University of Groningen

Investigation of hydrogen attack in 2.25Cr-1Mo steels with a high-triaxiality void growth model

van der Burg, M.W.D.; van der Giessen, E.; Brouwer, R.C.

Published in:
Acta Materialia

DOI:
[10.1016/1359-6454\(95\)00203-0](https://doi.org/10.1016/1359-6454(95)00203-0)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1996

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

van der Burg, M. W. D., van der Giessen, E., & Brouwer, R. C. (1996). Investigation of hydrogen attack in 2.25Cr-1Mo steels with a high-triaxiality void growth model. *Acta Materialia*, 44(2), 505 - 518.
[https://doi.org/10.1016/1359-6454\(95\)00203-0](https://doi.org/10.1016/1359-6454(95)00203-0)

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

INVESTIGATION OF HYDROGEN ATTACK IN 2.25Cr–1Mo STEELS WITH A HIGH-TRIAXIALITY VOID GROWTH MODEL

M. W. D. VAN DER BURG¹, E. VAN DER GIESSEN^{1†} and R. C. BROUWER²

¹Delft University of Technology, Laboratory for Engineering Mechanics, P.O. Box 5033, 2600 GA Delft and ²Shell Internationale Petroleum Maatschappij, P.O. Box 162, 2501 AN, The Hague, The Netherlands

(Received 9 February 1995; in revised form 20 April 1995)

Abstract—A model is presented to estimate the lifetime under hydrogen attack (HA) conditions. The first ingredient is the Odette–Vagarali model to calculate the equilibrium methane pressure as a function of hydrogen pressure, temperature, and type and composition of the carbides and the alloy. The second ingredient is a model for the growth to coalescence of methane-filled grain boundary cavities, possibly under the presence of (applied or residual) macroscopic stresses. This model is based on recent detailed numerical studies of the growth of voids under simultaneous grain boundary diffusion and creep of the grain material. A new, accurate analytical approximate void growth relation valid for high stress triaxialities is adapted for application to HA. The model is used to perform a study of HA, including a computation of Nelson curves, in 2.25Cr–1Mo steels with different types of carbides and for various applied stress states. Finally, the results of the model are presented in a concise, non-dimensional form that reveals the key parameters that determine HA life times.

1. INTRODUCTION

At high temperatures, pressure vessel steels such as 2.25Cr–1Mo exposed to hydrogen can be damaged by hydrogen attack (HA). Hydrogen diffuses into the steel where it reacts with the carbides. In the reaction, methane gas is formed which cannot diffuse through the material. Depending on temperature, hydrogen pressure and carbide stability, a high methane pressure can be formed and voids start to grow from the degrading carbides. Void growth takes place preferentially on grain boundaries, and is enhanced by macroscopic stresses due to e.g. the applied loading or residual stresses. Once the voids have grown so large that they coalesce, intergranular microcracks are formed. These microcracks degrade the material properties and may result in failure of the pressure vessel wall.

For carbon, Mo and Cr–Mo pressure vessel steels, safe operating temperatures and safe hydrogen pressures in order to avoid HA are given by the so-called Nelson curves [1]. The curves, which form the boundary between the temperature–hydrogen pressure region where failures have occurred and the region where safe operation is assumed, are empirical curves based on past service experience. The attractiveness of the Nelson curves—their simplicity and generality—is at the same time an important weakness. This is demonstrated for instance in case of the 0.5Mo

steels: after more than 20 years of service experience with the 0.5Mo steels, the Nelson line for the 0.5Mo steels had to be lowered to the curve of carbon steel due to failures in the temperature and pressure regime below the original 0.5Mo line. However, at the same time there is a vast amount of 0.5Mo equipment in service, which has been functioning satisfactorily over many years at temperatures and hydrogen pressures above the carbon steel line in the Nelson diagram. Due to the generality of the Nelson diagrams no distinction can be made between 0.5Mo steels that are apparently resistant and those that are susceptible to HA. Furthermore, Nelson curves are of limited use when new steel, such as modified 2.25Cr–1Mo, 2.25Cr–1Mo–V or 3Cr–1Mo–V, are introduced. Since there are no Nelson curves available for these steels, only accelerated short term exposure can be used to determine if the steels will be resistant to HA. At this moment, no proven techniques or models exist to extrapolate the short term test results to normal operating times and conditions. Also Nelson curves cannot be used in a “fitness for purpose” analysis of a steel that does exhibit HA damage. A better understanding of HA and more sophisticated models or assessment techniques are therefore needed for this purpose.

In order to develop a more fundamental understanding of HA and to be able to predict the limiting operating conditions of pressure vessel steels, several attempts have been made in the past to develop HA models. The basis of HA models has been the development, through the years, of several void growth

†To whom all correspondence should be addressed.

models based on diffusional and creep mechanisms. In their study [2] of HA, Shih and Johnson modeled void growth to be caused by two independent sources: growth by creep and growth by grain boundary diffusion. For the latter they adopted the model developed by Hull and Rimmer [3]. The possibility of synergistic effects due to the interaction between creep deformation and diffusional flow were not considered. Furthermore, their analysis essentially applied only to situations where the macroscopic stresses are negligible compared to the internal cavity pressure, so that the possible interaction with macroscopic creep deformations is also ignored. Parthasarathy [4] extended the void growth model of [2] by accounting also for surface diffusion; but, he too neglected the possible influence of macroscopic stresses. Shewmon [5] seems to have been the first to incorporate the interaction between HA and macroscopic stress. His void growth estimate is based on coupling grain boundary diffusive growth [3] to creep of the background material.

A few years before Shewmon's work [5], Needleman and Rice [6] had performed a very detailed study of cavity growth due to creep flow and diffusion along the grain boundary. Aiming at applications in the field of creep rupture, they assumed that void growth was driven by the (macroscopic) stresses remote from the void, which itself was not pressurized. By actually solving the coupled creep-diffusion problem, Needleman and Rice [6] demonstrated the possible interaction between creep and diffusive void growth which appears as a reduction of the actual diffusive path length due to local deformations. Sham and Needleman [7] extended this study into the range of higher triaxialities of the remote stress state, typical for creep crack growth conditions. They also managed to capture their numerical (finite element) results by an analytical expression for the void growth rate. These two works constitute the most accurate modelling of the problem until today. However, the results cannot directly be applied to HA conditions as the high internal methane pressure implies a much higher stress triaxiality than considered in [6] and [7] (as will be pointed out later in this paper, internal cavity pressure only would correspond to an infinite stress triaxiality). Therefore, Van der Giessen *et al.* [8] extended the work in [6] and [7] to essentially all stress triaxialities. They also proposed an extension of the analytical approximations to the computed growth rates that covers the entire stress triaxiality regime, and showed that these relations give a fairly accurate representation of the numerical results.

These relations proposed in [8] will be used in this paper to model void growth under HA conditions. However, they are expressed in terms of stresses remote from the (stress-free) cavity, whereas in HA situations the methane pressure acts on the cavity surface. In the next section we shall discuss how the necessary modification is carried through by way of a superposition argument.

The internal methane pressure in the cavities, being the primary driving force for void growth, is an important parameter in any HA cavity growth model. The methane pressure is controlled by the temperature, the hydrogen pressure and the stability of the carbides. The stability of the carbides is determined by the crystal structure of the carbide, the carbide composition and the alloy composition of the pressure vessel steel itself. Also, due to the high pressures (up to 10^3 MPa), the non-ideality of the methane gas has to be taken into account. All these effects have been incorporated in the present calculations, based on existing thermodynamic equations from [9] and [10].

In the subsequent section, the void growth model modified for HA will be used to predict the Nelson curves of a 2.25Cr-1Mo steel. The calculations will be carried out for three different types of carbides that may be present in the steel. The influence of macroscopic stresses caused by applied loads will be investigated. Finally, the results of the model will be presented in a dimensionless way. This singles out the controlling nondimensional groups of parameters in the model and casts the information in the most general form.

2. MODEL

At high temperatures and high hydrogen pressures, hydrogen molecules dissociate into hydrogen atoms and are absorbed to the steel surface. A number of the absorbed atoms form hydrogen molecules again and the molecules escape in the surrounding atmosphere. Other absorbed hydrogen atoms are absorbed into the steel. The hydrogen atoms readily diffuse over the interstitial sites (tetrahedral sites in case of ferritic steels, octahedral sites in austenitic steels) through the steel. At large discontinuities in the steel matrix, such as carbides, grain boundaries, or inclusions, hydrogen atoms can associate again and form hydrogen molecules. At high temperatures and hydrogen pressures, hydrogen gas can react with the carbides in the matrix, and methane gas is formed by the following chemical reaction:

with x the number of metal atoms (M) and y the number of carbon atoms (C) in the carbide. This reaction takes place preferentially at the least stable carbides. The methane molecules are much larger than the hydrogen atoms and cannot diffuse through the steel. Thus, a methane pressure builds up, determined by the equilibrium reaction above.

The equilibrium reaction consists of two consecutive reactions, i.e. carbide dissolution and formation of methane gas. The equilibrium constant of the total reaction can be expressed in terms of the Gibbs free energy of the carbides [11], the Gibbs energy of formation for methane gas, as well as in

terms of the activities of all the reacting atoms and molecules [9]. By equating these two expressions the methane fugacity can be calculated. However, due to high pressures inside the voids, the methane behaves as a non-ideal gas and therefore the methane fugacity is not simply equal to the methane pressure. The methane pressure can be calculated by using the simplified solutions of Odette and Vagarali [10], which are based on the equation-of-state for methane gas given by McQuarrie and Katz [12]. Appendix A summarizes the basic relations used in determining the methane equilibrium pressure p_{CH_4} . In the calculation of the methane pressure, time dependent effects during cavity growth are neglected. The rate of supply of carbon (from the carbides) and hydrogen (from the surrounding metal) is neglected in the model. The methane pressure p_{CH_4} is assumed to be always in equilibrium with the hydrogen pressure p_{H_2} and the carbides present in the steel. Also, the assumption has been made that only the carbides react with the hydrogen gas, whilst it may be possible that dissolved carbon in the steel react directly with the hydrogen (see, e.g. [2]).

The reaction of dissolved hydrogen with the carbides on a grain boundary leads to a grain boundary cavity containing a methane-hydrogen mixture at a relatively high pressure, determined by the partial pressures p_{CH_4} and p_{H_2} , respectively. The total pressure in this non-ideal mixture, p_m is approximately given by

$$p_m = p_{\text{CH}_4} + p_{\text{H}_2}. \quad (1)$$

In most works, e.g. [2, 4, 5], the hydrogen pressure has been neglected, since in many practical conditions it was assumed to be negligible compared to the methane pressure. As we will see later on, this is true for relatively less stable carbides, but not necessarily so for the more stable carbides. Hence, we shall use the total gas pressure according to equation (1) as the internal pressure in the cavity.

The carbides along the grain boundary are assumed to be identical and to be uniformly distributed, so that all cavities on the facet develop equally. It is assumed that all cavities are nucleated at the same instant, and that no new cavities nucleate afterwards. Let a be the cavity radius, $2b$ the spacing between two cavities, and ψ the tip angle of the spherical-caps

Fig. 1. Spherical cap-shaped cavities on a grain boundary facet.

shaped cavity (see Fig. 1). Then, the volume of a single cavity can be written as

$$V = \frac{4}{3}\pi a^3 h(\psi), \quad (2)$$

where $h(\psi)$ is the cavity shape parameter defined by

$$h(\psi) = [(1 + \cos \psi)^{-1} - \frac{1}{2} \cos \psi] / \sin \psi.$$

As discussed in detail by Chung *et al.* [13], the cavity tip angle ψ is determined by the surface free energy of the cavity relative to the corresponding energy of the grain boundary. To study the growth of these grain boundary cavities, it is appropriate to confine attention to a unit cell consisting of a cylinder with radius b containing a single cavity with radius a . The length of the cylinder is of the order of the grain size, and is assumed to be much larger than its radius b . A local coordinate system is introduced for each grain boundary facet with the x_1 -axis normal to the facet.

At temperatures typical for HA, the cavities grow by grain boundary diffusion (along with surface diffusion) and by creep of the adjacent grain material (elastic deformations are neglected in this analysis). For determining the growth rate of a single void, we adopt the results of detailed studies by Sham and Needleman [7] and, more in particular, by Van der Giessen *et al.* [8]. They have used numerical methods to investigate the growth by simultaneous creep and diffusion of a traction-free void in a long cylindrical unit cell subject to remote axisymmetric states of stress. It turns out that the accurate numerical results for the volumetric growth rate of a void can be approximated well by coupling relatively simple relationships for growth by creep and by diffusion. Thus, the total volumetric growth rate $\dot{V}$ is split up into a volumetric growth rate due to creep flow in the adjacent grains, $\dot{V}_{\text{cr}}$, and a contribution resulting from the diffusion of matter along the cavity surface into the grain boundary, $\dot{V}_{\text{diff}}$:

$$\dot{V} = \dot{V}_{\text{cr}} + \dot{V}_{\text{diff}}.$$

In order to be able to apply these relationships to HA, we need to account for two differences with the problem considered in [8]. First, we have to account for the internal gas pressure in the void. Second, we have to make a modification in order to account for the possible presence of surface tension effects, as being distinctly different from the surface energy effects that were already considered in [8]. We shall first briefly discuss how these aspects can be incorporated in the two distinct growth rate contributions separately, before discussing how the resulting contributions determine the actual total void growth rate.

In HA situations, the cavity contains methane-hydrogen gas under a hydrostatic pressure p_m and is also subjected to a remote stress state. The latter is assumed here to be axisymmetric and characterized by a remote stress S normal to the grain boundary facet and a remote transverse stress T in the plane of

Fig. 2. (a) Schematic of the stress situation for a unit cell containing a single cavity under HA conditions; (b) hydrostatic stress state that is superimposed on the stress state in (a); (c) the resulting stress state for the cavity with a stress-free surface.

the facet, as shown in Fig. 2(a). To apply the Van der Giessen *et al.* [8] relation for the growth rate due to creep on the present HA problem, we have to express the stress situation around the cavity surface, including the internal gas pressure along with the sintering stress, to the remote stress situation considered in [8]. The procedure to do so (see Fig. 2) makes use of the incompressibility of the grain material. The surface tension (i.e. surface stress) T_s is equivalent to a hydrostatic tension on the surface of $2T_s \sin \psi / a$. By superimposing a hydrostatic stress of $p = p_m - 2T_s \sin \psi / a$, so that the traction on the cavity surface vanishes, we obtain a remote stress situation that is characterized by remote (axisymmetric) stresses

$$\begin{aligned}\sigma_{11}^{\infty} &= S + p_m - 2T_s \sin \psi / a, \\ \sigma_{22}^{\infty} &= \sigma_{33}^{\infty} = T + p_m - 2T_s \sin \psi / a.\end{aligned}$$

Note that all other components of the remote stress tensor σ_{ij}^{∞} with respect to the local grain boundary base vectors are zero, $\sigma_{12}^{\infty} = \sigma_{13}^{\infty} = \sigma_{23}^{\infty} = 0$. Also note that these stresses remote from the cavity should be clearly distinguished from the actual local (highly nonuniform) stress distribution in the vicinity of the cavity. The remote mean stress σ_m^{∞} , defined by $\sigma_m^{\infty} = \sigma_{kk}^{\infty} / 3$ (summation over repeated indices implied), is

$$\sigma_m^{\infty} = \frac{1}{3}(S + 2T) + p_m - 2\frac{T_s}{a} \sin \psi, \quad (3)$$

and the remote effective stress $\sigma_e^{\infty} = \sqrt{3s_{ij}s_{ij}/2}$, in terms of the deviatoric stress components $s_{ij} = \sigma_{ij} - \sigma_{kk}\delta_{ij}/3$, is

$$\sigma_e^{\infty} = |\sigma_{11}^{\infty} - \sigma_{22}^{\infty}| = |S - T|. \quad (4)$$

Assuming the grains to deform by ideal or secondary creep according to the Norton power-law with creep exponent n , the creep strain-rates $\dot{\epsilon}_{ij}^{\infty}$ and the effective creep rate $\dot{\epsilon}_e^{\infty}$ due to these remote stresses are given by

$$\dot{\epsilon}_{ij}^{\infty} = \dot{\epsilon}_e^{\infty} \frac{3}{2} \frac{s_{ij}}{\sigma_e^{\infty}}, \quad \dot{\epsilon}_e^{\infty} = \dot{\epsilon}(\Theta) \left(\frac{\sigma_e^{\infty}}{\sigma_0} \right)^n. \quad (5)$$

Here, σ_0 is a reference stress parameter, and $\dot{\epsilon}(\Theta)$ is a temperature dependent reference strain-rate parameter.

Now the volumetric growth rate relations for creep proposed in [8] expressed in σ_e^{∞} , σ_m^{∞} and $\text{sign}(S - T)$, can be used for creep in HA situations. When the stress triaxiality $|\sigma_m^{\infty} / \sigma_e^{\infty}|$ is relatively low, or when the porosity level a/b is relatively small, the volumetric growth rate of the cavity due to creep flow, $\dot{V}_{cr}^L$, can be approximated well by

$$\begin{aligned}\dot{V}_{cr}^L &= 2\pi\dot{\epsilon}_m a^3 h(\psi) \text{sign}(\sigma_m^{\infty}) \\ &\times \left[\alpha_n + \beta_n \left| \frac{\sigma_e^{\infty}}{\sigma_m^{\infty}} \right|^n \right] \quad \text{if } |\sigma_m^{\infty} / \sigma_e^{\infty}| \geq 1; \quad (6)\end{aligned}$$

$$\begin{aligned}\dot{V}_{cr}^L &= 2\pi\dot{\epsilon}_m a^3 h(\psi) \text{sign}(\sigma_m^{\infty}) \\ &\times [\alpha_n + \beta_n]^n \left| \frac{\sigma_e^{\infty}}{\sigma_m^{\infty}} \right|^{n-1} \quad \text{if } |\sigma_m^{\infty} / \sigma_e^{\infty}| < 1, \quad (7)\end{aligned}$$

where $\dot{\epsilon}_m$ is a short hand notation introduced by

$$\dot{\epsilon}_m = \dot{\epsilon}(\Theta) \left| \frac{\sigma_m^{\infty}}{\sigma_0} \right|^n \quad (8)$$

("sign" denotes the sign of its argument). The constants α_n and β_n in (6) and (7) are defined by $\alpha_n = 3/(2n)$ and $\beta_n = (n-1)(n+0.4319)/n^2$. When $T > S$ and $\sigma_m^{\infty} > 0$, or $T < S$ and $\sigma_m^{\infty} < 0$, then β_n should be taken as $\beta_n = (n-1)(n+0.4031)/n^2$. However in the calculations we only used the first expression for β_n , which involves only a minor error. The relation (6), first derived by Budiansky *et al.* [14], is based on a cavity in an infinitely large creeping matrix, while (7) is an extension proposed by Tvergaard [15]. Elimination of $\dot{\epsilon}_m$ in favor of $\dot{\epsilon}_e^{\infty}$ ($\sigma_e^{\infty} \neq 0$) reveals that (7) is a linearization in $\sigma_m^{\infty} / \sigma_e^{\infty}$ of the normalized growth rate $\dot{V}_{cr}^L / \dot{\epsilon}_e^{\infty}$ according to (6) so that continuity in volumetric growth rates is assured. The normalization by $\dot{\epsilon}_m$ instead of by $\dot{\epsilon}_e^{\infty}$ ensures that the relationships (6) and (7) remain to be valid even if $\sigma_e^{\infty} = 0$ in case of remote hydrostatic tension (for instance, when $S = T = 0$ and $p_{CH_4} \neq 0$).

Van der Giessen *et al.* [8] have demonstrated that this void growth mode is changed rather abruptly at increasing stress triaxiality or increasing porosity a/b to another creep deformation mode. In that case, the volumetric growth rate due to creep $\dot{V}_{cr}^H$ is found to be approximated well by

$$\begin{aligned} \dot{V}_{cr}^H &= 2\pi\dot{\epsilon}_m a^3 h(\psi) \text{sign}(\sigma_m^\infty) \left[\frac{1}{1 - (0.87a/b)^{3/n}} \right. \\ &\times \left(\alpha_n + \frac{1}{n} \frac{\text{sign}(S - T)}{\text{sign}(\sigma_m^\infty)} \left| \frac{\sigma_e^\infty}{\sigma_m^\infty} \right| \right)^n \Bigg] \quad \text{if } |\sigma_m^\infty / \sigma_e^\infty| \geq 1; \quad (9) \\ \dot{V}_{cr}^H &= 2\pi\dot{\epsilon}_m a^3 h(\psi) \text{sign}(\sigma_m^\infty) \left[\frac{1}{1 - (0.87a/b)^{3/n}} \right. \\ &\times \left(\alpha_n + \frac{1}{n} \frac{\text{sign}(S - T)}{\text{sign}(\sigma_m^\infty)} \right)^n \left| \frac{\sigma_e^\infty}{\sigma_m^\infty} \right|^{n-1} \Bigg] \\ &\quad \text{if } |\sigma_m^\infty / \sigma_e^\infty| < 1. \quad (10) \end{aligned}$$

The derivation of (9) and (10) is described in [8], with, again, the solution for lower stress triaxialities (10) being a linearization of (9) in terms of $\sigma_m^\infty / \sigma_e^\infty$. Note that although the derivation in [8] was confined to stress states with $S > T$, the expressions (6)–(10) are now also properly formulated for $S < T$ using the symmetry properties outlined in [8].

The cavity grows not only by creep flow but also by diffusion of matter from the cavity surface into the grain boundary. This process was first modelled by Hull and Rimmer [3] based on the assumption that the grain material is rigid. To use the according volumetric growth rate relation in our HA situation, the diffusive driving stress has to be modified to account for the internal pressure p_m , the free surface energy γ_s and the surface tension T_s . An early adaptation of the Hull–Rimmer model to internal void pressure is due to Raj *et al.* [16], and has been used subsequently in [2]. Needleman and Rice [6] pointed out however that the void growth rate expression in [16] contained an incorrect factor $1 - f$. Furthermore, Raj *et al.* [16] assumed $\gamma_s = T_s$, while Herring [17] had indicated that, although this is true for fluids, surface free energy γ_s and surface tension T_s need not be the same for solids. In fact γ_s is always positive, whereas T_s may have either sign. Therefore, in the main body of [16] and subsequent works (e.g. [7, 15]) T_s has been put to zero. Needleman and Rice [6] briefly discuss the case with different values of γ_s and T_s , and when that result is modified for the presence of internal void pressure p_m according to (1), one obtains (see Appendix B) that the volumetric growth rate due to diffusion $\dot{V}_{diff}$ is given as

$$\begin{aligned} \dot{V}_{diff} &= 4\pi\mathcal{D}(\Theta) \\ &\times \frac{S + p_m - (1 - f)2\gamma_s \sin \psi / a - f2T_s \sin \psi / a}{\ln(1/f) - \frac{1}{2}(3 - f)(1 - f)}. \quad (11) \end{aligned}$$

Here, the grain boundary diffusion parameter is defined by $\mathcal{D}(\Theta) = D_B \delta_B \Omega / k\Theta$, where $D_B \delta_B$ is the boundary diffusivity, Ω is the atomic volume, and $k\Theta$ the energy per atom measure. The parameter f in (11) is determined by

$$f = \left(\frac{a}{L_{diff}} \right)^2, \quad (12)$$

where L_{diff} is the diffusion path length. For the rigid grain assumption, the diffusion path length is effectively equal to the cavity half-spacing b , so that

$f = (a/b)^2$ as in the Hull–Rimmer model [3]. However, if creep cannot be neglected, interaction between diffusion and creep occurs. As pointed out by Needleman and Rice [6], this results in a path length for diffusion that is significantly shortened, as creep locally accommodates the diffusional flow of matter in the vicinity of the cavity. This interaction then results in an increase of the volumetric growth rate. The two creep deformation modes mentioned above, involving growth rates $\dot{V}_{cr}^L$ and $\dot{V}_{cr}^H$, respectively, will give different interactions with diffusive void growth, leading to two diffusive growth rates $\dot{V}_{diff}^L$ and $\dot{V}_{diff}^H$, respectively. The numerical studies in [8] have shown that the interaction between creep flow and diffusion during cavity growth only leads to a significant effect on the volumetric growth rate in case of the deformation mode associated with the creep relation $\dot{V}_{cr}^L$ in (6) or (7). As shown already by Sham and Needleman [7], the associated volumetric growth rate $\dot{V}_{diff}^L$ is approximated well by taking the diffusion path length to be the minimum of $a + 1.5L$ or b , where L is the parameter

$$L = (\mathcal{D}\sigma_e^\infty / \dot{\epsilon}_e^\infty)^{1/3} \quad (\sigma_e^\infty \neq 0), \quad (13)$$

introduced by Needleman and Rice [6]. For the second creep mode, the interaction between diffusion and creep also exists, but the regime of interaction has been found to be relatively small. Van der Giessen *et al.* [8] demonstrate that by keeping the diffusion length equal to b , thereby neglecting this interaction all together, the subsequent error on the cavity growth rate $\dot{V}_{diff}^H$ remains negligible. Thus,

$$\begin{aligned} \dot{V}_{diff}^L &= \dot{V}_{diff}(f), \quad f = \max \left[\left(\frac{a}{b} \right)^2, \left(\frac{a}{a + 1.5L} \right)^2 \right]; \\ \dot{V}_{diff}^H &= \dot{V}_{diff}(f), \quad f = \left(\frac{a}{b} \right)^2. \end{aligned}$$

With reference to (11), note that both the surface free energy γ_s and a positive surface tension T_s tend to sinter-close the cavity. Only if $S + p_m$ exceeds the sintering stress σ_s , defined as

$$\sigma_s = (1 - f)2\gamma_s \sin \psi / a + f2T_s \sin \psi / a, \quad (14)$$

is the diffusive growth rate positive. Also note that the surface tension effects enter creep growth through σ_m^∞ according to (3).

Finally, as shown by Van der Giessen *et al.* [8], the total volumetric growth rate of the cavity can be obtained as

$$\dot{V} = \max[|\dot{V}_{cr}^L|, |\dot{V}_{diff}^L|, |\dot{V}_{cr}^H|, |\dot{V}_{diff}^H|]. \quad (15)$$

Surface diffusion along the void surface will also occur, and this process is assumed to be so rapid compared to the other mechanisms of matter transport that the spherical-caps shape of the cavity is maintained at all times. Experimental observations [18, 19] of the cavity morphology for the material to be studied later on supports this assumption. Based

on the above volumetric growth rate relations, we can follow the evolution of the cavity size in time by integration of

$$\dot{a} = \dot{V}/[4\pi a^2 h(\psi)],$$

with $\dot{V}$ according to (15), starting from the initial cavity radius a_1 .

The average creep strain-rate $\dot{\epsilon}_\perp$ in the plane of the grain boundary causes a change of the spacing $2b$ between cavities given by $b = b\dot{\epsilon}_\perp$. Because of axisymmetry and incompressibility, the in-plane strain-rate is determined by $\dot{\epsilon}_\perp = \dot{\epsilon}_{22}^\infty = \dot{\epsilon}_{33}^\infty = -\frac{1}{2}\dot{\epsilon}_{11}^\infty$ with the remote normal creep strain-rate $\dot{\epsilon}_{11}^\infty = \text{sign}(S - T)\dot{\epsilon}_e^\infty$ according to (5).

The cavities grow until coalescence occurs by failure of the ligament between cavities. In this study, coalescence is assumed to occur at $a/b = 0.9$; but, it is noted that the time to coalescence is not affected much by the precise critical value for coalescence. As cavitation is assumed to be uniform along a grain facet, cavity coalescence occurs at the same time everywhere along the facet, thus leading to instantaneous formation of a full-facet microcrack. Furthermore, following [2, 4, 5], we shall assume that the time to cavity coalescence is effectively used as an estimate of the ultimate time to failure.

The rate of cavity growth is strongly determined by temperature because of the strong temperature dependence of (i) the formation of methane and therefore the methane pressure (see Appendix A) and (ii) of the creep and grain boundary diffusion processes. This latter dependence is incorporated through the temperature dependence of the reference creep strain-rate parameter $\dot{\epsilon}(\theta)$ in (5) and of the diffusion parameter $\mathcal{D}(\theta)$ in (11). They are written here in the form

$$\dot{\epsilon}(\theta) = \dot{\epsilon}_0 \frac{\theta_0}{\theta} \exp\left[\frac{Q_V}{R} \left(\frac{1}{\theta_0} - \frac{1}{\theta}\right)\right], \quad (16)$$

$$\mathcal{D}(\theta) = \mathcal{D}_0 \frac{\theta_0}{\theta} \exp\left[\frac{Q_B}{R} \left(\frac{1}{\theta_0} - \frac{1}{\theta}\right)\right]. \quad (17)$$

Here, $\dot{\epsilon}_0$ and $\mathcal{D}_0$ are the values of the reference creep strain-rate parameter and the boundary diffusion parameter, respectively, at the reference temperature θ_0 , Q_V and Q_B are the respective activation energies, and R is the gas constant. Following Needleman and Rice [6] and Frost and Ashby [20], the reference creep strain-rate parameter $\dot{\epsilon}_0$ and the boundary diffusion parameter $\mathcal{D}_0$ are taken to be given by

$$\dot{\epsilon}_0 = A \frac{D_{V0} \mu b}{k \theta_0} \left(\frac{\sigma_0}{\mu}\right)^n \exp\left[\frac{-Q_V}{R \theta_0}\right],$$

$$\mathcal{D}_0 = \frac{D_{B0} \delta_B \Omega}{k \theta_0} \exp\left[\frac{-Q_B}{R \theta_0}\right],$$

where A is a creep constant, subscript V refers to volume (or lattice) diffusion, subscript B refers to boundary diffusion, μ is the elastic shear modulus,

b is the length of the Burger's vector and k is Boltzmann's constant.

There are a number of essential differences between the present model and earlier investigations as in Refs [2], [4] and [5]. The main differences are in the void growth model. In the models of Shih and Johnson [2] and Parthasarathy [4], the contribution to cavity growth due to creep is based on the analysis (see, e.g. [21]) of a thick-walled sphere under internal pressure, while the interaction between creep void growth and diffusive void growth is neglected all together. The influence of remotely applied stresses is not taken into account. Shewmon's [5] model, on the other hand, does account for the effect of remote applied stresses. The diffusive contribution to void growth in his model is also based on the Hull-Rimmer [3] model as here, and for the additional contribution by creep he follows a more simple approximate approach by Edwards and Ashby [22]. The numerical model recently used by Van der Giessen *et al.* [8] has provided much more detailed insight in void growth under high triaxialities, and the void growth relations (6)–(15) based on [8] are significantly more accurate than those in [5]. It should be noted that Parthasarathy [4] actually takes into account the contribution of surface diffusion to cavity growth, based on considerations by Chuang *et al.* [13] for cavity growth controlled by surface diffusion. However it is reported in [4] that grain boundary diffusion, as considered in our model, rather than surface diffusion is the controlling mechanism for diffusive void growth in 2.25Cr-1Mo steels.

3. RESULTS FOR 2.25Cr-1Mo STEELS

The model will be applied to investigate HA of 2.25Cr-1Mo steels under different loading conditions. We have taken the following material parameters. The initial half-spacing b_1 between cavities is taken equal to the average half-spacing between carbides mentioned in [4], $b_1 = 8 \times 10^{-6}$ m. The initial cavity radius is taken to be $a_1 = 0.05 \times 10^{-6}$ m in most computations, just as in [4]. The equilibrium cavity tip angle ψ is taken as $\psi = 78.5^\circ$ (cf. [13]). The surface energy is estimated by Parthasarathy and Shewmon [9] as $\gamma_s = 1$ J/m². As mentioned above, the value of the surface tension T_s at grain boundary cavities is largely unknown. In order to get an indication of the effect of surface tension, we shall either take the same value as the surface energy (cf. [16]), i.e. $T_s = 1$ J/m², or neglect it, $T_s = 0$, as in [6]. The diffusion parameters are taken from Parthasarathy [4], where the grain boundary diffusion coefficient is given as $\mathcal{D}_0 = 1.7 \times 10^{-35}$ m⁵/Ns at $\theta = 725$ K, and the corresponding activation energy is $Q_B = 206 \times 10^3$ J/mol. The creep parameters are taken from Kleuh [23]: $n = 6.5$ and $\dot{\epsilon}_0 = 3.8 \times 10^{-60}$ s⁻¹ at $\theta = 727$ K when the reference stress is taken as $\sigma_0 = 1$ N/m². For the corresponding activation energy for creep we have used $Q_V = 251 \times 10^3$ J/mol from [20]. It is emphasized

that accurate values of most of these parameters are difficult to obtain; the above-mentioned values serve merely as representative values.

Literature from various sources (e.g. [24]–[33]) shows that 2.25Cr-1Mo steels, depending on the composition and the thermal history of the steel, can contain the following five carbide types (in order of increasing stability): M_3C , M_2C , M_7C_3 , $M_{23}C_6$ and M_6C . The absolute stability of the carbides formed, depends not only on the crystallographic structure, but also on the alloy content of the carbides themselves. The carbide stability increases with increasing Cr, Mo and V content. In the present study, void growth calculations are carried out for M_3C , M_7C_3 and $M_{23}C_6$. The presence of the M_6C carbides is neglected as these carbides do not play a role in the HA of the steel due to their stability. The reaction of hydrogen with the small M_2C carbides has not been modelled as no information was readily available on the thermodynamic properties of these carbides.

The cited literature shows that, as an indication, the different carbides in a 2.25Cr-1Mo pressure vessel steel have carbide compositions as stated in Table 1. In calculating the carbide stability, both the Cr content and the Mo content in the carbide has to be taken into consideration. However, thermodynamic data on carbides containing Mo were not available, and therefore the influence of Mo on the carbide stability has been neglected in the calculations. The thermodynamic data used in the calculations have been taken from Lundberg *et al.* [11] and Parthasarathy and Shewmon [9].

As mentioned before, temperature effects are crucial for HA. On the one hand, creep and diffusion processes are strongly enhanced by increasing temperature [cf. (16) and (17)]. However, on the other hand, it should be noted that when the temperature increases, the methane pressure p_{CH_4} decreases for thermodynamic reasons. This is illustrated in Fig. 3 where isopressure lines of p_{CH_4} are shown as a function of temperature Θ , ranging from $\Theta = 550$ to 800 K, and hydrogen pressure p_{H_2} , ranging from $p_{H_2} = 1$ MPa to $p_{H_2} = 20$ MPa. The generated methane pressures differ significantly among the different carbide types. Comparison between the methane pressures of the less stable carbide M_3C in Fig. 3(a), and those of the more stable M_7C_3 in Fig. 3(b) shows that they can differ by an order of magnitude. The pressures generated by $M_{23}C_6$ carbides [Fig. 3(c)] are even lower at the same hydrogen pressure and temperature. Figure 3 also shows that the sensitivity of the

Fig. 3. Methane pressure p_{CH_4} as a function of temperature Θ and hydrogen pressure p_{H_2} for: (a) M_3C carbides; (b) M_7C_3 carbides; and (c) $M_{23}C_6$ carbides.

methane pressure to the hydrogen pressure decreases with increasing hydrogen pressure.

The growth of cavities is studied for the three types of carbides specified above. For each type of carbide, different values of the sintering stress in (14) are considered by taking either $\gamma_s = T_s = 1$ J/m², or $\gamma_s = 1$ J/m², $T_s = 0$, or by completely neglecting the sintering stress. In the absence of any macroscopic stress ($S = T = 0$), the internal void pressure p_m must exceed the sintering stress in order that cavities can develop. The results of the cavity growth calculations are depicted in Fig. 4, where the time to failure t_f is

Table 1. Composition of the carbides M_3C , M_7C_3 and $M_{23}C_6$

	Cr (%)	Fe (%)	Mo (%)
M_3C	30	69	1
M_7C_3	60	36	4
$M_{23}C_6$	50	28	22

Fig. 4. Time to failure t_f as a function of temperature Θ and hydrogen pressure p_{H_2} for: (a) carbide M_3C ; (b) carbide M_7C_3 ; and (c) carbide $M_{23}C_6$. Growth is driven solely by the internal methane-hydrogen pressure p_m ($S = T = 0$). The dotted lines correspond to cases where $\gamma_s = T_s = 0$.

plotted in Nelson curves as a function of temperature and hydrogen pressure. The calculations have been carried out for a 20×26 grid of hydrogen pressure and temperatures; the discrete nature of that grid is responsible for the "zig-zags" in Fig. 4 and subsequent figures. The times to failure when $\gamma_s = 1 \text{ J/m}^2$ for $T_s = 0$ or 1 J/m^2 are nearly identical, as shown by the solid contour lines in Fig. 4. In those cases, there is a region in each of the Nelson curves where cavity growth is prevented by the sintering effect. The failure

times in the absence of sintering stress are drawn by dashed lines. It is seen that, if cavitation occurs, the ultimate times to failure are not influenced by the sintering stresses due to surface free energy or surface stress at the cavity surface. The explanation for this is that, according to (11), the sintering stress σ_s is relevant only in the initial stages of cavitation when the cavity has still a small radius a . When the cavity radius a increases, the influence of the sintering stress decreases rapidly. In view of the fact that diffusive cavity growth according to (11) is very fast when $a/b < 0.1$, the influence of the sintering stress on the time to coalescence is negligible. According to (3), the surface tension affects creep growth as well; but, the creep contribution to cavity growth tends to become significant only when a/b is sufficiently large, and the influence of the surface tension has become negligible by then.

Consistent with the observations in Fig. 3 regarding the stability of the three types of carbides, the results in Fig. 4 show that the failure times depend sensitively on the type of carbide. For the ranges of temperature and hydrogen pressure considered here, the less stable carbide M_3C can lead to failure within typical lifetimes of components, whereas the predicted lifetimes for $M_{23}C_6$ carbides are two orders of magnitude longer.

In Fig. 4 we have also made an attempt to identify the dominant cavity growth mechanism. The criterion used for that, is based on the value of the ratio of the growth rate $\dot{V}_{cr}$ due to creep and the total growth rate $\dot{V} = \dot{V}_{cr} + \dot{V}_{diff}$ at the instant where $a/b = 0.2$. If $\dot{V}_{cr}/\dot{V} > 0.67$ at $a/b = 0.2$, growth is said to be "creep controlled", while the "diffusion controlled" regime is taken to correspond to $\dot{V}_{cr}/\dot{V} < 0.33$. Coupled growth is said to take place in the intermediate regime $0.33 < \dot{V}_{cr}/\dot{V} < 0.67$. It is emphasized that this classification is not at all a strict one, particularly since it is based on instantaneous growth rates at an admittedly rather arbitrary instant ($a/b = 0.2$). In fact, the computations commonly indicate that diffusive growth dominates during the very early stages of growth, while in the course of the process, it is taken over by creep void growth. Nevertheless, the classification is useful when comparing the different cases in Fig. 4 (as well as in Fig. 5 and Fig. 7 later on).

The experimental determination of the initial cavity size and spacing is not very accurate. Therefore, we have used the model to get some insight in the influence of the initial cavity radius a_i on the time to failure. It is found that for values $a_i < 0.4 \mu\text{m}$, the resulting contours of time to failure in the Nelson diagrams do not differ significantly from those in Fig. 4. This is consistent with findings of Shih and Johnson [2]. However, reducing the initial cavity radius a_i increases the initial sintering stress, leading to an enlarged region in the Nelson diagrams where cavities cannot open.

Based on the cavity growth relations (5)–(14), it is

expected that the growth of methane-filled cavities will be enhanced by applied remote stresses S and T . As an example, Fig. 5 shows times to failure for the case of a (constant) applied uniaxial stress $S = 50$ MPa ($T = 0$). This stress is below the allowable design stress for 2.25Cr-1Mo steel in the temperature range investigated here [34]. Since the applied stress is larger than the (initial) sintering stress in this case, all cavities will open and grow. Figure 5 mainly shows times to failure for M_3C carbides; for the other two types of carbide, only the isochronous failure lines of 10^6 hrs are plotted. Enhancement of the void growth by the applied stress occurs especially in the low hydrogen pressure-high temperature regime of the Nelson diagram, where, as shown in Fig. 3(a), the methane pressures are relatively low. In that regime, lifetime is reduced significantly as compared with the case $S = 0$ in Fig. 4(a). On the other hand, for lower temperatures and higher hydrogen pressures, the methane pressures are high [Fig. 3(a)] and the influence of the remote stress applied here is completely negligible. It should be noted however that the influence of the remote uniaxial stress is significant even in temperature-hydrogen pressure regimes where the methane pressure p_{CH_4} is more than five times larger than S . This is to be attributed to the highly nonlinear dependence of the creep growth rates on mean and effective stress in (6)–(10). As a consequence, the regime where growth is diffusion controlled has shrunk relative to that in Fig. 4(a). Evidently, as the methane pressure differs among the carbide types, the influence of the applied stresses also differs. This is strikingly clear when comparing the 10^6 hrs-contours in Fig. 5 for M_7C_3 and $M_{23}C_6$ carbides with the Nelson curves corresponding to $S = 0$ in Fig. 4(b) and (c), respectively.

In Fig. 5, the applied stress S has a constant value

Fig. 5. Time to failure t_f as a function of temperature Θ and hydrogen pressure p_{H_2} for carbide M_3C . Cavity growth is driven by the internal pressure and by a remote normal stress of $S = 50$ MPa, $T = 0$. The isochronous failure lines of 10^6 hrs for the M_7C_3 carbide and the $M_{23}C_6$ carbide are also plotted.

irrespective of the hydrogen pressure. For many engineering components, however, the remote stresses are basically proportional to the hydrogen pressure p_{H_2} . For instance, in a high-temperature pressure vessel where the radius of the vessel is, say, 10 times the wall thickness, the hoop stress is of the order of 10 times the vessel pressure, thus leading to, e.g. $S = 10p_{H_2}$. Based on the previous observations relating to Fig. 5, one should expect that when such proportional remote stresses become of the same order of magnitude as the internal gas pressure p_m , the lifetime can be diminished significantly compared to when the applied stresses are neglected all together. To trace the potential areas in $\Theta - p_{H_2}$ space, Fig. 6 shows the ratio of generated methane pressure and hydrogen pressure, for the three types of carbides. Next, as an example, we investigate the influence of proportional remote stresses by taking $S = 10p_{H_2}$ ($T = 0$). In this case, enhanced cavity growth due to the remote applied stress will take place in regimes in Fig. 6 where $p_{CH_4}/p_{H_2} < 10$ roughly, so that S exceeds the methane pressure p_{CH_4} . For M_3C , in Fig. 6(a), this is only when the temperature is sufficiently high, say above 700 K, more or less irrespective of p_{H_2} . For lower temperatures, the M_3C methane pressures are mostly so high that the applied stresses can be neglected. By contrast, according to Fig. 6(b), enhancement of cavitation for M_7C_3 carbides can be neglected only at sufficiently low temperatures, while for the least aggressive carbide $M_{23}C_6$ in Fig. 6(c), the applied stress will enhance growth in the whole range. The times to failure for M_7C_6 corresponding to Fig. 6(b) with $S = 10p_{H_2}$ are depicted in Fig. 7. Comparing Fig. 7 with the corresponding Nelson curves in the absence of applied stress [Fig. 4(b)] shows a drastically different picture (note that $\gamma_s = T_s = 0$ has been taken in Fig. 7 so that all cavities will develop). While M_7C_3 carbides were seen in this latter figure to be quite resistant to cavitation under the mere influence of methane pressure, Fig. 7 shows that realistic levels of additional, remote stresses can reduce the lifetimes significantly. In fact, for hydrogen pressures below 5 MPa, the three carbides show the same time to failure. For higher values, M_7C_3 and $M_{23}C_6$ behave virtually the same while M_3C give around one order of magnitude shorter lifetimes.

4. NONDIMENSIONAL RESULTS

The results presented in the previous section show that, due to the highly nonlinear processes involved, the predicted Nelson curves for a particular Cr-Mo steel depends strongly on the carbide types, on the compositions of these carbides, and on the presence of additional macroscopic stresses (either stresses due to the applied loading of the component or residual stresses). This implied that Nelson curves, for a given macroscopic stress state, are only valid for steels with

Fig. 6. Ratio of methane pressure and hydrogen pressure, p_{CH_4}/p_{H_2} , as a function of temperature Θ and hydrogen pressure p_{H_2} for: (a) carbide M_3C ; (b) carbide M_7C_3 ; and (c) carbide $M_{23}C_6$.

identical compositions and identical heat treatments. Deviations from the alloy composition and the normal heat treatment may result in the formation of slightly different carbides, and therefore in a significantly different resistance to HA.

Rather than performing an enormous parameter study for a range of carbide types, loading conditions, material properties, etc., we here present the predictions of our model in a more general yet concise way. We shall do so by first reducing the set of governing parameters by the introduction of nondimensional

groups. Careful examination of the void growth expressions (6)–(15) reveals that the dimensionless volumetric growth rate $\dot{V}/(a^3\dot{\epsilon}_m)$ can be given in the following form:

$$\frac{\dot{V}}{a^3\dot{\epsilon}_m} = \frac{\dot{V}}{a^3\dot{\epsilon}_m} \left(\frac{a}{b} \frac{\sigma_e^\infty}{\sigma_m^\infty}, \text{sign}(S - T), \left(\frac{a}{L_{m0}} \right), \frac{\Theta}{\Theta_0}, \frac{Q_v - Q_B}{3R\Theta_0}, n, \psi, \frac{\gamma_s/a}{\sigma_m^\infty}, \frac{T_s/a}{\sigma_m^\infty} \right), \quad (18)$$

where the carbide dependent methane pressure is contained in σ_m^∞ according to (1) and (3). In (18), L_{m0} is the value of the parameter L_m defined by

$$L_m = (\mathcal{D}|\sigma_m^\infty|/\dot{\epsilon}_m)^{1/3}, \quad (19)$$

at the reference temperature Θ_0 . It relates the rates of diffusion and creep similar to the parameter L in (13), but is based on the remote mean stress σ_m^∞ instead of the remote effective stress σ_e^∞ (this is useful for HA since σ_e^∞ can become zero). This parameter has the physical dimension of length and can be normalized by another typical length scale in the problem, such as the cavity size a or the half cavity spacing b . Note however, that a physical interpretation for L_m is lacking, as discussed also in [8].

For the evolution in time, a time scale is introduced by defining a reference time t_{ref} as

$$t_{ref} = \frac{b_I^3}{\mathcal{D}_0|\sigma_m^\infty|},$$

where, as before, the subscript I indicates the initial value. This reference time t_{ref} is based on the rate of diffusion at the reference temperature Θ_0 . Most of the nondimensional groups in (18) are assumed to be constant during the process. First, the temperature is assumed to be constant, so that also the methane pressure for a given carbide type and hydrogen

Fig. 7. Time to failure t_f as a function of temperature Θ and hydrogen pressure p_{H_2} for M_7C_3 carbides. Cavity growth is driven by methane–hydrogen pressure and by a normal stress of $S = 10p_{H_2}$, $T = 0$. The isochronous failure lines of 10⁶ hrs for the carbide M_3C and the carbide $M_{23}C_6$ are also plotted.

pressure are constant during the process; thus, σ_e^∞ and σ_m^∞ can be regarded as given constants. The ratio a/b increases continually and the sintering stresses decrease with increasing cavity radius a . As mentioned in the previous section, the initial cavity radius a_1 does not affect the total time to coalescence significantly when $(a/b)_1 < 0.05$, nor does the value of the surface energy and surface tension (as long as the cavity can grow). Hence, it follows from (18) that the time to failure t_f with respect to the reference time t_{ref} is determined by the following nondimensional parameter set:

$$\frac{t_f}{t_{\text{ref}}} = \frac{t_f}{t_{\text{ref}}} \left(\frac{\sigma_e^\infty}{\sigma_m^\infty}, \text{sign}(S - T), \frac{b_1}{L_m}, n, \psi \right). \quad (20)$$

Note that the temperature dependence of creep and diffusion is implied in b_1/L_m , and in the reference time t_{ref} . As the process is virtually independent of the initial cavity radius a_1 , we have normalized the length parameter L_m in (20) by the initial half spacing b_1 rather than a_1 .

For simplicity, we shall confine attention in the following to a typical cavity tip angle ψ of 78.5° [13]. Furthermore, we shall presume that σ_m^∞ is always positive under HA conditions; the stress state dependence of the failure time according to (20) reduces to a dependence on $(\sigma_e^\infty/\sigma_m^\infty)\text{sign}(S - T)$. Thus, we are left with just three-nondimensional parameters determining the time to failure,

$$\frac{t_f}{t_{\text{ref}}} = \frac{t_f}{t_{\text{ref}}} \left(\Sigma, \frac{b_1}{L_m}, n \right); \quad (21)$$

namely Σ , defined through

$$\Sigma = (\sigma_e^\infty/\sigma_m^\infty)\text{sign}(S - T) = \frac{S - T}{(S + 2T)/3 + p_{\text{CH}_4}}, \quad (22)$$

the ratio of creep and diffusion rates expressed through b_1/L_m , and the creep exponent n . Note that the axisymmetric stress state Σ follows from substitution of the expressions (3) and (4) into $(\sigma_e^\infty/\sigma_m^\infty)\text{sign}(S - T)$.

The results can be represented by surfaces of constant value of t_f/t_{ref} in the three-dimensional space spanned by these three parameters. In Fig. 8, we present three orthogonal cross-sections of this space. The stress state dependence of failure times is scanned by considering reciprocal stress triaxialities ranging from $\Sigma = -1.5$ (corresponding to pure axisymmetric transverse tension), via hydrostatic loading $\Sigma = 0$, to a state characterized by $\Sigma = 3$ (corresponding to uniaxial tension). The value of b_1/L_m is taken to run over eight decades from $\log(b_1/L_m) = -4$ to $\log(b_1/L_m) = 4$, while the creep exponent n ranges from $n = 4$ to 9. Figure 8(a) shows a cross-section at a fixed stress state specified through $\Sigma = 0.5$. Figure 8(b) presents a cross-section for $n = 6$, and finally, Fig. 8(c) corresponds to $\log(b_1/L_m) = 2.5$.

In Fig. 8 the dominant void growth mechanism is identified in a similar way as in the previous section: void growth is termed ‘‘creep controlled’’ if

Fig. 8. Normalized time to failure t_f/t_{ref} as a function of the three (nondimensional) parameters: stress triaxiality Σ , the ratio of diffusion and creep rates b_1/L_m , and the creep exponent n . In (a), the stress triaxiality is $\Sigma = 0.5$, in (b) the creep exponent $n = 6$, and in (c) $\log(b_1/L_m) = 2.5$. The dashed lines in each figure indicate how the three cross-sections (a)–(c) fit together.

$\dot{V}_{cr}/\dot{V} > 0.67$ at $a/b = 0.2$, while the “diffusion controlled” regime is taken to correspond to $\dot{V}_{cr}/\dot{V} < 0.33$. It is seen in Fig. 8(a) and (b), that when $\log(b_1/L_m) \approx 1$ or lower, cavity growth is mostly determined by diffusion. It is interesting to note that Needleman and Rice [6] in their study of creep rupture under uniaxial tension (no internal void pressure) used the parameter a_1/L to indicate when creep contributed to void growth. A noteworthy conclusion from Fig. 8(a) is that t_f/t_{ref} as a function of b_1/L_m is virtually independent of n ; but, it should be realized that the creep exponent is implicit in b_1/L_m [see (8) and (19)]. In Fig. 8(b) when $\Sigma = -1.5$, there is no grain boundary normal stress in the model (only axisymmetric transverse tension), and hence no grain boundary diffusion occurs [cf. (11)]. In the creep controlled regime where the value of b_1/L_m is small, the creep rate drops sharply and therefore the failure times t_f/t_{ref} become relatively high. With increasing value of Σ , the grain boundary normal stress rapidly becomes more important, and diffusion becomes dominant at sufficiently low values of b_1/L_m . The time to failure in the diffusion controlled regime is nearly independent of b_1/L_m , as is also clear in Fig. 8(a).

A dependence of the lifetimes on the creep exponent n will only appear when creep contributes significantly to growth. Therefore in Fig. 8(c), a section is shown for $\log(b_1/L_m) = 2.5$, where growth is creep controlled. Again we see that, despite the fact that the creep exponent n is an independent group determining the failure time in (20), its influence is not large. Apparently, the failure time is mainly determined by rate of creep compared to the rate of diffusion, which is expressed in b/L_m rather than by the value of n itself. However note in Fig. 8(c), that with increasing n , also the sensitivity of the lifetime on the stress state increases.

Of course, these nondimensional plots can be used to construct Nelson curves for a specific material and a specific remote loading state, as in Figs 4, 5 or 7. Since the latter figures were all for $n = 6.5$, Fig. 8(b) is particularly convenient. Knowing the methane pressure and the remote applied stresses, as well as the material parameters for any temperature, the two dimensionless parameters Σ and b_1/L_m can be computed and the normalized time to failure is read from the plot.

5. CONCLUSION

In this paper, we have discussed a model for HA based on a combination of an equilibrium reaction model for the hydrogen-to-methane reaction and a recent model for the growth of cavities due to creep and diffusion. One key improvement of the model over currently existing models is the accuracy of the void growth model for the entire range of internal methane-hydrogen gas pressures relative to macro-

scopic (applied or residual) stresses present remote from the cavities. This is of substantial importance in view of the fact that the growth rate of cavities in a creeping matrix is very strongly dependent on the overall stress triaxiality, or in other words for HA, the parameter Σ defined in (20). Indeed, Van der Giessen *et al.* [8] have shown that other void growth models may predict growth rates that are several orders of magnitude in error, depending on the stress triaxiality and the porosity level.

The application of this model to 2.25Cr-1Mo steel has shown that the time to failure is very sensitive to the type and composition of the carbides in the material, since these determine their reactivity and thereby the equilibrium methane pressure. A similar sensitivity should be expected for other materials. It also implies a possibly strong sensitivity to the actual heat treatment (see also Ref. [24]). Unfortunately, these kinds of information are not available in the standard, empirical Nelson-curves. This predicted sensitivity may also provide one possible explanation for the fact that some 0.5Mo steels show an inferior resistance to HA than others.

Another aspect that has become clear from this study is that the presence of—what we have called macroscopic—stresses (S, T) remote from the cavity may significantly influence the time to failure. This is an effect that has not gained much attention in the HA literature (other than, as far as we know, [4]), nor is this accounted for in the traditional Nelson curves. Such stresses could be either due to the applied loading or may be present as residual stresses. Their relevance in HA depends primarily on their value relative to the methane pressure p_{CH_4} through the triaxiality parameter Σ , and secondly, through the length parameter L_m . It is clear that this effect is coupled with the mentioned sensitivity to carbide type and composition. Hence, we conclude that close attention should be paid not only to stress concentrations in components but particularly to weldments and/or heat affected zones where the carbide composition may be expected to deviate from that in the base material and where residual stresses will be present.

It should be mentioned at this point that in the present considerations, we have tacitly assumed that the stresses (S, T) remote from the cavity are equal to the actual macroscopic stresses. As has been first pointed out by Dyson [35] for creep rupture, this need not be the case when the growth rate of the cavities would be considerably faster than the creep rate of the surrounding material. This may arise, for instance, when the rate of diffusion is much larger than the creep rates, or when the cavities are subjected to different internal methane pressures. Because of compatibility, internal stress redistributions will then have to take place in the material which may lead to the stresses around the cavities differing considerably from the applied macroscopic stress state. The results presented here for the influence of macroscopic

stresses should therefore be considered merely as a qualitative illustration. A more elaborate study of these aspects, in the spirit of the multi-grain work in [36], is currently being carried out and will be reported elsewhere.

Acknowledgements—The research of Marc van der Burg is sponsored by Shell Research, Amsterdam, The Netherlands. Helpful discussions with Dr A. G. Varias and R. W. J. Koers are gratefully acknowledged.

REFERENCES

1. *American Petroleum Institute Publication*, Vol. 941, 4th edn (1990).
2. H.-M. Shih and H. H. Johnson, *Acta metall.* **30**, 537 (1982).
3. D. Hull and D. E. Rimmer, *Phil. Mag.* **4**, 673 (1959).
4. T. A. Parthasarathy, *Acta metall.* **33**, 1673 (1985).
5. P. G. Shewmon, *Acta metall.* **35**, 1317 (1987).
6. A. Needleman and J. R. Rice, *Acta metall.* **28**, 1315 (1980).
7. T.-L. Sham and A. Needleman, *Acta metall.* **31**, 919 (1983).
8. E. van der Giessen, M. W. D. van der Burg, A. Needleman and V. Tvergaard, *J. Mech. Phys. Solids* **43**, 123 (1995).
9. T. A. Parthasarathy and P. G. Shewmon, *Metall. Trans. A* **15A**, 2021 (1984).
10. G. R. Odette and S. S. Vagarali, *Metall. Trans. A* **13A**, 299 (1982).
11. R. Lundberg, M. Waldenstrom and B. Uhrenius, *CAL-PHAD* **1**, 159 (1977).
12. D. A. McQuarrie and J. L. Katz, *J. Chem. Phys.* **44**, 2393 (1966).
13. T.-J. Chuang, K. I. Kagawa, J. R. Rice and L. Bank-Sills, *Acta metall.* **27**, 265 (1979).
14. B. Budiansky, J. W. Hutchinson and S. Slutsky, in *Mechanics of Solids: The Rodney Hill 60th Anniversary Volume* (edited by H. G. Hopkins and M. J. Sewell), p. 13. Pergamon Press, Oxford (1982).
15. V. Tvergaard, *J. Mech. Phys. Solids* **32**, 373 (1984).
16. R. Raj, H. M. Shih and H. H. Johnson, *Scripta metall* **11**, 839 (1977).
17. C. Herring, in *The Physics of Powder Metallurgy*, p. 143. McGraw-Hill, New York (1951).
18. T. A. Parthasarathy, H. F. Lopez and P. G. Shewmon, *Metall. Trans. A* **16A**, 1143 (1985).
19. P. G. Shewmon, *Mat. Sci. Tech.* **1**, 1 (1985).
20. H. J. Frost and M. F. Ashby, *Deformation-Mechanism Maps*, p. 62. Pergamon Press, Oxford (1982).
21. I. Finnie and W. R. Heller, *Creep of Engineering Materials*. McGraw-Hill, New York (1959).
22. G. H. Edward and M. F. Ashby, *Acta metall.* **27**, 1505 (1979).
23. R. Kleuh, *Int. J. Pressure Vess. Piping* **8**, 165 (1980).
24. R. G. Baker and T. Nutting, *J. Iron and Steel Inst.* p. 257 (1959).
25. Jun Yu, *Commun. Metall. Trans. A* **20**, 1561 (1989).
26. *American Petroleum Institute Publication*, Vol. 945 (1975).
27. K. W. Andrews, H. Hughes and D. J. Dyson, *J. Iron and Steel Inst.* p. 337 (1972).
28. R. Petri, E. Schnabel and P. Schwaap, *Arch. Eisenhüttenwes.* **51,8** 355 (1980).
29. H. K. D. H. Bhadesia and R. C. Thomson, *private communication*. To be published.
30. T. Imanaka and J. Shimomura, *5th Int. Conf. Pres. Ves. Technol. Materials and Manufacturing* **2**, 617 (1984).
31. R. L. Kleuh and R. W. Swindeman, *Metall. Trans.* **17**, 1027 (1987).
32. B. J. Shaw, *1984 Pressure Vessel and Piping Conference and Exhibition*, p. 117 (1984).
33. T. Takano, H. Suzuki, K. Tsukada and K. Sato, *Transactions ISIJ* **24**, B237 (1984).
34. H. E. Boyer, *Atlas of Creep and Stress-Rupture Curves*. ASM International, Ohio (1988).
35. B. F. Dyson, *Metal Sci.* **10**, 349 (1976).
36. E. Van der Giessen and V. Tvergaard, *Acta metall. mater.* **42**, 959 (1994).

APPENDIX A

At high temperature and pressures the non-ideality of the methane gas has to be taken into account. Odette and Vagarali [10] derived an equation of state for methane, and, based on this equation-of-state, they derived approximate solutions for three different fugacity ranges. The fugacity of methane can be converted to methane pressure using

$$f_{\text{CH}_4} = p_{\text{CH}_4} e^{C(T)p_{\text{CH}_4}} \quad (\text{A1})$$

where

$$C(T) = 0.005 \text{ MPa}^{-1} \quad \text{for } f_{\text{CH}_4} < 10^3 \text{ MPa}$$

$$C(T) = \frac{1.1875}{T} + 3.0888 \times 10^{-3} \text{ MPa}^{-1}$$

$$\text{for } 10^3 \text{ MPa} < f_{\text{CH}_4} < 10^4 \text{ MPa}$$

$$C(T) = \frac{2.375}{T} + 1.1776 \times 10^{-3} \text{ MPa}^{-1}$$

$$\text{for } f_{\text{CH}_4} > 10^4 \text{ MPa}$$

which can easily be solved numerically.

The methane that generates HA is considered in this paper to be formed by the reaction of hydrogen with a carbide. The reaction of hydrogen with a mixed (alloy) carbide is given by

with M^i the metal, x the number of metal atoms and y the number of carbon atoms in the carbide and y_1 and y_2 are the concentration parameters of metal M^1 and M^2 , respectively ($y_1 + y_2 = 1$).

The reaction constant of the reaction (A2) for one mole of metal atoms depends on the Gibbs energy of formation for the carbide $\Delta G_{(\text{M}_1^1 \text{M}_2^2)_x \text{C}_y / x}$, and the Gibbs energy of formation of methane ΔG_{CH_4} , as,

$$K(T) = e^{(\Delta G_{(\text{M}_1^1 \text{M}_2^2)_x \text{C}_y / x} - (y/x) \Delta G_{\text{CH}_4}) / (RT)} \quad (\text{A3})$$

The Gibbs energy of formation of the alloy carbide is not known. However Lundberg *et al.* [11] developed an expression for the Gibbs free energy of alloy carbides in terms of the Gibbs free energies of the pure carbides:

$$G_{(\text{M}_1^1 \text{M}_2^2)_x \text{C}_y / x}^0 = y_1 G_{\text{M}^1 \text{C}_y / x}^0 + y_2 G_{\text{M}^2 \text{C}_y / x}^0 + RT[y_1 \ln(y_1) + y_2 \ln(y_2)] + y_1 y_2 A_0.$$

The Gibbs free energies of the pure carbides depend on the type of carbide, the kind of metal atoms in the carbide and on the temperature. The Gibbs energy of formation for the carbide, $\Delta G_{(\text{M}_1^1 \text{M}_2^2)_x \text{C}_y / x}$, is

$$\begin{aligned} \Delta G_{(\text{M}_1^1 \text{M}_2^2)_x \text{C}_y / x} &= y_1 (G_{\text{M}^1 \text{C}_y / x}^0 - G_{\text{M}^1}^0 - (y/x) G_{\text{C}}^0) \\ &+ y_2 (G_{\text{M}^2 \text{C}_y / x}^0 - G_{\text{M}^2}^0 - (y/x) G_{\text{C}}^0) \\ &+ RT[y_1 \ln(y_1) + y_2 \ln(y_2)] \\ &+ y_1 y_2 A_0. \end{aligned} \quad (\text{A4})$$

For Fe and Cr carbides the Gibbs energies of formation of

the carbides M_3C , M_7C_3 and $M_{23}C_6$, where M^i can be either Fe or Cr (in J/mol metal atoms), are

$$\begin{aligned} G_{FeC_{1/3}}^0 - G_{Fe}^0 - 1/3G_C^0 &= 13320 - 64.720T + 7.4834T \ln(T) \\ G_{FeC_{3/7}}^0 - G_{Fe}^0 - 3/7G_C^0 &= 16730 - 12.42T \\ G_{FeC_{6/23}}^0 - G_{Fe}^0 - 6/23G_C^0 &= 5760 - 5.01T \\ G_{CrC_{1/3}}^0 - G_{Cr}^0 - 1/3G_C^0 &= -850 - 14.58T \\ G_{CrC_{3/7}}^0 - G_{Cr}^0 - 3/7G_C^0 &= -16000 - 7.62T \\ G_{CrC_{6/23}}^0 - G_{Cr}^0 - 6/23G_C^0 &= -13100 - 3.33T \quad (A5) \end{aligned}$$

with T in K, $\Delta G_{(M_1^1 M_2^2)C_{y/x}}$ in J/mol, $G_{MC_{y/x}}^0$ the Gibbs free energy per metal atom of the $M_x^i C_y$ carbide, $G_{M^i}^0$ the Gibbs free energy of M^i in $j = \alpha$ or γ , and G_C^0 the Gibbs free energy of carbon in graphite. The constant A_0 has the value

$$\begin{aligned} A_0 &= 1790 \text{ J/mol metal atom} \quad \text{in case of } M_{y_1}^1 M_{y_2}^2 C_{1/3} \\ A_0 &= 750 \text{ J/mol metal atom} \quad \text{in case of } M_{y_1}^1 M_{y_2}^2 C_{3/7} \\ A_0 &= 1110 \text{ J/mol metal atom} \quad \text{in case of } M_{y_1}^1 M_{y_2}^2 C_{6/23} \end{aligned} \quad (A6)$$

By inserting (A5) and (A6) into (A4) the Gibbs energy of formation of the alloy carbide is obtained. The Gibbs energy of formation of one mole of methane from carbide and hydrogen gas is given by [9, 11] as

$$\Delta G_{CH_4} = -69120 - 65.35T + 51.25T^{10} \log(T).$$

By inserting both Gibbs energies in (A3), the reaction constant for dissolution of the alloy carbide in methane can be calculated. The equilibrium constant of the reaction (A3) can also be written in the standard manner in terms of the activities a_{M^i} and $a_{M_2^2}$ of the metals in the matrix, the activity $a_{(M_1^1 M_2^2)C_{y/x}}$ of the carbide, and the fugacities f_{CH_4} and f_{H_2} of methane and hydrogen gas, respectively. The hydrogen fugacity is equal to the hydrogen pressure for the temperature and pressure range of interest to this paper. Values for the activity coefficients $a_{M_1^1 M_2^2 C_{y/x}}$, a_{Fe} and a_{Cr} have been taken from [9]. The activity coefficient of the alloy carbide is set to unity, Raoultian behaviour is assumed for α -Fe, and the activity coefficient of Cr in α -Fe is taken to be 10, thus

$$a_{(M_1^1 M_2^2)C_{y/x}} = 1, \quad a_{Fe} = 1 - c_{Cr}, \quad a_{Cr} = 10c_{Cr},$$

where $c_{Cr} = Cr/(Cr + Fe)$ atom percent in steel. The temperature dependence of the activities has been neglected. From (A3), the methane fugacity can now be expressed in the Gibbs energy of the reaction and the activities as follows:

$$f_{CH_4} = \frac{f_{H_2}^2 (a_{(M_1^1 M_2^2)C_{y/x}})^{x/y} e^{((x/y)\Delta G_C - \Delta G_m)/RT}}{[(a_{M_1^1})^{y_1} (a_{M_2^2})^{y_2}]^{x/y}}. \quad (A7)$$

Together with (A1), this result (A7) can be used to calculate the equilibrium methane pressure p_{CH_4} in a void, depending on temperature, hydrogen pressure, carbide type, carbide composition and the alloy composition of the matrix.

APPENDIX B

The formulation of the volumetric growth rate expression (11) for growth by grain boundary diffusion in the presence of internal void pressure and for distinct values of the surface energy and surface tension has been the subject of some confusion in the literature (see discussions in [16] and [6]). It seems worthwhile, therefore, to briefly outline the derivation of (11). As discussed in detail in [6] and [13], the diffusional transport of matter along the grain boundary $z = 0$ (see Fig. B1) is governed by

Fig. B1. Schematic of the axisymmetric problem of grain boundary diffusion away from a cavity of radius a .

$$\frac{1}{r} \frac{d}{dr} (rj) + 2v_z = 0; \quad (B1)$$

$$j = -\frac{D_B \delta_B}{k\theta} \frac{d\mu}{dr}; \quad (B2)$$

$$\mu = \mu_0 - \Omega \sigma_{zz}, \quad (B3)$$

expressing conservation of matter, the kinetic diffusion equation and the chemical potential along the stressed grain boundary, respectively. Here, j is the volumetric flux of matter, v_z and σ_{zz} are the normal velocity and normal stress along the grain boundary and μ is the chemical potential per atom, all being functions merely of the radial coordinate r . The boundary conditions for the differential equations (B1)–(B3) are

$$j = 0 \quad \text{at } r = b;$$

$$\mu = \mu_0 - \Omega \left(p_m - 2 \frac{\gamma_s}{a} \sin \psi \right) \quad \text{at } r = a, \quad (B4)$$

where the latter stems from the chemical potential along the curved void surface due to the specific free energy content $p_m - 2\gamma_s \sin \psi / a$ of the surface (γ_s is the surface free energy, and p_m is the void pressure). Adopting the Hull and Rimmer [3] assumption that the grain material is undeformable, so that v_z is the same for all r , these equations can be readily solved to give the following relation between v_z and the normal stress distribution:

$$\begin{aligned} \mathcal{D} \sigma_{zz}(r) &= -\mathcal{D} (p_m - 2\gamma_s \sin \psi / a) \\ &\quad + v_z \left[b^2 \ln \left(\frac{r}{a} \right) - \frac{1}{2} (r^2 - a^2) \right] \end{aligned} \quad (B5)$$

($\mathcal{D} = D_B \delta_B \Omega / k\theta$). This stress distribution is linked to the remote stresses S and T , and the internal pressure p_m by way of the vertical equilibrium condition

$$\pi b^2 S + (p_m - 2T_s \sin \psi / a) \pi a^2 = 2\pi \int_a^b \sigma_{zz}(r) r dr, \quad (B6)$$

where in the second term the surface tension T_s is accounted for. It is emphasized that for solids, γ_s and T_s are not identical, as they are for fluids ([6, 17]). Making use furthermore of the balance of mass leading to $\dot{V} = 2v_z \pi b^2$, one finds from (B5) and (B6) that the volumetric growth rate $\dot{V}$ is given by

$$\dot{V} = 4\pi \mathcal{D} \frac{S + p_m - (1-f)2\gamma_s \sin \psi / a - f2T_s \sin \psi / a}{\ln(1/f) - \frac{1}{2}(3-f)(1-f)},$$

with $f = (a/b)^2$.