Investigation of models for hydrogen attack of steel

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Hydrogen attack of steels at elevated temperature caused by methane formation at internal surfaces occurs in different stages. Several models have been proposed which are based on specific mechanisms. In this paper general equations for the chemical reaction and for creep expansion of pores are used and it is left to the numerical analysis to pinpoint the mechanisms which are controlling the processes. The numerical analysis of experimental data for a limited temperature and pressure range not only verifies several mechanisms of the earlier models, but also shows additional features such as a rise of the methane pressure from a definite minimum value to a peak resulting from the superposition of a rapidly decreasing methane production rate and creep expansion of bubbles by diffusion.

1. Introduction
The properties of carbon and low alloy steels may deteriorate when exposed for a period of time to pressurized hydrogen at elevated temperatures even without the action of an external load. This is caused by a reaction of hydrogen with carbon of the steel at internal surfaces which results in a build-up of methane pressure, expansion of cavities, localized decarburization, a loss of strength, an apparent bulk embrittlement, swelling and ultimately fracture. In normalized steels the cavities assume a spherical shape. The growth of these "bubbles" occurs in several different stages [1]. The initial stages of attack, which are significant for service life prediction, received special attention in the past that led to the development of several different models [2]. They may be classified as nucleation models and growth models [3–5]. Of these two, the growth models are most advanced and are able to predict the time for a given degree of attack within an order of magnitude [4]. These models take into account the rate of the methane reaction, and unconstrained as well as constrained creep expansion of the bubbles. The models suggest that at a given hydrogen pressure, initially methane pressure builds up at submicroscopic voids along interface boundaries which act as high energy hydrogen traps. At first methane pressure is balanced by surface tension, so growth is low. At this "incubation" stage action is reversible with external hydrogen pressure and has little effect on the mechanical properties. When the cavities reach a critical size, they grow rapidly by diffusion processes until they reach a size where dislocation creep mechanisms become operative and expansion occurs at increasing rates. Eventually, exhaustive of carbon, interconnection of cavities, and venting of methane may take place.

In this paper a different approach to model analysis is taken by not assuming a specific model for the kinetics of the chemical reaction or of creep expansion. A general creep law and a power law for the reaction rate is used to calculate the methane pressure in the bubbles as a function of the total bubble volume. Evaluation of experimental data provide the constants for the rate equations which in turn may give an indication of the mechanisms involved in the process. This allows a comparison with models which have been proposed in the literature.

2. General model of hydrogen attack
The total methane production rate may be a function of the surface area over which it occurs, the

diffusion rate of carbon, the diffusion distance of carbon, or the rate of solution of carbides in addition to hydrogen pressure, carbon activity, methane pressure and test temperature. The surface area may be the entire surface area of the bubble or only the surface area of a ring section created by the intersection of the bubble with a grain boundary if boundary diffusion is controlling. Since it is unknown which of these processes is rate controlling, it is assumed that the methane production rate is a general power function of the bubble radius or bubble volume. Thus,

$$\frac{dv_g}{dt} = \mu_0 k\, v_b^m \qquad (1)$$

where μ_0 is the rate of surface reaction per unit area, k is a geometric factor, v_b is the bubble volume, v_g is the gas volume at one atmosphere pressure, and m is a constant. For constant temperature and identical symmetry one may write

$$k_g = \mu_0 k \qquad (1a)$$

The rate of volume expansion of a spherical cavity in an infinite medium as a result of internal pressure p is given by

$$\frac{dv_b}{dt} = \frac{3}{2} B \left[\frac{3}{2n}\right]^n v_b p^n = k_b v_b p^n \qquad (2)$$

where v_b is the volume of the bubble, t is the time, p is the gas pressure and B and n are constants [6]. The pressure, p, is a function of the rate of methane formation while the volume of the bubble is a function of the pressure. The volume expansion rate and the gas production rate are correlated on the basis of Boyle's law:

$$p = v_g/v_b \qquad (3)$$

Total differentiation of Equation 3 with respect to time and substitution for the pressure from Equation 3 gives

$$\frac{dp}{dt} = \frac{1}{v_b} \frac{dv_g}{dt} - \frac{p}{v_b} \frac{dv_b}{dt} \qquad (4)$$

Dividing Equation 4 by the bubble growth rate dv_b/dt and substitution of Equation 2 gives the differential equation

$$\frac{dp}{dv_b} = \frac{k_v}{k_p} \frac{v_b^{m-2}}{p^n} - \frac{p}{v_b} \qquad (5)$$

This equation can be solved by conversion to a linear differential equation. Thus,

$$p\, v_b = (K_1 v_b^{n+m} + K_2)^{1/(n+1)} \qquad (6)$$

with the constants K_1 and K_2, where

$$K_1 = \frac{(n+1)}{(n+m)} \frac{k_g}{k_b} \qquad (6a)$$

and K_2 is a numerical value.

Equation 6 gives the pressure as a function of the size of the cavity at constant test temperature and hydrogen pressure.

3. Analysis and discussion

To evaluate Equation 6 reference is made to experimental work by Roth [7] and Schroeder [8], who provided data on decarburization and volume growth. Assuming that surface decarburization is minimal and the entire carbon lost is converted to methane which is trapped in the bubbles, one can calculate a methane pressure corresponding to the total bubble volume.

It has been shown that as a result of the bubble growth processes involved a stable number of bubbles is established in the early stages of attack [4]. Therefore it is possible to correlate methane pressure and total bubble volume using Equation 6.

It should be noted that for chemical analysis of the carbon retained in the steel a colorimetric method was used by Roth to avoid errors in the assay which may have arisen in the conventional combustion method due to the methane trapped in the bubbles.

Data used for evaluation are for a commercial SAE 1020 steel containing in weight per cent 0.21 C, 0.52 Mn, 0.04 Si, 0.032 S, 0.013 P, a recarburized vacuum-melted iron, Ferrovac 1020, containing 0.02 C, 0.001 Mn, 0.006 Si, 0.007 S, 0.002 P, and 0.01 Mo, and an alloy steel containing 1.14 Cr, 0.53 Mo, 0.10 C, 0.46 Mn, 0.80 Si, 0.010 S, 0.011 P. Data points used in this evaluation are only those whose metallographic inspection showed that decarburization was uniform throughout the test section and surface decarburization was not an influencing factor.

Fig. 1 shows data points for the product of pressure and bubble volume plotted against bubble volume and curves obtained from evaluation of Equation 6. One observes an initial rapid increase of pressure with increasing bubble volume followed by a more or less rapid leveling off to constant values. The approach to constant values indicates a trend towards exhaustion of the gas reaction and an expansion of the bubbles at constant gas volume and decreasing gas pressure. It is interesting to note
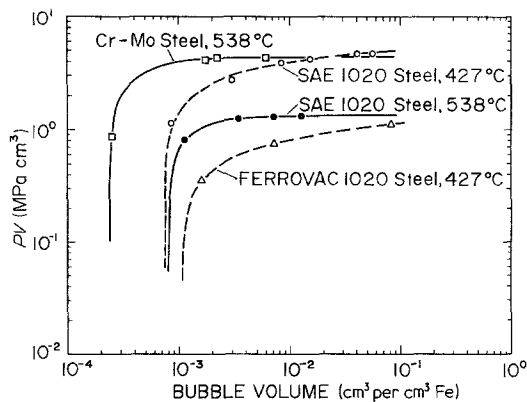
Figure 1 The product of methane pressure and bubble volume as a function of the bubble volume resulting from exposure of steels to hydrogen at 6.2 MPa pressure at elevated temperatures.

Figure 2 Methane pressure against bubble volume of steels which were exposed to hydrogen at 6.2 MPa pressure and different temperatures.

that as the creep strength of the test material increases the gas pressure to produce a given bubble size increases [9]. Related to this trend is the fact that there is a minimum bubble volume and corresponding methane pressure at which the pressure build-up begins. This minimum bubble volume is smaller and the methane pressure higher as the creep strength of the test material increases either by alloying or due to lowering of the temperature. It is interesting to observe that the shape of the curves for identical test temperature is similar regardless of material composition.

Fig. 2 shows the methane pressure as a function of bubble volume and computer-drawn curves with the aid of Equation 6. The curves start at a minimum bubble volume at which the pressure rises sharply with increasing bubble size. After reaching a peak it drops to become asymptotic to a slope of -1 indicating constancy of the product of pressure and volume and thus exhaustion of the gas reaction. The peaks of the pressure for the different materials are higher and the corresponding bubble volumes smaller as the creep resistance of the material increases.

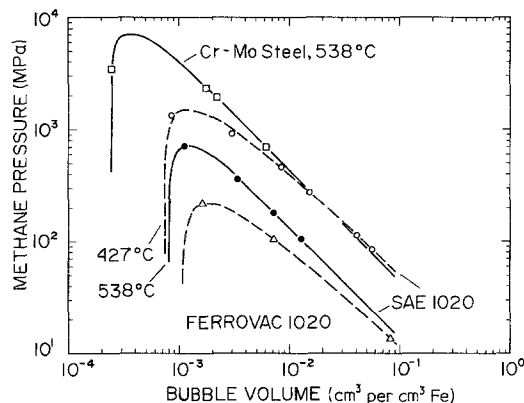To evaluate the experimental data numerically according to Equation 6 creep exponents of $n =$ 1, 5 and 6 were assumed and the constants m, K_1 and K_2 determined for the best fit of data. A value of $n = 1$ indicates creep by diffusion while $n = 5$ or 6 applies for dislocation creep mechanisms. All creep exponent values chosen gave a trend of the curves as indicated in Figs. 1 and 2. However, the minimum deviation was obtained for $n = 1$ while for $n > 1$ a reasonable, though not as good fit could be obtained for bubble volume data points beyond the peak pressure values. The numerical values of the constants which resulted in the curves shown in Figs. 1 and 2 are listed in Table I. The power value, m, for the gas reaction is negative. Equation 1 shows that for this case the gas reaction decays rapidly with increasing bubble volume rather than increase according to any geometrical parameter of the bubble. Also listed in Table I are numerical values for the minimum bubble volume which is determined by the constants K_1 and K_2.

Equation 6a can be used to determine the activation energy for the gas reaction from the temperature dependence of μ_0 and B. For diffusion creep with $n = 1$ and an activation energy of $310\,\mathrm{kJ\,mol^{-1}}$ for creep [10] the activation energy for the gas reaction is calculated as 93.2 $\mathrm{kJ\,mol^{-1}}$. This compares favourably with the

TABLE I Data for hydrogen attack at 6.2 MPa hydrogen pressure

Test material	Temperature (° C)	m	K_1	K_2	V_{min} (cm³ per cm³ Fe)
Ferrovac 1020	427	-1.03	-8.162	10.02	1.06×10^{-3}
Carbon Steel	427	-1.15	-16.16	47.58	7.49×10^{-4}
Carbon Steel	538	-2.35	-1.20×10^{-4}	1.81	8.06×10^{-4}
Chrom. Steel	538	-2.13	-1.60×10^{-3}	19.45	2.43×10^{-4}

activation energy for diffusion of carbon in alpha-iron of $84\,kJ\,mol^{-1}$ [11]. For $n = 5$ or $n = 6$ representing dislocation creep mechanisms, the calculated activation energy ranges from 236 $kJ\,mol^{-1}$ to $270\,kJ\,mol^{-1}$.

The numerical results lend support to the explanation of several model characteristics within the range of hydrogen pressure and temperature of the experimental data. Creep by diffusion controls the expansion of bubbles during both the stage of increasing pressure as well as the following stage of attack in which the chemical reaction becomes exhausted. During this latter stage of attack creep by dislocation motion occurs parallel with diffusion creep. Control by diffusion creep commences at a definite minimum bubble size and a corresponding minimum gas pressure. This corroborates earlier suggestions that initial expansion of bubbles is controlled by surface tension until a critical size is reached where diffusion and dislocation mechanism can commence [1].

The rapid decrease of the reaction rate of the methane formation and the magnitude of the activation energy indicate that carbon diffusion and exhaustion of carbon sources are factors which dominate the gas producing reaction. Geometric factors such as dispersion of carbon sources and geometry of diffusion path play also a role. Additional experimental data are needed for further analysis.

4. Conclusions

The proposed general model for hydrogen attack which takes into account an unspecified rate of gas producing reaction and an unspecified rate of bubble expansion does provide specific information on the particular mechanisms involved upon numerical analysis of experimental data. It verifies several model characteristics proposed in earlier publications such as a critical minimum bubble size and minimum methane pressure from which on creep becomes a controlling factor; diffusion and exhaustion of carbon as controlling the chemical reaction rate, and the parallel action of creep by diffusion and dislocation mechanisms in late stages of attack. It also shows that a monotonous

decay of the methane production combined with bubble expansion by diffusion creep results in an initial increase to peak values of the methane pressure in the bubbles followed by a decay to values of constant product of pressure and volume resulting from the exhaustion of the chemical reaction.

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