

THE INFLUENCE OF GASEOUS HYDROGEN ON THE FRACTURE PROCESS IN Fe-2.6%-Si SINGLE CRYSTALS

H. Vehoff, W. Rothe, and P. Neumann

Max-Planck-Institut für Eisenforschung, 4000 Düsseldorf, F.R.G.

ABSTRACT

In hydrogen-assisted cracking the kinetics of crack growth and of the embrittlement process are strongly influenced by the microstructure. Therefore crack growth measurements were carried out with properly oriented Fe-2.6%-Si single crystals in ultra high vacuum as well as in high purity low pressure hydrogen gas. The brittleness of the fracture can be characterized quantitatively by the ratio $a_n = 2\Delta a / \Delta \delta$, where Δa is the crack growth increment and $\Delta \delta$ is the plastic crack tip opening increment. It is found, that a_n depends strongly on temperature and hydrogen pressure. It is shown, however, that a_n is a unique function of θ only, where θ is the surface coverage of hydrogen at the crack tip, which in turn depends on temperature and hydrogen pressure. $\theta(T, P_{H_2})$ can be described by a Langmuir isotherm for dissociative adsorption with a heat of desorption which is equal to the deepest adsorption state $E_d(\beta_2)$ of hydrogen on a Fe(100)-surface.

KEYWORDS

Single crystal; FeSi-alloy; stable crack growth; gaseous hydrogen; vacuum; hydrogen embrittlement; adsorption; surface coverage; heat of desorption.

INTRODUCTION

The embrittling effect of hydrogen on the fracture behavior of steels has been studied extensively over several decades. Different mechanisms are found to be operative in different ranges of hydrogen pressure (Oriani, 1978; Tetelman, 1974; Riecke, 1978). At low partial pressures of hydrogen (less than 0.1 MPa), hydrogen interacts with the metal and lowers the cohesive strength of the lattice (Oriani and Josephic, 1977). The decohesion theory postulates that regions exist near the crack tip with hydrogen concentrations, which are several orders of magnitude larger than the lattice concentration of hydrogen. These high concentrations can only be explained by trapping of hydrogen at dislocations, microcracks, grain boundaries or other traps (Kumnick and Johnson, 1980). Therefore the microstructure strongly influences the embrittlement process and the crack growth kinetics. Thus it can be expected, that the experimental study of the mechanism of gaseous hydrogen embrittlement is facilitated by studying the process at the crack tip in

its simplest form under the most simple boundary conditions (Lynch, 1979). For these reasons FeSi-single crystals were used, since the microprocesses for ductile and brittle fracture are well known in this alloy (Vehoff and Neumann, 1979, 1980). Near the typical V-shaped crack tips, which are found in properly oriented FeSi-single crystals (Neumann, Vehoff, and Fuhlrott, 1977), a high concentration of hydrogen is expected only at the dislocation cores (Hirth and Carnahan, 1978) or on the crack tip surface. Stable crack growth tests in tension are carried out at different temperatures and hydrogen pressures in order to investigate the influence of the hydrogen concentration at the crack tip on the brittleness of the fracture process and on the crack growth kinetics (Williams and Nelson, 1970; Gangloff and Wei, 1977). The experimental results are used to obtain a quantitative relationship between the surface coverage of hydrogen at the crack tip and the brittleness of the fracture process.

EXPERIMENTAL PROCEDURE

Crack growth tests on pre-cracked Fe-2.6%-Si single crystals are carried out in a closed loop hydraulic system under plastic strain control. The crack growth tests were done in tension. After a constant increment of the plastic crack tip opening $\Delta\delta$, a striation was produced on the fracture surface by unloading the specimen. The distance between these striations characterizes the crack advance Δa after a constant plastic crack tip opening increment $\Delta\delta$. The ratio of Δa (the projection of the striation spacing on the plane perpendicular to the specimen axis) and $\Delta\delta/2$, $a_n = 2\Delta a/\Delta\delta$, characterizes the fracture process. a_n is a measure of the brittleness of the fracture process. $a_n = \sqrt{2}$ characterizes perfectly ductile rupture by alternating slip for the orientation used. $a_n \rightarrow \infty$ characterizes perfectly brittle fracture. For more details of the measurement of a_n , and the specimens used, see Vehoff and Neumann (1980). Care must be taken, however, since this definition of a_n for tensile crack growth is not identical with the definition of a_n for cyclic crack growth, which was used in previous papers.

In vacuum below a critical crack tip opening rate $\dot{\delta}_c(T)$ the crack propagates in a ductile manner (Vehoff and Neumann, 1980). Below $\dot{\delta}_c(T)$, a_n does not depend on temperature and on the crack tip opening rate in vacuum as well as in air (Neumann, Fuhlrott, and Vehoff, 1979). In this work $\dot{\delta} = 0.1 \mu\text{m/s}$ was chosen. This value is smaller than $\dot{\delta}_c(T)$ for all temperatures examined. Crack growth would be perfectly ductile, $a_n = \sqrt{2}$, in all experiments, if they would have been carried out in vacuum instead of the hydrogen environment. Therefore all embrittling effects characterized by $a_n > a_n^{\text{duct}} = \sqrt{2}$ are due to the hydrogen environment.

The experiments were carried out in an ultra high vacuum chamber. After pre-cracking, the specimen chamber is evacuated to pressures of less than 1 μPa . Then hydrogen gas (99.999% purity) purified by a gas purifier (Oxisorb) and by a liquid nitrogen cold trap is filled into the specimen chamber. The residual gas purity is controlled by a mass spectrometer. In order to minimize the contamination of hydrogen due to surface reactions with the walls of the specimen chamber the gas flow is controlled to give residual impurity concentrations of less than 0.1% in the hydrogen gas at all pressures. Whenever the test pressure is changed, the specimen chamber is evacuated to pressures of less than 1 μPa .

At all temperatures the specimen as well as the walls of the specimen chamber are held at the same temperature in order to obtain thermal equilibrium. This is very important for hydrogen pressures of less than 1 Pa, because in this pressure range the mean free path in the gas is larger than the specimen chamber dimensions.

RESULTS AND DISCUSSION

Figure 1a shows the V-shaped crack tip, which was opened up in vacuum until $\Delta\delta = 40 \mu\text{m}$. Afterwards the crack was further opened up in gaseous hydrogen by $\Delta\delta = 5 \mu\text{m}$ yielding a total $\Delta\delta$ of 45 μm . Figure 1b shows the corresponding force-plastic elongation curve. In vacuum the low a_n -value of 1.4 (perfectly ductile) corresponds to a crack tip opening angle of $\alpha = 71^\circ$ (equal to the angle between two (112)-slip planes). In Fig. 1a these parts of the fracture surface, from which the two slip bands emanate, form an angle of 71° . In hydrogen higher a_n -values corresponding to lower crack tip opening angles are found (in Fig. 1a the sharp crack extends down into the area between the two slip bands). The increase in a_n compared to the vacuum value therefore indicates a change in the crack growth mechanism.

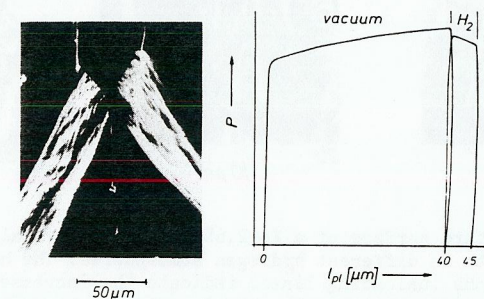


Fig. 1. Crack tip and plastic zone at the side surface of a FeSi-single crystal (Orientation: $\langle 100 \rangle$ specimen axis, $\langle 110 \rangle$ direction of the crack front). The crack tip opening angle changes from 71° in vacuum to a smaller value in gaseous hydrogen (Fig. 1a). Figure 1b shows the corresponding force-plastic elongation curve.

Figure 2 shows six photographs of a (100)-fracture surface, which were taken after crack growth at different hydrogen pressures. The photographs in the lower row are higher magnifications of the photographs above. The horizontal lines in the upper photographs (unloading lines) indicate the increase in crack length Δa after a constant increment of the plastic crack tip opening $\Delta\delta$ ($\Delta\delta = 10 \mu\text{m}$ used in our experiments). It is clearly visible, that Δa and hereby a_n is a function of the hydrogen pressure. With increasing hydrogen pressure the normalized crack advance a_n increases. Along with the increase of a_n , the surface roughness decreases with increasing hydrogen pressure.

For temperatures higher than 410 K, no effect of the hydrogen pressure is found in the pressure range examined ($P_{\text{H}_2} < 10 \text{ kPa}$). Below 290 K, a_n is a function of T, P_{H_2} and $\dot{\delta}$. Between 290 and 410 K, a_n is found to be independent of $\dot{\delta}$ for the rates used ($0.01 \mu\text{m/s} < \dot{\delta} < 10 \mu\text{m/s}$), and a function of T and P_{H_2} only. Therefore for this temperature range it is concluded that the hydrogen gas is in local equilibrium with the surface coverage θ at the crack tip. For different temperatures and pressures the same microstructural features are found on the crack surface, if only a_n is constant. We therefore suppose that the surface coverage of hydrogen at the crack tip θ is directly correlated with a_n : $a_n = f(\theta(T, P_{\text{H}_2}))$.

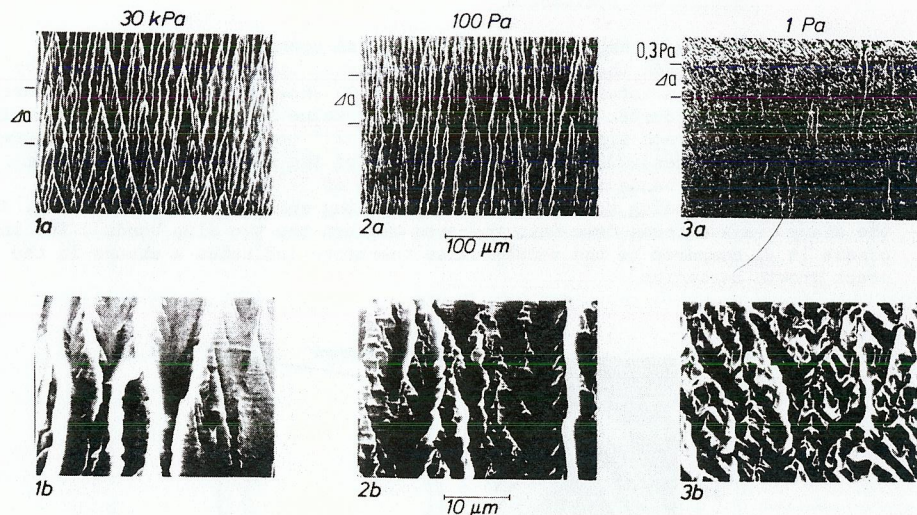


Fig. 2. (100)-fracture surface of a Fe-2.6%Si single crystal taken after stable tensile crack growth in different hydrogen atmospheres. The horizontal lines in the upper photographs (unloading lines) indicate the increase in the crack length Δa after a constant increment of the plastic crack tip opening $\Delta\delta$ ($\Delta\delta = 10 \mu\text{m}$, $\dot{\delta} = 0.1 \mu\text{m/s}$, $T = 303 \text{ K}$).

This assumption is confirmed by the following quantitative considerations.

For the dissociative adsorption of a monolayer the rate of adsorption r_a is given by the relationship (Clark, 1970)

$$r_a = \sigma \cdot (1-\theta)^2 \cdot n \cdot \exp(-E_a/kT), \quad (1)$$

where σ is the condensation coefficient, n is the number of H_2 molecules impinging on unit surface per second and E_a is the activation energy of adsorption.

From kinetic gas theory it follows that

$$n = P_{\text{H}_2} \cdot (2\pi mkT)^{-1/2}, \quad (2)$$

where m is the mass of the hydrogen molecule.

The rate of desorption r_d for dissociative adsorption is given by

$$r_d = k_d \cdot \theta^2 \cdot \exp(-E_d/kT), \quad (3)$$

where k_d is the evaporation coefficient and E_d is the activation energy of desorption.

For thermal equilibrium, equations (1) - (3) lead to the relationship

$$\sqrt{P_{\text{H}_2}} = b(T) \cdot \theta / (1-\theta), \quad (4)$$

where

$$b(T) = \sqrt{k_d/\sigma} \cdot (2\pi mkT)^{1/4} \cdot \exp(U/2kT),$$

and

$$U = E_a - E_d$$

is the heat of desorption.

The simplest possible assumption concerning $f(\theta)$ is a linear relationship

$$a_n = f(\theta) = \beta \cdot \theta + c \quad (5)$$

with

$$c = a_n^{\text{duct}} - \beta \cdot \theta_{\text{thr}} \quad (a_n^{\text{duct}} = \sqrt{2} \text{ for the orientation used}),$$

where θ_{thr} is the critical surface coverage for which the fracture mode changes from ductile to brittle.

For $\beta\theta \gg c$, equation (4) and (5) combines to

$$1/\sqrt{P_{\text{H}_2}} = 1/b(T) (\beta/a_n - 1). \quad (6)$$

Plotting $1/\sqrt{P_{\text{H}_2}}$ versus $1/a_n$ for constant temperatures must yield a straight line.

Figure 3 shows the results. The six straight lines intersect the abscissa at approximately the same value. This proves that a_n is proportional to θ with the same proportional factor β at all temperatures examined (Eq. (6)). Experiments in the transition range from ductile to brittle fracture (small θ -values) are in progress.

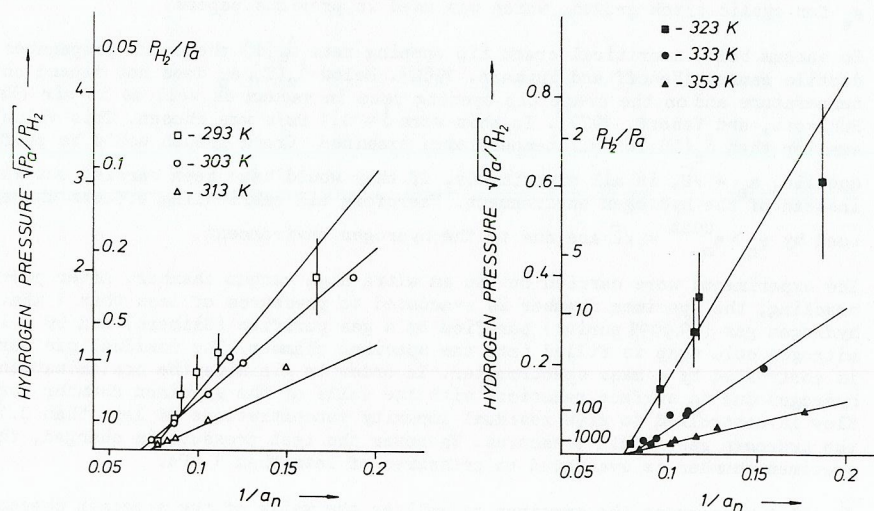


Fig. 3. $1/\sqrt{P_{\text{H}_2}}$ versus the reciprocal crack growth increment $1/a_n$ for different temperatures. The straight lines are fitted from equation (6).

For constant a_n equation (4) leads to

$$\log(P_{H_2}/Pa) = 2 \log(\theta/(1-\theta)) + \log(b_1(T)) + U/(kT) \log(e), \quad (7)$$

with

$$b_1(T) = (k_d/\sigma) (2\pi mkT)^{1/2} / Pa.$$

For high U -values ($U \gg kT$) the last term dominates and a plot of $\log(P_{H_2}/Pa)$ versus the reciprocal absolute temperature must give a straight line. Figure 4 shows the experimental results for two different a_n -values. The data are obtained from the fitted lines in Fig. 3. The error bars in Fig. 4 indicate the error due to the worstly fitted line in Fig. 3. The slopes of the lines in Fig. 4 give an activation energy $U = -102 \pm 10$ kJ/mol, which agrees with the desorption energy of hydrogen from Fe(100)-surfaces $E_d(\beta_2) = 100$ kJ/mol, measured by Boszos and co-workers (1978) from thermal desorption spectra.

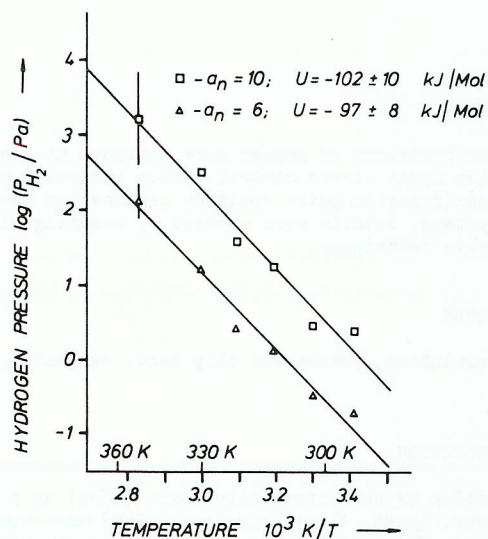


Fig. 4. The logarithms of the hydrogen pressures $\log(P_{H_2}/Pa)$, for which a constant a_n -value is obtained as a function of temperature. The data points are calculated from the fits given in Fig. 3. The straight lines are fitted from equation (7).

Thus our experiments show that in the pressure and temperature range examined the brittleness of a stationarily growing crack, characterized by a_n , is a unique linear function of the hydrogen coverage at the crack tip.

Experiments with temperatures below 290 K in which the hydrogen coverage is not in equilibrium with the gas phase for the δ -values used are in progress.

SUMMARY

1. At temperatures $T > 290$ K the brittleness of the fracture process in Fe-2.6%-Si single crystals characterized by the normalized crack growth increment a_n , is independent of the crack tip opening rate δ ($0.01 \mu m < \delta < 10 \mu m$), and only a function of temperature and hydrogen pressure.
2. For constant a_n the microstructure of the fracture surfaces is similar for different pressures and temperatures in the range examined.
3. The normalized crack growth increment a_n is found to be a unique, linear function of the surface coverage of hydrogen at the crack tip θ .
4. The temperature and pressure dependence of a_n , since a_n is proportional to θ , can be described by a Langmuir isotherm for dissociative adsorption with a heat of desorption, which agrees with the deepest adsorption state $E_d(\beta_2)$ of hydrogen on Fe(100)-surfaces.

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