JOURNAL OF MATERIALS SCIENCE 14 (1979) 2703–2708

Kinetic aspects of slow crack growth in the gaseous hydrogen embrittlement of steels

K. SIERADZKI
Department of Materials Science and Engineering, Iowa State University and Ames Laboratory, USDOE, Ames, Iowa 50011, USA

P. FICALORA
Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York 13200, USA

An explanation of the slow crack-growth phenomenon in gaseous hydrogen embrittlement is suggested on the basis that chemisorption is the rate-limiting step. The basis of the analysis is the existence of a mobile adsorbed species which is a prerequisite to the occurrence of slow crack growth. The disappearance of the mobile species with increasing temperature results in the observed crack-velocity dependence on temperature. The analysis is able to account qualitatively for the observed dependence of crack velocity with pressure in the different temperature regions of crack growth.

1. Introduction

In our discussion of the slow crack-growth phenomenon in the gaseous hydrogen embrittlement (ghe) of steels we will be concerned with the identification of those processes responsible for determining the rate of crack growth. Generally, the overall transport processes involved in an embrittlement effect will be dependent upon the source of the embrittling species. That is, the rate-determining step in an embrittlement process will depend upon whether hydrogen originates in the environment surrounding the metal or is present in solution within the metal lattice. Thus it is necessary, when considering the kinetics of hydrogen embrittlement to restrict the discussion in this manner.

The kinetics of ghe are usually investigated experimentally via the sustained load slow crack-growth test. Specimens used are typically fracture mechanics compact tension type which have been fatigue precracked. Often the precracking is accomplished in an environmental chamber which can be evacuated. Following precracking, the chamber is backfilled with hydrogen gas to the desired test pressure. Subsequently, a load is slowly applied until the first detectable sign of cracking occurs. Once this condition is obtained the load is maintained at a constant value. The data are displayed as the logarithm of the crack velocity as a function of the stress intensity factor K. Observable growth occurs at a stress intensity value defined as the threshold stress intensity, K_{Th}. At low K levels the crack velocity is heavily K dependent (stage I); at intermediate K levels the crack-growth rate is approximately constant and K independent (stage II); and at still higher K levels crack acceleration occurs resulting in unstable fracture as K approaches K_{IC} (stage III). It is generally accepted that the crack acceleration in stage I is due to a combination of chemical and mechanical effects, whereas stage II growth rates are chemically controlled, and stage III crack acceleration is mechanically controlled. At present there exists no explanation which can either quantitatively or qualitatively account for the observed $\dot{a}(K,P,T)$ in any of the three stages of crack growth.

There seems to be, in the literature on this subject, general agreement that the following transport processes are involved in the ghe of steels and may be represented by the following series of consecutive steps: (a) physisorption, (b) chemisorption (this may include a molecular

0022–2461/79/112703–06 $02.60/0

chemisorption followed by surface migration and dissociative chemisorption); (c) absorption (solution); (d) lattice diffusion. Since there is no *a priori* way of telling which of these transport steps is rate determining, in the next section, we refer to certain critical experimental observations to aid us in its identification. This is accomplished by further restricting the discussion to stage II crack growth where it is assumed that $\dot{a}_{\mathrm{II}} = \dot{a}(P, T)$.

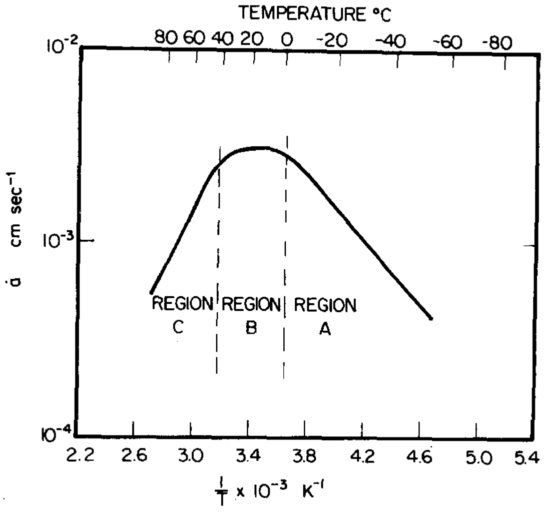

Figure 1 Temperature dependence of the slow crack-growth rate in 4130 steel (after Williams and Nelson [1]).

2. Observed kinetics

There have been a number of recent investigations exploring stage II crack-growth kinetics in steels during ghe. Williams and Nelson [1] investigated the embrittlement of 4130 steel. They found that in the temperature range of 80 to 25° C the crack-growth rate increased with decreasing temperature, and in the range of 0 to − 80° C the rate decreased with decreasing temperature. Their results at a single pressure are illustrated in Fig. 1, and may be expressed for other pressures in the general form, $\dot{a} \propto P_{\mathrm{H}_2}^{n}$, where n is equal to 0.5 in region A, 1.0 in region B, and 1.5 in region C. Of course, relations of this form are meaningful only if the crack velocities are taken from the stage II portion of the log $\dot{a}$–K curve where approximate K independence is observed, However, their work was done at constant K (using a tapered double cantilever beam specimen) so that it is not clear as to whether or not the K value at which the testing was done corresponded to stage II growth. Wei and co-workers [2, 3] have investigated crack-growth kinetics in the ghe of 18 Ni (200) and 18 Ni (250) maraging steels. Their results, definitely for stage II, are in agreement with the low-temperature (region A) results of Williams and Nelson. For region B, Wei and co-workers found $0.8 < n < 1.2$, and for region C no slow crack growth was observed at all. On the other hand, Kerns and Staehle [4], Johnson [5]. and Sieradzki and Ficalora [6] have reported results in region B which are in close agreement with those of Williams and Nelson. The general state of affairs of the kinetics in ghe is described in Table I, which indicates that region A and region B behaviour may be represented by

$$\begin{aligned} &\dot{a} \propto P_{\mathrm{H}_2}^{n}; \quad n \simeq 1 \text{ (stage II region B)} \\ &\dot{a} \propto P_{\mathrm{H}_2}^{1/2} \quad \text{(stage II region A).} \end{aligned} \tag{1}$$

The occurrence of the fractional exponents reported by some investigators (Table I) is discussed at the end of this section.

Table II contrasts various transport processes with respect to their feasibility as serving as the rate-controlling step in ghe in terms of critical experimental observations. For example, if the crack velocity in stage II is examined as a function of temperature, a rather sharp maximum is observed as illustrated in Fig. 1. If diffusion were rate limiting, a monotonic increase in crack velocity with temperature (in the range $-80°\mathrm{C} \leqslant T \leqslant 80°\mathrm{C}$)

TABLE I A summary of kinetic investigations for the ghe of steels

Investigator(s)	Materials	Temperature dependence		
		Region A	Region B	Region C
Williams and Nelson [1]	4130 Steel	$\dot{a} \propto P_{\mathrm{H}_2}^{1/2}$	$\dot{a} \propto P_{\mathrm{H}_2}^{1}$	$\dot{a} \propto P_{\mathrm{H}_2}^{3/2}$
Hudak and Wei [2] Gangloff and Wei [3]	18-(200) and 18-(250) Maraging Steel	$\dot{a} \propto P_{\mathrm{H}_2}^{1/2}$	$\dot{a} \propto P_{\mathrm{H}_2}^{n}$ $0.8 < n < 1.2$	No slow crack growth observed
Kerns and Staehle [4]	4335 Steel	–	$\dot{a} \propto P_{\mathrm{H}_2}^{0.95}$	–
Johnson [5]	H-11 Steel	–	$\dot{a} \propto P_{\mathrm{H}_2}^{1}$	–
Sieradzki and Ficalora [6]	4340 Steel	–	$\dot{a} \propto P_{\mathrm{H}_2}^{1}$	–

TABLE II Contrasting transport processes as rate-limiting steps in the ghe of steels

Rate-limiting step/experimental observation	No observed incubation	Crack velocity behaviour with temperature	Activation energy for crack growth
Adsorption	Consistent	?	Consistent
Lattice diffusion	Consistent (Rice [8])	Inconsistent	Consistent

would be expected. Since this does not occur, lattice diffusion cannot serve as the rate-limiting step. A comparison of the activation energies for adsorption and diffusion with that of the crack velocity turns out not to be informative with respect to the identification of the rate-limiting step. Srikrishnan and Ficalora [7] have pointed out that the activation energies for adsorption and diffusion in the H_2/Fe system are too close to allow for a definitive conclusion based on such evidence. The lack of an observed incubation period does not serve to differentiate between adsorption and diffusion either. As Rice [8] has pointed out, required diffusion distances may be quite small (~ twice the crack-tip opening displacement) resulting in what may appear experimentally as no incubation period.

Tien *et al.* [9] have developed a kinetic model for hydrogen transport in ghe first proposed by Bastien and Azou [10]. This concept involves hydrogen transported in the form of Cottrell atmospheres on moving dislocations. They argue that this is the rate-determining step in the ghe of steels. According to their model, hydrogen transported this way can be deposited when moving dislocations intersect a void or when moving dislocations annihilate. In this manner they postulate that hydrogen may precipitate at discontinuities leading to substantial non-equilibrium pressures for purely kinetic reasons. Oriani and Josephic [11, 12] have emphasized that ghe behaviour is observed if specimens are first preloaded and subsequently subjected to a gaseous hydrogen environment. Although the arguments of Oriani and Josephic are meant to apply to K threshold or equilibrium conditions (in terms of possible mechanisms for ghe), transport processes must still be operative for cracking to occur. This seems to preclude the operation of the model suggested by Tien *et al.* Johnson and Hirth [13] have analysed such kinetic pressure models in terms of hydrogen transport via moving dislocations. They conclude that only very small pressure increases (~ 1%) over the external hydrogen test pressure can occur. Furthermore, they show that the model predicts that dynamic pressure increases are directly proportional to the strain rate and point out that hydrogen embrittlement effects increase with decreasing strain rates.

In an indirect way the evidence strongly suggests that a surface process is rate limiting during sustained load cracking. Fig. 1 indicates that there is a temperature dependent change occurring in the rate-controlling step. In region A the crack-growth process is activated; whereas in region B the cracking process becomes non-activated. If a surface process is rate controlling, this transition in the rate-limiting step should be a function of both temperature and pressure. Indeed, some results of Gangloff and Wei [3] schematically illustrated in Fig. 2, indicate that this is the case. For each pressure, three regions of temperature dependence were

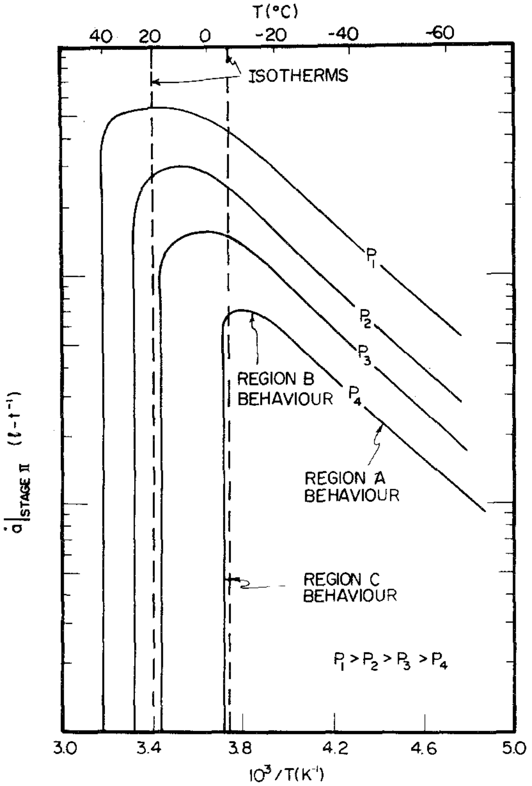

Figure 2 Schematic illustration of the P_{H_2}–T effect on crack-growth rate (after Gangloff and Wei [3]).

observed. In the next section we discuss the strong parallelisms which exist between ghe and the adsorption of hydrogen on iron. We also show how a knowledge of this adsorption leads to the qualitative crack velocity–pressure relations observed in stage II.

We return now to the matter of the fractional pressure exponents as observed by some investigators in region B. Gangloff and Wei [3] have previously addressed this issue. Fig. 2 illustrates that unique values of the pressure exponent (n) may be expected only when the isothermal lines intersect curves (defining stage II crack growth) such that the points belong to a common region of temperature dependence. The crack velocities in relations of the type $\dot{a} \propto P^n_{H_2}$ (for any region) are restricted in that all the growth rates must be limited by the same rate-controlling step. Strictly this may preclude the comparison of crack velocities over large pressure ranges at the maxima (or in region B) along an isotherm. If, however, one chooses to use isotherms in describing region B behaviour then the maximum at the highest and lowest pressures can serve as temperature limits for the isothermal lines. The isotherm defined by the maximum at the highest pressure may pass through C regions of the lower pressures leading to pressure exponents $n \geqslant 1$. On the other hand, the isotherm defined by the maximum at the lowest pressure may pass through A regions of the higher pressures leading to $1 \geqslant n > \frac{1}{2}$. Over smaller pressure ranges, the two "limiting" isothermal lines approach each other and n approaches unity from both sides. In general, the temperature difference (ΔT) between the isothermal lines will be a function of the material investigated. For some materials (over small enough ranges in pressure) a negligible ΔT may occur so that pressure exponents equal to unity may be observed in region B. We expect this to have been the case for the materials tested (at the pressures tested) by Williams and Nelson [1], Kerns and Staehle [4], Johnson [5] and Sieradzki and Ficalora [6] (Table I).

3. Adsorption as the rate-limiting step

Information regarding the nature of the adsorption of hydrogen on iron is very important in the understanding of the sustained load cracking results described in Table I.

Hydrogen is known to chemisorb readily on an iron surface from temperatures of at least 500 to 600 K down to liquid nitrogen temperatures [14, 16]. Porter and Tompkins [17] have found that the adsorption of hydrogen on iron obeys a Temkin isotherm and these results have been confirmed by Pecora and Ficalora [16]. An investigation concerning the effect of gaseous additives (SO_2, O_2, CO_2, N_2O, and H_2S) on hydrogen adsorption was performed by Srikrishnan and Ficalora [7]. Their results clearly indicate that there exists a strong parallelism between the effects of impurity gases on hydrogen adsorption and crack-growth studies performed in a hydrogen environment with the same gaseous impurities. Using a magnetization technique developed by Selwood [18], Artyukh *et al.* [19] and Pecora and Ficalora [16] have investigated the adsorption of hydrogen on an iron surface. Above room temperature, the magnetization change, which is proportional to the amount of hydrogen chemisorbed, was found to increase, and below room temperature a decrease was observed. This behaviour was attributed to two different types of adsorbed species; a low temperature H^+ or H_2^+ species, and a high temperature H^- species which compete to produce no net change in magnetization at room temperature. These results have recently been duplicated using a different magnetization technique [20] (i.e. vibrating magnetometer).

This evidence indicating two different types of adsorbed species of hydrogen, finds much support in the literature. The low temperature or type C adsorbed state, (not to be confused with the labelling of regions in Fig. 1), which we identify as the H_2^+ or H^+ species, desorbs rapidly with increasing temperature. This species has a very low activation energy for adsorption $E_a^c \sim 0\,kJ\,mol^{-1}$, and a heat of adsorption, $\Delta H_a^c \sim -25$ to $-30\,kJ\,mol^{-1}$ [21, 22]. At higher temperatures, the type A adsorption, which we equate to the H^- species, predominates. It is characterized by an activation energy $E_a^A \sim 25$ to $38\,kJ\,mol^{-1}$ [17] and a heat of adsorption $\Delta H_a^A \sim -126\,kJ\,mol^{-1}$ [21]. Owing to the large differences in the heats of adsorption, the C species may be considered mobile while the A species is rather immobile.

The adsorption of hydrogen on iron can be schematically represented by the following reaction,

$$P_{H_2} \xrightarrow{K_1} [H_2]_{VDW} \underset{k_1}{\overset{K_2}{\leftrightarrows}} \frac{2}{X}[H_X^+]_C \underset{k_2}{\leftrightarrows} 2[H^-]_A; \quad 1 \leqslant X \leqslant 2 \qquad (2)$$

where K_1 and K_2 are equilibrium constants and

k_1 and k_2 are rate constants. Molecular hydrogen in the gas phase rapidly forms a Van der Waals (VDW) type physisorbed state. It is followed by a type C adsorption (surface reaction) which is followed by a type A adsorption at rates dependent upon temperature and pressure. We have chosen to designate the C species as $[H_X^+]$ to indicate that this species is either an H^+ or a stretched H_2^+ (chemisorbed) species. The subscript X should be interpreted as being equal to or very close to unity. The activation energy for C adsorption is very small and the heat of adsorption is such that coverage can be maintained at low temperatures (and at pressures relevant to ghe studies) so that $\theta^C \simeq 1$. The types C and A adsorptions will in general occur on physically distinct sites, so that $\theta^C \simeq 1$ represents fully occupied C sites. At these same temperatures $\theta^A \ll 1$ since E_a^A is large and the rate of adsorption (or migration) to A sites is governed by the Boltzmann factor. At temperatures near room temperature the activation energy for desorption from the C sites (~ 25 kJ mol^{-1} is low enough to permit rapid desorption and migration to A sites governed by the exponential in the equation for desorption. This means that $\theta^C < 1$ and there is a slower uptake (capture rate) from the gas phase to the C sites at these temperatures.

The A species with its high heat of adsorption is relatively immobile on the surface and is postulated to be the embrittling species. It is the mobility of the C species through which the type A forms which allows the build up of high enough concentrations of $[H^-]_A$ at the crack tip region such that an observable embrittling effect is produced. Even though $[H^-]_A$ forms well above room temperatures, the adsorption does not proceed via the mobile precursor state (type C) so that large enough concentrations of $[H^-]_A$ will not necessarily exist at critical regions, for slow crack growth to occur. This phenomenon manifests itself in the decrease of crack velocity with increasing temperature (region C) in sustained load slow crack-growth testing. The weaker embrittlement occurring at these temperatures relates to the poorer mobility of the A species and the gradual disappearance (with temperature) of the C species.

We assume that for a particular material and at a particular value of stress intensity, K, the fractional coverage, θ^A, must reach a value corresponding to a critical concentration at the crack tip region before crack growth occurs. The crack growth rate may then be expressed as

$$\dot{a} \propto \left[\frac{\partial \theta^A}{\partial t}\right]_{\theta_{\text{crit}}} \tag{3}$$

At low temperatures (Fig. 1, region A) the rate of formation of the A species, $d\theta^A/dt$, is governed by the reaction

$$\frac{2}{X}[H_X^+]_C \xrightarrow[k_2]{} 2[H^-]_A,$$

and the adsorption of the VDW layer and the type C species is rapid so that

$$[H_2]_{VDW} = K_1 P_{H_2}$$

and,

$$\begin{aligned}[H_X^+]_C &= (K_2[H_2]_{VDW})^{X/2} \\ &\approx (K_1K_2P_{H_2})^{1/2}; \qquad X = 1.\end{aligned} \tag{4}$$

The rate of chemisorption of the A species is given by

$$k_2\,(K_1K_2P_{H_2})^{1/2}$$

or

$$\dot{\theta}^A = k' P_{H_2}^{1/2} \exp(-E_a/RT), \tag{5}$$

so that we obtain a relation of the form

$$\dot{a} \propto P_{H_2}^{1/2} \left.\begin{matrix}\text{region A}\\ \text{stage II.}\end{matrix}\right\} \tag{6}$$

At higher temperatures (region B) we are concerned only with the A species which forms via the mobile C state, since the mobility of the C state is assumed to be a prerequisite to slow crack growth. At these temperatures the filling of the C sites becomes rate determining so that the rate of chemisorption is

$$k_1K_1P_{H_2},$$

and

$$\dot{a} \propto P_{H_2} \left.\begin{matrix}\text{region B}\\ \text{stage II.}\end{matrix}\right\} \tag{7}$$

Equations 6 and 7 are to be compared to Equation 1. The activation energies predicted by the analysis are consistent with those observed in regions A and B during sustained load cracking [1–3].

The analysis also allows us to make some interesting observations. For typically B and C temperature regions the activated step may become rate determining if the hydrogen pressure is high enough. The increased pressure will tend to keep the C sites full and counteract the effect of temperature which tends to empty the C sites. Converseley, for typically A temperature regions the $H_{2(g)} \leftrightharpoons 2[H^+]_C$ reaction could become rate determining at very low pressures ($\ll 1$ Torr) since the filling of the C sites is again difficult under these conditions. This is probably not relevant to ghe since at these lower pressures and temperatures no cracking is likely to occur due to the difficulty in maintaining large concentrations of the A species under these conditions.

4. Conclusions

We have suggested that in ghe, sustained load cracking in stage II may be represented by a function of the form $\dot{a} \propto P_{H_2}^n$ where n has unique values (0.5 in region A and 1.0 in region B) under a prescribed set of conditions. This further supports experimental results first reported by Williams and Nelson [1]. The analysis presented provides strong evidence that a surface process is crack-growth rate limiting in that a consistent picture in terms of pressure functionalities and activation energies results.

Perhaps the most interesting concept incorporated in to the analysis is the required presence of a mobile species for slow crack growth to occur. This concept could be tested by studying embrittlement with other gases which adsorb strongly enough on iron so that the ad-atom can be considered immobile. Unfortunately, such an approach involves the intrinsic assumption that the embrittlement mechanism not change from one gas species to another.

Acknowledgements

The authors are grateful for the support of the Niagara Mowhawk Power Corporation in sponsoring this research. K. S. also wishes to acknowledge the support of the Ames Lab of the USDOE during the preparation of the manuscript.

References

1. D. P. WILLIAMS and H. G. NELSON, *Met. Trans.* **1** (1970) 63.
2. S. J. HUDAK and R. P. WEI, *Met. Trans.* 7A, (1976) 235.
3. R. P. GANGLOFF and R. P. WEI, *Met. Trans.* **8A** (1977) 1043.
4. G. E. KERNS and R. P. STAEHLE, *Scripta Met.* **6** (1972) 1189.
5. H. H. JOHNSON, "Hydrogen in Metals", edited by I. M. Bernstein and A. W. Thompson (ASM, Metals Park, Ohio, 1974) p. 35.
6. K. SIERADZKI and P. J. FICALORA, "Environmental Degradation of Engineering Materials", edited by M. R. Louthan and R. P. McNitt (Virginia Polytechnic Institute, 1977) p. 523.
7. V. SRIKRISHNAN and P. J. FICALORA, *Met. Trans.* 7A (1976) 1669.
8. J. R. RICE, US AEC Report no. 26 (1974).
9. J. K. TIEN, A. W. THOMPSON, I. M. BERNSTEIN and R. J. RICHARDS, *Met. Trans.* 7A (1976) 821.
10. P. BASTIEN and P. AZOU, "Proceedings of the First World Metal Congress" (ASM, Metals Park, Ohio, 1951) p. 535.
11. R. A. ORIANI and P. H. JOSEPHIC, *Acta Met.* **22** (1974) 1065.
12. *Idem, ibid* **25** (1977) 979.
13. H. H. JOHNSON and J. P. HIRTH, *Met. Trans.* 7A (1976) 1543.
14. D. O. HAYWARD and B. M. W. TRAPNELL, "Chemisorption" (Butterworth, London, 1964) p. 67.
15. P. H. EMMETT and R. W. HARKNESS, *J. Amer. Chem. Soc.* **57** (1935) 1631.
16. L. M. PECORA and P. J. FICALORA, *Met. Trans.* 8A (1977) 1841.
17. A. S. PORTER and F. C. TOMPKINS, *Proc. Roy. Soc. London* **A217** (1953) 529.
18. P. W. SELWOOD, "Chemisorption and Magnetization" (Academic Press, New York, 1975).
19. E. N. ARTYUTH, N. K. LUNEV and R. T. RUSOV, *Kinet. Katal.* **13** (1972) 741.
20. C. RANSOM, Dissertation, Syracuse University (1979).
21. G. C. BOND, "Catalysis by Metals" (Academic Press, New York, 1962) p. 93.
22. M. R. SHANABARGER, *Surface Sci.* **52** (1975) 689.

Received 13 March and accepted 11 April 1979.