( Cr_2C \), 4\( \times \)10\(^{-4}\) for \( Cr-C_3 \) and 8\( \times \)10\(^{-4}\) for \( Cr_3C_2 \). For a recent review see Ref. [15].

The fugacity of \( CO \) is plotted as a function of temperature and \( p_{O_2} \), for reactions of \( O_2 \) with \( Cr_2C_6 \), \( Cr_3C_2 \), \( Cr_2C_2 \) and \( C \), in Fig. 1. Note that \( Cr_2C_6 \) gives the smallest values for the fugacity and \( C \) the highest. Typically, at 1000 K, the values for \( Cr_2C_6 \) are about 10\(^{-9} \) at \( p_{O_2} = 1 \), and 10\(^{-4} \) at \( p_{O_2} = 10^8 \). For pure \( C \) the fugacities are a factor of \( 3 \times 10^4 \) higher, at 1000 K.

At this point it would be interesting to estimate the virtual CO pressure in experiments of Bricknell and Woodford [5]. Their technique for controlling \( p_{C} \) was to pack the Ni-specimens which contained some C in Ni: NiO powder at 1273 K, which fixed the \( O_2 \) activity at \( p_{O_2} = 3 \times 10^{-11} \), and then see if bubbles were produced in the boundaries and they were. Assuming a carbon activity of one, we obtain from Fig. 1, that \( f_{CO} = 7 \times 10^3 \). If instead we assume that \( a_C \), the carbon activity, was equal to the average C concentration (100 ppm by weight), then \( a_C = 5 \times 10^{-4} \), which reduces \( f_{CO} \) to 3.4. At these low pressures once may assume the \( f' = 1 \), which would mean an effective \( CO \) pressure, \( p_{CO} = 0.34 \) MPa (using equation 8). Since cavities were observed under these conditions, one may infer that \( a_C > 5 \times 10^{-4} \) because of non-equilibrium segregation in the boundaries. There is also the possibility that \( CO_2 \) instead of \( CO \) was being produced. That reaction at 1273 K and \( p_{O_2} = 3 \times 10^{-4} \), yields \( p_{CO} = 21 \) MPa, which is a stress large enough to cause cavitation in pure nickel. The enhancement factor, when \( CO_2 \), rather than \( CO \), is the reaction product, is given in Fig. 2, and was obtained by considering reaction (R4).

The assumptions made in the calculation of curves in Figs 1 and 2 need to be re-emphasized. The activities of \( Cr \), \( C \) and the carbides have been assumed to be unity. While this is probably true for the carbides, since they do not dissolve significant amount of impurities, the activities of \( Cr \) and \( C \) would depend on the alloy composition and whether or not the boundary segregation of these impurities is in equilibrium with the matrix. Decreasing \( C \) activity decreases the driving force for cavity nucleation. We than CO is the reaction product, is given in Fig. 3. Note that the enhancement factor decreases as \( T \) decreases, [4]. Possibly a more accurate estimate of activities in real alloys can be done, but, in the author's view a systematic experimental study on the ternary Ni-Cr-C system is first necessary before attempting to apply the analysis to more complex alloys. Another assumption, that \( Cr \) rather than \( Cr_2O_3 \) is the reaction product, is justified on the basis that excess \( Cr \) is usually present in the nickel-base alloys. However, for sake of completeness, analytical expressions for \( f_{CO} \) for this and the other reactions, are given in Table 2.

The fugacity of gases, \( f \), can be related to their partial pressure, \( p \), through the expression in equation (8). For low values of \( f \), up to a few atmospheres, the behavior should remain ideal, and the activity coefficient \( f' = 1 \). In the following section we describe a method for obtaining approximate values of \( f' \) at large partial pressures of the gas.

3. FUGACITY OF NON-POLAR GASES AT HIGH TEMPERATURE AND PRESSURE

3.1. Equation of state

At high pressures the compressibility, and, therefore, the free energy of gases becomes pressure depen-

<table>
<thead>
<tr>
<th>Table 1. Free energy of formation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>CO (g)</td>
</tr>
<tr>
<td>CO (g)</td>
</tr>
<tr>
<td>Cr, (g)</td>
</tr>
<tr>
<td>Cr, (g)</td>
</tr>
<tr>
<td>Cr, (g)</td>
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<tr>
<td>Cr, (g)</td>
</tr>
</tbody>
</table>
Fig. 1. CO fugacities as a function of temperature and oxygen pressure for different oxidation reactions.

For ideal non-polar, the interaction between the molecules may be described by van der Waals' equation. This concept was used by Maron and Turnbull [17] to express the equation of state of a non-polar gas as:

\[ pV = RT + \sum_{a \leq b} z_{ab} p \]  \hspace{1cm} (9)

where \( z(T) \) are the virial coefficients. It was shown that (9) was obeyed by several gases (H\(_2\), CH\(_4\), He, CO\(_2\), HNO\(_3\), C\(_3\)H\(_4\), O\(_2\), CO, C\(_2\)H\(_6\), C\(_2\)H\(_4\)) in the range 203 to 873 K, and 1 to 1000 bars.

Equation (9) can be substituted in equations (cG/cp)\(_T\) = V and \( \delta G = RT \ln f \), and equation (8) to
give:
\[ \ln I = \sum_{n=1}^{4} \frac{p_n^n}{nRT} \]  

Maron and Turnbull argue that equation (10) should be universal if \( p \) and \( T \) are normalized with respect to the critical values, \( p_c \) and \( T_c \), in van-der Waals' equation such that
\[ p_n = \frac{p}{p_c} \quad \text{and} \quad T_n = \frac{T}{T_c} \]  

where \( p_n \) and \( T_n \) are the reduced or normalized quantities. With these substitutions (10) becomes
\[ \ln I = \sum_{n=1}^{4} a_n \frac{p_n^n}{nRT} \]  

where
\[ a_n = \chi_n(T_n) \frac{p_n^n}{T_n} \]  

Maron and Turnbull have shown that the above parametric description fits the \( P, I, T \) data to an accuracy of better than 5%. The coefficients \( a_n \) are listed in Table 3.

Table 2. Equilibrium values of CO fugacity for different oxidation reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( f_{CO} ) expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(g) + 3/2O2(g) = CO2(g)</td>
<td>( f_{CO} = p_{02}^{1/2} \times 2.9 \times 10^{-2} \exp(282.2 \text{ kJ mole}^{-1} \text{ RT}) )</td>
</tr>
<tr>
<td>Cr23C(s) + 3O2(g) = 23Cr(s) + 6CO(g)</td>
<td>( f_{CO} = 8.2 \times 10^{-1} p_{02}^{1/2} \frac{a_{Cr}^{1/2}}{a_{O2}^{3/2}} \exp(58 \text{ kJ mole}^{-1} \text{ RT}) )</td>
</tr>
<tr>
<td>2Cr2C(s) + 3O2(g) = 14Cr(s) + 6CO(g)</td>
<td>( f_{CO} = 8.9 \times 10^{-1} p_{02}^{1/2} \frac{a_{Cr}^{1/2}}{a_{O2}^{3/2}} \exp(62.6 \text{ kJ mole}^{-1} \text{ RT}) )</td>
</tr>
<tr>
<td>Cr2C(s) + O2(g) = 3Cr(s) + 2CO(g)</td>
<td>( f_{CO} = 1.3 \times 10^{-2} p_{02}^{1/2} \frac{a_{Cr}^{1/2}}{a_{O2}^{3/2}} \exp(77.3 \text{ kJ mole}^{-1} \text{ RT}) )</td>
</tr>
<tr>
<td>C(s) + 3/2O2(g) = CO(g)</td>
<td>( f_{CO} = 3.8 \times 10^{-3} p_{02}^{1/2} \exp(111.6 \text{ kJ mole}^{-1} \text{ RT}) )</td>
</tr>
<tr>
<td>4Cr2C6 + 8O2 = 46Cr2O3 + 24CO</td>
<td>( f_{CO} = 3.9 \times 10^{-21} \frac{p_{02}^{1/2} \exp(220.8 \text{ kJ mole}^{-1} \text{ RT})}{a_{Cr2C6}^{1/2} a_{O2}^{3/2}} )</td>
</tr>
</tbody>
</table>

Table 3. Numerical expressions for the coefficients \( a_n \) in equation (13). These numbers are not dimensionless; they have been calculated such that \( R = 0.082054 \text{ liter bar K mole}^{-1} \) and \( p \) and \( T \) are expressed in bars and liters in equations (9)–(13)

\[ a = A_0 + \sum_{n=1}^{4} A_n T^n \]

<table>
<thead>
<tr>
<th>( A_0 )</th>
<th>( A_1 )</th>
<th>( A_2 )</th>
<th>( A_3 )</th>
<th>( A_4 )</th>
<th>( A_5 )</th>
<th>( A_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_1 )</td>
<td>1.0196 x 10^{-2}</td>
<td>-2.1420 x 10^{-2}</td>
<td>0</td>
<td>-3.2548 x 10^{-2}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( a_2 )</td>
<td>0</td>
<td>0</td>
<td>3.6991 x 10^{-3}</td>
<td>0</td>
<td>-4.3022 x 10^{-3}</td>
<td>0</td>
</tr>
<tr>
<td>( a_3 )</td>
<td>0</td>
<td>0</td>
<td>-1.251 x 10^{-4}</td>
<td>0</td>
<td>4.6438 x 10^{-4}</td>
<td>0</td>
</tr>
<tr>
<td>( a_4 )</td>
<td>0</td>
<td>0</td>
<td>1.7019 x 10^{-6}</td>
<td>0</td>
<td>-1.221 x 10^{-6}</td>
<td>0</td>
</tr>
</tbody>
</table>
we obtain the plots shown in Fig. 3 for the fugacity data, according to equation (14). The fit with (14) is quite good when \( p_0 < 75 \), but above that the value of \( I \) given by (14) overestimates the data. By extrapolation, we may assume that the value of \( I \), if calculated from equation (14), will always be \( \geq \) to the actual value. If this value is substituted in equation (8), then we shall obtain the lowest possible value for \( p \).

The universality of equation (14) is checked by calculating \( A \) for CO and CH\(_4\) at different temperatures. These results, on the basis of the straight lines drawn in Fig. 3, are tabulated in Table 4. A mean value of \( A = 8.57 \times 10^{-2} \) is obtained with a maximum deviation of less than 7%.

The equilibrium values for \( p_{CO} \) are obtained by applying equations (14) and (8) to the fugacity curves in Fig. 1. The results for the reactions (R1) and (R5) are shown in Fig. 4. Remember that these are subject to the assumptions discussed in this section. In general we expect that the numbers are quite good as long as \( p_{CO} \) is less than \( 3 \times 10^3 \) bars. When the estimated \( p_{CO} \) is greater, then the real values are likely to be even higher than those derived in Fig. 4. Nevertheless results in Fig. 4 provide some interesting insights. When \( p_{CH_4} = 1 \), the CO pressure will be greater than \( 10^3 \) MPa, a value which is even larger than the stress applied in most stress-rupture tests. The pressure falls sharply when the \( p_{CO} \) drops below \( 10^{-8} \) bars. As a guideline, one can expect that when \( p_{CO} \) is below \( 10^{-10} \) bars, the oxidation reaction would be thermo-chemically limited, while above \( 10^{-8} \) bars the kinetics of the reaction may be more important. Also, for a fixed value of \( p_{CO} \), the environmental attack should be most severe at intermediate temperatures; at high temperatures \( p_{CO} \) becomes small, while at the lower temperatures the kinetics becomes slow. The question of kinetics is discussed in the next section.

4. KINETICS

4.1 The heterogeneous nucleation model

The mechanism of cavity nucleation in creep-fracture remains controversial. Limited observations suggest that cavities do not nucleate below a threshold stress [21], that they increase in number with time [22] and that triple junctions formed by second phase particles and grain boundaries are the preferred sites for nucleation. There is more in the literature.

Table 4. A tabulation of the constant \( A \) in equation (14) based upon thermodynamic data for CO and CH\(_4\).

<table>
<thead>
<tr>
<th>( T ) K</th>
<th>( p ) (range) bars</th>
<th>( p_0 ) (range)</th>
<th>( A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO 673</td>
<td>25-1200</td>
<td>5.02</td>
<td>9.18 \times 10^{-2}</td>
</tr>
<tr>
<td>CO 573</td>
<td>25-1200</td>
<td>4.27</td>
<td>8.46 \times 10^{-2}</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>153</td>
<td>2.53</td>
<td>4.37 \times 10^{-2}</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>573</td>
<td>3.01</td>
<td>8.34 \times 10^{-2}</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>473</td>
<td>2.48</td>
<td>8.35 \times 10^{-2}</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>8.57 \times 10^{-2}</td>
</tr>
</tbody>
</table>
the site of nucleation. Note that \( \tau \) is dimensionless. It has been shown that the smallest values of \( F_i \) should be achieved at junctions of particles and grain boundaries [10], as shown in Fig. 5. \( F_i \) would depend on the dihedral angles \( \alpha, \beta, \) and \( \gamma \) all of which must satisfy equilibrium, while at the same time, the radius of curvature \( r \) is uniform at all surfaces of the boundary. The particle shape and the surface energies will influence \( F_i \), which in certain instances may even become zero (for example in a matrix matrix matrix, triple grain junction \( F_i \) becomes zero if \( \alpha < \pi/3 \)). Also, \( F_i \) may well vary from one particle to another giving rise to a distribution in the values for nucleation time. Experience suggests that nucleation time would be within the realm of measurement at temperatures near \( 0.5 \cdot 10^6 \text{ Torr} \) when \( \tau \) is of the order of \( 10^9 \cdot 10^{10} \text{ atomic volumes} \) [10].

The oxidation reaction can hasten the nucleation time because the critical nucleus size will become smaller according to [20] and because the large CO molecules may accelerate cluster growth by trapping vacancies.

4.2 Diffusion reaction.

Nucleation and growth of cavities by \( CO \) involves several sequential reactions. For example, as shown in the schematic in Fig. 6, dissociation of oxygen to atomic \( O \) at the surface diffusion of \( O \) along the boundary to the carbide precipitates production of \( CO \) by oxidation and clustering of \( CO \) with each other and with other vacancies to form cavities and diffusion of \( CO \) back out to the surface. In principle any one of the above reactions can become rate limiting. Different scenarios and conditions are summarized in Table 5. The reactions are still qualitative because at this point rigorous analysis including diffusion interface reaction kinetics and cluster formation would not lead to further insights. Instead we wish to emphasize the need for more definitive and simple experiments.

Some general statements can be made on the basis of the listing in Table 5. High \( \Omega \) solubility coupled with low \( CO \) solubility in the interface will promote nucleation and vice versa. A small carbide spacing this should be about equal to the distance of the

\[
\tau = \left( \frac{\gamma}{\sigma \cdot \rho \cdot p} \times F_i \right) \Omega_k
\]

where \( \gamma \) is the surface energy, \( \Omega_k \) is the weighted molecular volume and \( F_i \) is a factor which depends on the site of nucleation. Note that \( \tau \) is dimensionless.
carbides from the surface) will also promote nucleation, while presence of trace impurities which inhibit $Q$ diffusion will suppress nucleation. Because CO molecules are large they would induce considerable strain energy which should relieve by having vacancies or other CO molecules next to it. This would give rise to a large binding energy and help nucleation. The O=O bond is quite strong, 4.7 eV and there may be instances where dissociation of $O_2 \rightarrow 2Q$ may become important.

The solubility of Q and CO are likely to be strongly influenced by the hydrostatic component of the applied stress (because the partial molar volume of solution may be large), which means that the stress-state can affect environmental attack. In general a tensile mean stress, as found at notch roots, will promote nucleation.

Theoretically, the highest gas pressures which can be achieved will be those calculated from thermodynamics in the previous section. In practice they may be lower because of the kinetic reasons described above. Another limit on the maximum pressure is the yield strength of the material; if it becomes greater than a critical value then the void will begin to grow plastically. An approximate value for this critical pressure can be obtained by drawing an analogy with a thick ful and systematic experimental work is obvious.

According to the above consideration, the critical pressure then the void will begin to grow plastically. The need for further care will be achieved will be those calculated from thermodynamics in the previous section. The fatigue life first begins to drop when $p_{O_2}$ is low, while $p_{CO}$ becomes large but insensitive to $p_{O_2}$ when $p_{O_2} > 10^{-4}$ (see Fig. 4), because fugacity begins to rise non-linearly with pressure. The need for further careful and systematic experimental work is obvious.

Whereas the thermodynamic criterion may provide a qualitative explanation for environmental attack in

$$p_{\text{max}} = \frac{1}{2}Y \left[ 1 + \ln \left( \frac{Y}{\alpha} \right) \right]$$

The 'burst' pressure can be estimated by setting $\alpha$ equal to (particle spacing) (particle size). Assuming the latter to be about 5, we get that $p_0 \approx 4$.

A good discussion of the kinetics of void growth in the H$_2$ attack (CH$_4$) problem in steels can be found in Ref. [24].

5. SUMMARY

Oxidation of carbides (or carbon) by oxygen transported from the surface via grain boundaries can produce CO at high pressures. This pressure adds to tensile applied stress in promoting nucleation and growth of cavities. Reasonable thermodynamic calculations have been done, which show that the gas pressure can be as large as 1000 MPa when Cr$_2$C$_3$ is oxidized at 1000 K and $p_{O_2} = 1$. At $p_{O_2} = 10^{-8}$, the pressure reduces to about 100 MPa and at $p_{O_2} = 10^{-12}$ to about 1 MPa. From thermodynamic considerations it would appear that environmental effect would begin at about $p_{O_2} > 10^{-10}$ bars. The only data of this type in the literature, by Shahinian et al. [2, 3], is in agreement with this. They found that low cycle fatigue life of Ni at 823 K [2] changes sigmoidally with increasing $p_{O_2}$. The fatigue life first begins to drop when $p_{O_2} > 10^{-9}$ and then saturates when $p_{O_2} > 10^{-4}$. This would also be expected from the thermodynamic calculations: $p_{CO}$ would be much smaller than the applied stress when $p_{O_2}$ is low, while $p_{CO}$ becomes large but insensitive to $p_{O_2}$ when $p_{O_2} > 10^{-4}$ (see Fig. 4), because fugacity begins to rise non-linearly with pressure. The need for further careful and systematic experimental work is obvious.

Whereas the thermodynamic criterion may provide a qualitative explanation for environmental attack in

<table>
<thead>
<tr>
<th>Table 5: Kinetic limitations to cavity nucleation</th>
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<tbody>
<tr>
<td>Condition</td>
</tr>
<tr>
<td>Slow O diffusion</td>
</tr>
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<td></td>
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<tr>
<td></td>
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<tr>
<td>Slow (interface limited) Oxidation reaction</td>
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<td></td>
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<tr>
<td>Fast cluster growth for cavity nucleation</td>
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<tr>
<td></td>
</tr>
<tr>
<td>Slow CO diffusion</td>
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</table>
7. ADDITIONAL REMARKS

Structural nickel base alloys contain a considerable amount of Cr and Al, partly to enhance creep resistance but also to provide a protective oxide on the surface against corrosion. A tenacious oxide layer would reduce the oxygen activity at the oxide-metal interface to a near equilibrium level, for example, about \(10^{-20}\) to \(10^{-21}\) at 1000 to 1300 K assuming a CrCrO\(_3\) interface. Such low \(p_0\), would preclude the cavitation mechanism discussed so far. Why then are structural alloys environment sensitive? The question can be answered in several ways.

Perhaps the most important reason is that deformation can break the surface layer permitting subsurface diffusion of oxygen. Grain boundary sliding can produce offsets at the surface. Propagation of creep cracks, or crack-tip sharpening in fatigue loading, can continually expose fresh metal surface. Circumstantial support for this idea comes from the experience [26] that often notch sensitivity and environmental sensitivity of alloys goes hand in hand. Also alloys which show stress-rupture strengthening in oxygen with smooth tensile specimens, may exhibit oxygen attack if notched specimens are used. Presumably localized slip at notch root breaks the oxide scale. Experience also suggests [26] that nickel-base alloys which have excellent resistance to simple corrosion, can be quite susceptible to stress corrosion cracking at elevated temperature.

In addition to the internal gas production, internal oxidation of impurities or carbides, which produces new oxide precipitates or an oxide shell on existing precipitates can also promote cavity nucleation. The reason is that, nearly always, oxide dispersion alloys have poor resistance to cavitation. Apparently, at least in alloys of Cu and Ni, oxide precipitates are poorly adhered to the metal. Internal oxidation of impurities in the boundaries could occur at fairly low activities of oxygen, although, again, if a very stable oxide such as Al\(_2\)O\(_3\) or Cr\(_2\)O\(_3\) forms on the surface then some mechanism must be available for penetrating the oxide layer.

There are two other interesting observations in this context. Oxide dispersion strengthened Ni alloys (Ni-Cr-ThO\(_3\)), with equiaxed grain structure are known to be much less environment or notch sensitive than the precipitation strengthened alloys: presumably these are already prone to cavitation because they contain oxide particles so that oxygen attack can do no further harm. The second observation is that whenever environmental attack is severe, the addition of trace B and Zr has a dramatic beneficial effect. In Ni-C alloys this effect has been correlated to the obstruction of \(Q\) diffusion in the presence of B. But it is not possible that the same mechanism operates in the structural alloys too? I am also led to think that the beneficial effect of B in austenitic stainless steels which contain some carbon, may also be of a similar kind.

Finally the kinetics of oxidation of metal surfaces is a complex process even in simple cases [27, 28]. Our current understanding of the oxidation of a binary alloy such as Ni-Cr is so inadequate that we cannot even begin to make judgments about the oxidation kinetics of multi-component engineering alloys [29]. For example, a Cr\(_2\)O\(_3\) layer on chromium may be tenacious but in a Ni-Cr alloy the oxide scale can contain two or more layers of different compositions (because of kinetic considerations [27]) and therefore, it may be more susceptible to cracking due to lattice mismatch, thermal stresses and deformation.

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