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鋼鐵氫致裂縫成長之新看法

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Some New Aspects of Hydrogen-Assisted Crack Growth in Steels

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摘　要

論文描述氫脆在肥粒鐵鋼材中造成破裂機構的相關現象。裂縫前進的特徵是以在準劈裂區域上的條紋沿裂縫方向垂直傳遞。試片開口的效應可證實拉伸應力對裂縫生長的促進。本文亦對含3%矽之鐵合金中，寬尺度（0.3nm間距）及窄尺度（30nm間距）兩種條紋作出觀察。

關鍵詞彙：氫脆化，肥粒鐵，鐵矽合金，氫致脆裂，準劈裂，條紋

ABSTRACT

The paper describes features associated with the "brittle" cracking mechanism of hydrogen embrittlement in ferritic steel. Such crack advance is characterised by the presence of striations on "quasi-cleavage" facets running roughly orthogonal to the crack propagation direction. A notch effect is observed, from which is deduced that the cracking is promoted by tensile stress. In iron-3% silicon, observations have been made of both coarse-scale (0.3μm spacing) and fine-scale (30nm spacing) striations.

Key words: Hydrogen Embrittlement, Ferrite, Fe-Si Alloy, Hydrogen-Assisted Crack, Quasicleavage, Striations.

INTRODUCTION

It is clear that in many examples of "corrosion-fatigue" crack propagation in steels, the "corrosion" component is associated not with the anodic dissolution of material *from* the growing crack tip, but with the cathodic generation of hydrogen, which enters the material *ahead of* the crack tip and facilitates decohesion. The mechanisms leading to such decohesion are not fully agreed: views range from attribution to a "brittle" cracking mechanism, akin to cleavage fracture in mild steel,[1,2,3] to a mechanism involving the easier generation of slip dislocations from the crack tip.[4] In a number of quenched-and-tempered steels, the crack follows an intergranular path, which is attributed to interactions between hydrogen and trace impurity elements segregated at grain boundaries.[5]

The present paper addresses a particular aspect of hydrogen-assisted crack growth in steels which relates to a "brittle", "striated" mode of crack advance observed in high-chromium ferrite, such as the alpha-phase in duplex stainless steel. For such material, similar fracture surfaces are observed for fatigue-

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cracks propagated in high-purity water, in brine and in hydrogen gas.[6,7] In each case, "brittle" striations are observed and the "cyclic cleavage" is attributed to sequential increments of "hydrogen embrittlement". Rather similar features have been observed on "quasi-cleavage" facets in hydrogen-charged mild steel, tested in tension at low strain rate, and on facets in hydrogen-charged silicon-iron.[8,9] The paper briefly summarises these earlier results and draws attention to new findings in silicon-iron. (see also[10,11]).

EXPERIMENTAL

The composition of the mild steel was 0.15C, 0.71 Mn, 0.19Si, 0.009P, 0.01S and the heat-treatment given to it was 6h at 1050°C, followed by furnace cooling to produce an average grain size of 100μm. Testing was carried out on uniaxial specimens and notched specimens, both uncharged and charged electrolytically from 0.8N sulphuric acid solution, "poisoned" with trace amounts of arsenic. Diffusive hydrogen concentrations of 1.7ppmw (2mAmm^{-2} for 1h), 3ppmw (2 mAmm^{-2} for 2h), and 4.15ppmw (6 mAmm^{-2} for 2h) were determined at room temperature, using a modified mercury replacement method. Tests were carried out over a temperature range from 20°C to -130°C at a nominal strain-rate of $3.6\times10^{-4}s^{-1}$. Fracture surfaces were examined using a Camscan scanning electron microscope (SEM), fitted with an energy-dispersive X-ray microanalysis (EDX) system.

The fractography for silicon-iron was carried out on large, nominally-flat cleavage facets, obtained by inducing internal hydrogen cracks in quasi-single-crystals. Polycrystalline Fe-3Si sheet was cold-rolled to a reduction of 20% and was then annealed at 1200°C to produce a microstructure with grains extending through the sheet thickness. Test specimens, measuring 4×4×10mm were polished to 1200 SiC grit and were charged, at 5 mAmm^{-2} in 0.8 N H_2SO_4 "poisoned" with 4mgl^{-1} As_2O_3. After a period of time, orthogonal traces of cracks were observed on the specimens' surfaces. Specimens were notched parallel to one set of traces and were then fractured at -196°C. Fracture surfaces were examined, using a conventional JEOL 5200 SEM, operating at 25kV, and a high-resolution Hitachi S 4000 SEM fitted with a field-emission gun (FEG), operating at 15-25kV. On this latter instrument, electron diffraction backscatter patterns (EBSP) could be obtained, over a scan area of approx. 0.2μm×0.4μm. The surfaces were also examined, using a Nanoscope III atomic force microscope (AFM) and a Nanoscope II scanning tunnelling microscope (STM).

RESULTS

The RA% of charged, mild steel uniaxial tensile specimens exhibits a broad minimum over the temperature range -33°C to -80°C (RA% approx. 40%) whereas the RA% for uncharged specimens over this range remains high (greater than 65%): see Fig. 1. The fracture surfaces of charged specimens in this range exhibit "quasicleavage" facets, with river-lines radiating outwards from a central particle, of a few μm in diameter. Such particles were identified as MnS, using EDX analysis. Running roughly orthogonal to these river-lines were "striations"; sometimes matching on both sides of the fracture surface; sometimes not matching. The spacing of these striations was of order 1-5μm and, on cursory examination, there was no major difference in the spacing of striations at -33°C and those at -80°C: see Fig. 2. Etch-pitting of the fracture surface revealed that the facets corresponded macroscopically to {001} planes and

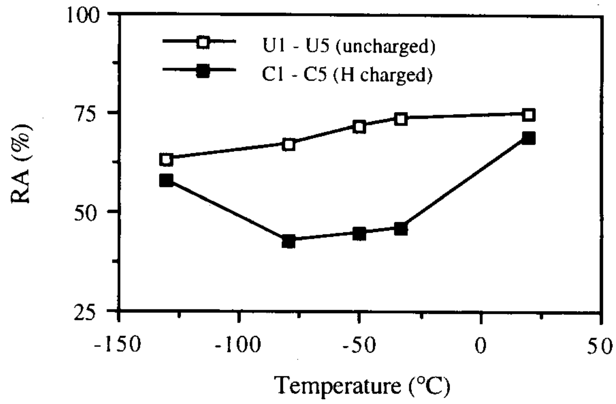
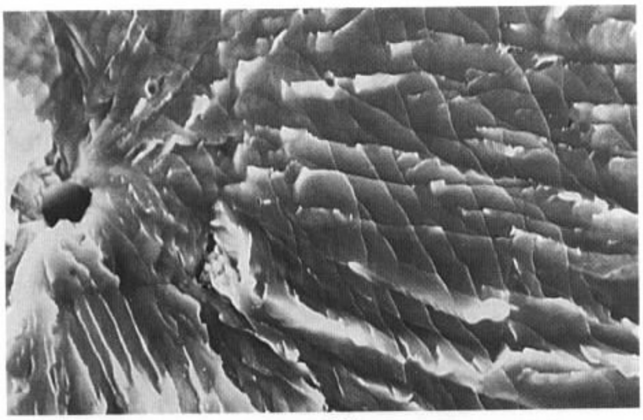
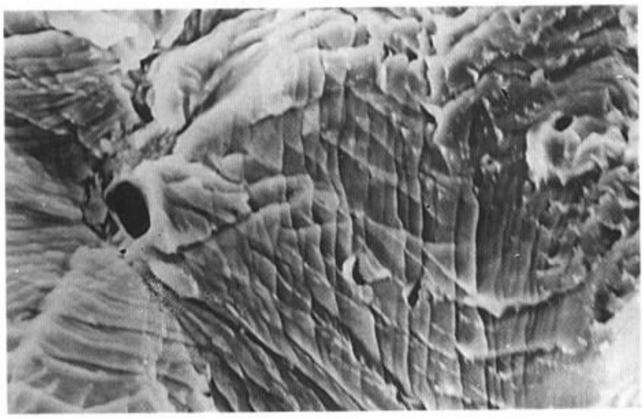


圖 1 充氫與未充氫試片之面積收縮率隨溫度的變動

Fig. 1 Variation of RA% with temperature for uncharged tensile specimens and hydrogen-charged specimens (courtesy Y.Togn).



(a)



(b)

圖 2 充氫軟鋼中準劈裂區域上之條紋
(a)在-30°C (b)在 80°C

Fig. 2 Striations on "facets in hydrogen-charged mild steel a) at -30°C, (b) at 80°C.

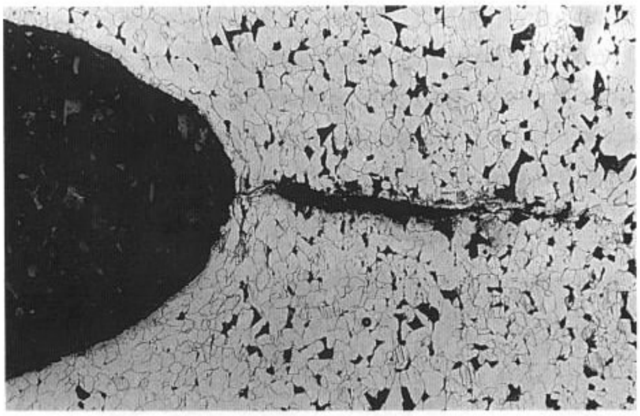


圖 3 充氫軟鋼試片在室溫下拉伸之截面圖。在此溫度，單軸向拉伸試片出現75%的面積收縮率和100%的纖維式破壞

Fig. 3 Section through notched tensile specimen of hydrogen charged mild steel, tested at room temperature. At this temperature, a uniaxial specimen exhibits 75% RA (see Fig. 1) and 100% fibrous fracture. (courtesy Y.Tong).

that the striations were parallel to <110>, with the crack propagation directions (cpd) being <110>. Metallographic sections revealed that the cracks apparently propagated in a discontinuous manner.[8] An important finding was that quasi-cleavge facets could be obtained in notched specimens at a temperature for which uniaxial specimens exhibited fully ductile behaviour, with 75%RA: see Fig. 3. Uncharged, uniaxial specimens fractured at -196°C again exhibited {001} cleavage facets, with the cpd apparently <110>, but no striations could be detected.

The hydrogen-charged Fe-3Si specimens exhibited internal cracks, nucleated from inclusions of approximately 10μm in size and containing Mn, S and Al. These internal cracks had a square symmetry, revealed as the boundary between the internal crack, induced at room temperature, and the subsequent fast cleavage fracture, produced at -196°C: see Fig. 4. The internal cracks were attributed to hydrogen-assisted "stable" crack growth (H-SCG) and examination of their surfaces in the SEM revealed river lines radiating outwards from the inclusion nucleation site, together with striations, lying roughly orthogonal to the river-lines, spaced at 0.3μm. The crack front was jogged on the 0.3μm scale and was not precisely parallel to the striations, which were inclined at a small angle to the front: see Fig. 5. Closer examination in the FEG SEM showed a fine structure between the 0.3μm striations, consisting of irregular rounded steps on a scale of some 15-30nm. No striations were observed on the "fast cleavage" fracture surfaces obtained at -196°C. Electron back-scatter patterns (EBSP) were obtained from the fracture surfaces corresponding to "fast cleavage" and to H-SCG. The orientation between the specimen surface and the microscope axis was used to confirm the {001} cleavage plane in both cases. The EBSP for the "fast cleavage" fracture was sharp, whereas that for the H-SCG fracture was diffuse: see Fig. 6.

The AFM results confirmed the presence of striations on H-SCG facets, of spacing approximately 0.3μm and height approximately 0.05μm. The AFM probe was not sufficiently sharp to resolve fine detail between the 0.3μm striations, but use of the STM revealed the presence of finer features, having a spacing of some 15-30nm and a height of 15-20nm: see Fig. 7. Transmission electron microscopy (TEM) was used to examine the region around a (ductile, shear) crack tip in a TEM thin foil. Slip within the plastic zone ahead of the crack tip was found to be

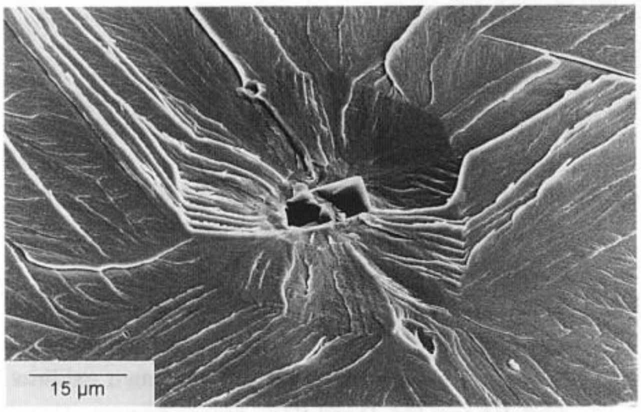


圖 4 氫裂縫起始於矽鐵合金中之非鐵金屬的夾雜物。在-196°C時，一些裂縫產生後，試片接著以快速的劈裂破壞。

Fig. 4 Hydrogen crack initiated at a non-metallic inclusion in silicon-iron. After some cracking, the specimen was fractured by fast cleavage fracture at -196°C. (courtesy T.J. Marrow).

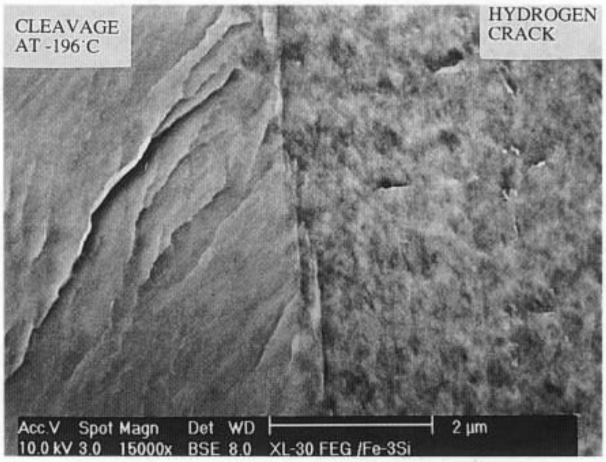


圖 5 矽鐵合金中的『寬』尺度(0.3μm)條紋。注意裂縫前端出現階梯狀的外觀

Fig. 5 "Coarse"-scale (0.3μm) striations in iron-silicon alloy. Note the "jogged" nature of the crack front. (courtesy T.J. Marrow).

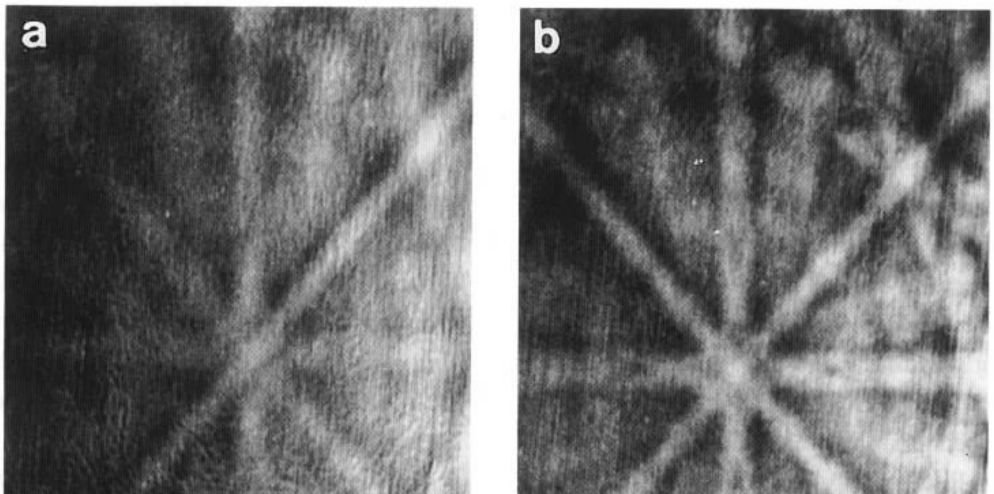


圖 6 氫裂縫（較模糊）及快速劈裂（較清晰）的背向散射電子圖形

Fig. 6 Electron back-scattered patterns (EBSP) for hydrogen crack (diffuse) and fast cleavage (sharp): (courtesy T.J. Marrow).

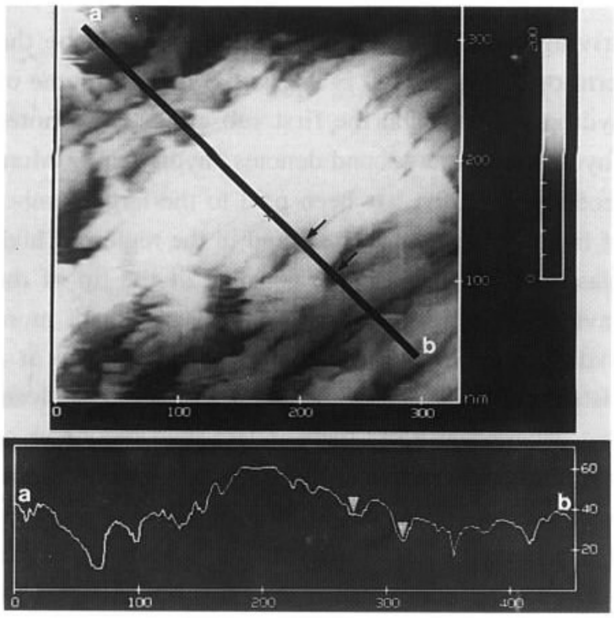


圖 7 掃描穿隧式電子顯微鏡對『窄』尺度(30nm)條紋的觀察

Fig. 7 Scanning Tunnelling Microscope (STM) observations of "fine"-scale (30nm) striations (courtesy T.J. Marrow).

planar, with slip-spacings of approximately 15-20nm. Both {110} and {112} slip-plane traces were observed.

DISCUSSION

The striations seen on hydrogen-induced fracture surfaces in both mild steel and silicon iron are similar to those observed in chromium-rich ferrites and in other experiments on silicon iron.[2,9] The crystallography is such that the facets correspond macroscopically to {001} planes, with striation directions parallel to $<1\bar{1}0>$ and cpd parallel to <110>. There is evidence for slip on {112} planes at room temperature from the present TEM results and there is further evidence that {112} slip is significant at low temperatures. The EBSPs indicate that the striations are associated with plastic strain (because the pattern is blurred), although the same crystallography is obtained for "fast cleavage" at -196°C, where the EPSB remains sharp. There is superficial similarity between the striations observed on the hydrogen-induced facets and "striations" observed on the fatigue surfaces of fcc metals, which exhibit planar slip (underaged Al-Cu alloys; austenitic stainless steel and Cu-Al alloys, having low stacking-fault energy). These have been attributed to "alternating slip" mechanisms, giving rise to macroscopic {001} surfaces.[12,13,14]

It is of interest that the observed crystallography is consistent with the movement of (a/2) $<\bar{1}\bar{1}1>$ slip dislocations on {112} planes, either to give symmetrical crack-tip blunting and opening, or a fine-scale "zigzag". Specifically, for the (001) plane, we have the movement of (a/2) [111] on $(\bar{1}\bar{1}2)$ and (a/2) $[\bar{1}\bar{1}1]$ on (112) to give

$$(a/2)\,[111] + (a/2)\,[\bar{1}\bar{1}1] \rightarrow a\,[001] \qquad (1)$$

The line of intersection of (112) and $(\bar{1}\bar{1}2)$ is $[1\bar{1}0]$ which then gives the line vector of the dislocations. It is then of great interest that both dislocations are *pure edge*, since $[\bar{1}\bar{1}1]$ is orthogonal to $[1\bar{1}0]$ and [111] is also orthogonal to $[1\bar{1}0]$. The cpd is [110], which is orthogonal to $[1\bar{1}0]$ whilst still lying in (001). The situation is therefore one of *plane strain* with the crack blunting in "2D" when viewed in the $(1\bar{1}0)$ plane. This seems to be a rather simple opening and may account for Gerberich's observations of a chevron form to his striations when he tried to propagate cracks in silicon-iron on (001) with the crack front [010] and the cpd [110].

Equation 1) is appealing, but does not, as written, correspond to symmetrical crack blunting which is more appropriately written as:

$$(a/2)\,[111] + s(a/2)\,[11\bar{1}] \rightarrow (a/2)\,[001] + (a/2)\,[00\bar{1}] + a\,[110] \qquad (2)$$

Note the 180° change in sign of the second slip dislocation. Equation 1) might, however, be regarded as the plane strain version of Cottrell's mechanism for the nucleation of fast fracture, which could account for the similarity in crystallography of facets for "fast cleavage" at -196°C to that for hydrogen-induced fracture. More probably in Fe-3Si at -196°C and in high-chromium ferrites, fast cleavage is initiated by mechanical twins rather than by slip dislocations. In bcc metals, the twinning shear is (a/6) <$\bar{1}\bar{1}$1> with habit planes of the form {112}. Hence, equation 1) might become:

$$(a/6)\,[\bar{1}\bar{1}1] + (a/6)\,[111] \rightarrow (a/3)\,[001] \qquad (3)$$

again with lowering of energy and crystallographic features identical to those associated with equation 1). Such "fast cleavage" runs at high speed and is not associated with significant plasticity: it exhibts a sharp EBSP, see Fig. 6b.

The features to be reconciled with any proposed mechanism of hydrogen-induced fracture include the following:

- observations of striations, spaced at approximately 1μm - 0.3μm
- effect on striation spacing of test temperature
- evidence of a "notch effect" in mild steel
- fine-scale detail within the striations
- jogs on the crack front

In all cases we assume a supersaturation of hydrogen in a crack/cavity. This may be a crack propagating in a hydrogen atmosphere, a crack in which cathodic electrochemical processes are liberating hydrogen, a cavity/weakly-bonded inclusion subjected to high hydrogen pressure from charging (the Fe_3Si), or a cavity subjected to high hydrogen content, induced by the "sweeping-in" of hydrogen by dislocations. (mild steel[8]).

The hydrogen-filled crack/cavity is then subjected to transverse tensile stress. Plastic deformation is induced at the ends of the cavity. This has two effects. It produces high plastic strains (dislocation density) *at* the tip of the cavity, which decrease rapidly away from the tip; *and* it induces a high tensile stress, σ_{11}, and high hydrostatic stress $\sigma_H = 1/3(\sigma_{11} + \sigma_{22} + \sigma_{33}) = \sigma_{22}$ in plane strain. The peak value of σ_{11} is of order 3-4σ_Y where σ_Y is the uniaxial yield stress, and is located (as is the peak value of σ_H) at a distance 1.9δ ahead of the tip, where δ is the crack-tip opening-displacement, CTOD. For a long period of time, it was argued that hydrogen would also accumulate mainly at this position because the driving force for such accumulation would be the term $\sigma_H.V_H$, where V_H is the partial molar volume of hydrogen (Note that the first subscript "H" denotes "hydrostatic"; the second denotes "hydrogen"). More recently, attention has been paid to the large number of hydrogen "traps" to be found in the region of high plastic strain (dislocation density) *at* the tip of the cavity and it has been shown that *very* much more hydrogen would be expected *at* the tip than at a distance, 1.9δ, ahead of the tip. Calculations indicate that, whereas at 25°C there is less than one order of magnitude difference between hydrogen concentrations at the two types of site, the effect at -120°C is such that there are several orders of magnitude difference between the concentration at the tip and at 1.9δ ahead.[15]

Any mechanism must therefore envisage the supersaturation of hydrogen in the stressed crack/cavity entering through the tip and becoming "trapped", significantly within 0.2δ–δ of the tip. Significant points are that hydrogen-induced quasi-cleavage cracking is observed in a notched testpiece at a temperature at which a smooth uniaxial specimen fails by ductile fracture and that striations are observed on the "quasi-cleavage" facets. In many experiments, the spacings of striations, as revealed in conventional SEMs, is of order 1μm, but the more recent observations in silicon-iron, using the FEG SEM, AFM and STM, show major striations spaced at 0.3μm, of height approximately 50nm and finer-scale striations, spaced at 30nm, of height 15-30nm. The TEM image of plastic zones in the wake of a plastic crack exhibits slip-planes spaced at some 15-30nm.

The behaviour of notched specimens *vis-a-vis* uniaxial tensile specimens indicates that hydrogen-induced quasicleavage is a process which responds to the level of tensile stress, rather than to that of shear stress, i.e. it is propagation-controlled. The fractography indicates that the nucleation site is a second-phase particle: a nonmetallic inclusion. The situation is apparently similar to that pertaining to fast, transgranular cleavage in low carbon steels and in steel weld metals: the initiating particles in wrought steel are usually carbides; in weldmetals, they are usually brittle, oxide or silicate, inclusions. If the size of the initiating nucleus is *a*, the *local* stress σ_F ahead of a notch required to produce cleavage fracture is given by:

$$\sigma_F \geq \{(\pi E/2a)\,\gamma_w\}^{0.5} \qquad (4)$$

where E is Young's modulus and γ_w is the *local* work of fracture (some 9 - 14 Jm^{-2}). From stress analysis, σ_F is calculated from the expression:

$$\sigma_F = Q_F\,\sigma_Y \qquad (5)$$

where Q_F is the value of "stress intensification factor" at fracture, and is a function of the size of the plastic zone at which fracture occurs. In general, Q is likely to vary between 1.0 and 2.5 for the notch geometry used.

We now consider three situations: a hydrogen-filled cavity in a stress-free specimen; a hydrogen-filled cavity in a uniaxial specimen, and a hydrogen-filled cavity in a notched specimen. The excess hydrogen in the cavity exerts a pressure p and some enters the traps located within a distance approximately 0.2δ–δ ahead of the cavity crack tip. The pressure, now reduced to p' because hydrogen is lost to traps, simply adds to the applied stress to increase the stress intensity factor at the cavity-crack tip. The hydrogen ahead of the tip may reduce the local work of fracture, to γ_H, by interacting with the bonding electrons in 3d (or hybridised 3d/4s) levels. In the most generalised form, equation 4) may then be re-written, to treat hydrogen-induced quasi-cleavage, in the form:

$$\sigma_{F(H)} + p' \geq \{(\pi E/2a)\,\gamma_H\}^{0.5} \qquad (6)$$

where $\sigma_{F(H)}$ is the reduced value of σ_F in the presence of hydrogen.

If the notched specimen were not charged with hydrogen, i.e. the local work-of-fracture remained at γ_w, it would not fail by fast cleavage at room temperature, i.e. $\sigma_F \geq 2.5\ \sigma_Y$. Typical figures might be σ_F = 800 MPa, σ_Y = 180 MPa. Since quasi-cleavage *is* observed when hydrogen is present, it follows that, if γ_w is not affected, the value of p must be of order 350MPa. Quasi-cleavage is also produced in hydrogen-charged, uniaxial specimens at -50°C where σ_Y is 220 MPa. As at room temperature, the value of σ_F for fast cleavage in a mild steel of 100μm grain size is approximately 800MPa, so the required value for p, (with γ_w unchanged) is 580 MPa. It is extremely difficult to contemplate pressures of this order since the specimens are in contact with atmospheric pressure (1atm = 0.1 MPA). Moreover it is difficult to understand how a higher pressure can be generated at -50°C than at room temperature. The conclusion is that γ_w is reduced to a lower value, γ_H, by the uptake of hydrogen into traps immediately ahead of a cavity tip.

The extent of the region of "high" plastic strain is calculated[15] to lie in the range 0.2δ to δ (CTOD) which may be written in terms of stress intensity, K, as:

$$0.2\delta\text{–}\delta = (0.1\text{-}0.5)K^2/\sigma_Y E \qquad (7)$$

If the half-length of the nucleating inclusion is taken as 3μm (see Figs. 3, 4) and $\sigma_{F(H)}$ is taken as (a maximum of) 450MPA, since the hydrogen-charged notched specimen <u>does</u> crack at room temperature (where σ_Y = 180MPa) the range 0.2δ–δ is 6-30nm i.e. comparable with the spacing of the fine striations observed in Fe3Si using FEG SEM, AFM or STM-techniques. The conclusion is that hydrogen is "soaked-up" in traps ahead of the cavity tip to a concentration such that γ_w is lowered to *a* vlaue γ_H such that equation 6) is satisfied. At a higher temperature, $Q\sigma_Y$ is smaller, from equation 5) the value of tensile stress developed is smaller, and γ_H may have to be reduced further to give quasi-cleavage, e.g. in charged, unstressed tests.

The picture so far is one of a discontinuous, but near-continuous, "smooth" process. The time taken for hydrogen levels to be replenished over a distance of 15-30nm is small and, provided that p′ does not decrease significantly as the cavity advances 15-30nm, the condition for further crack advance is soon re-established. The TEM studies indicate slip planes at spacings of order 15-30nm, which might be indicative of some crack-tip emission after each small crack advance and arrest. An alternative explanation is that dislocations are attracted, by image forces, to the free cavity durfaces after the cavity tip has advanced,[11] so that the fine-scale striations simply reflect the slipband spacings behind the crack tip.

These fine-scale phenomena do not, however, agree entirely with the observations made (admittedly at coarser scale) in mild steel[8] or, by other workers, in iron-silicon[2,9]. Here, the striations are spaced at distances 1μm or greater (up to 5μm); metallographic observations suggest dicontinuous propagation in "jumps" at this coarser scale, and acoustic emission (AE) "events" in iron-silicon are associated with these apparently larger striation spacings.[9] Such "large jumps" take approximately 13s, so that, *pro rata*, advance over 15-30nm would take only a few tenths of a second, (ignoring the complexities of hydrogen diffusion kinetics in a highly-dislocated region. It is of interest to address the question of why these larger spacings are observed. One clue is given by the finding that there is little temperature variation of the "large" striation spacing, Figs 2a, 2b, so that they are more likely to be associated with microstructural features than with characteristics of hydrogen diffusion to produce a "saturated" (embrittled) region.

The inherent ("in-grown") dislocation density in an annealed mild steel is approximately 10^{12} m^{-2}, i.e. the average spacing is 1μm. These "in-grown" dislocations accommodate small misorientations between "clumps" in the grain, and in general, with mixed (edge and screw) character. Regions subjected to plastic strain are arranged in a cell structure of size somewhat less than 1μm diameter, see Fig. 8. Whatever new dislocation arrays are produced ahead of a (slowly-moving) hydrogen-induced cavity-crack, there will be some perturbation as the cavity-crack tip approaches "pre-existing" dislocation sources or intersects cell walls. The "creeping" hydrogen-induced growth (of maximum step height 15mm) could operate sources, spaced at roughly 1μm (perhaps 0.3μm in Fe3Si, see below) intervals, which might produce sufficient dislocations to give an opening of at least 50nm. The cavity-crack then experience a greater overall "opening" (displacement of faces) giving rise to detectable AE amplitude, explaining why AE "events" are associated with 1μm or more "jumps". The larger opening is also just detectable on the optical microscope scale: 50nm is 0.1mm at × 2000. In both mild steel and other work on silicon-iron, the striation spacings are greater by a factor of 3-10 than those observed in the Fe3Si experiments reported in this paper. Loosely, it is anticipated therefore that the AE "events" will be of higher amplitude than the Fe-3Si figures here suggest, and that "discontinuities" in mild steel will be easier to observe in the optical microscope.

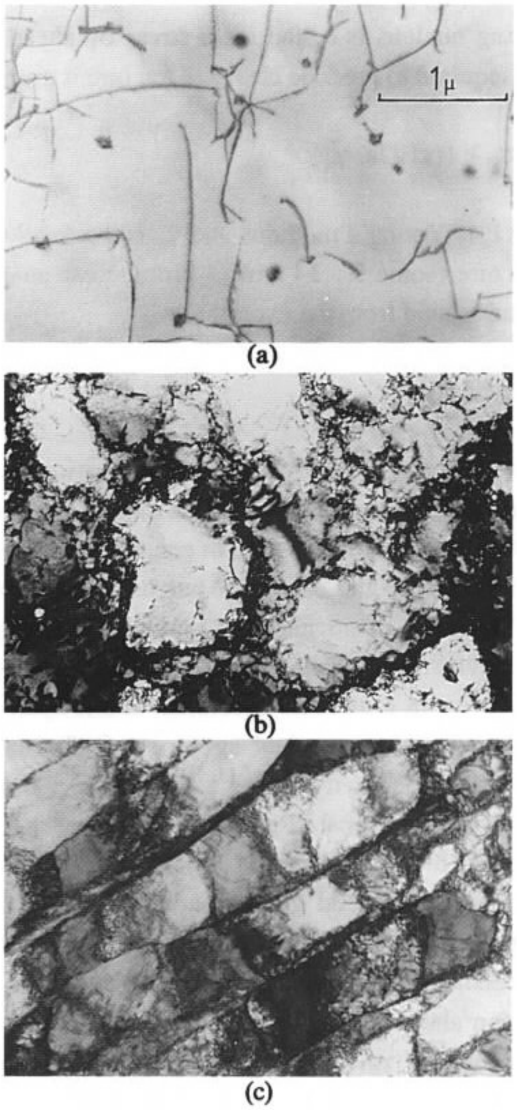


圖 8 軟鋼中的差排結構。(a)退火狀況(b) 10%塑性應變狀況(c) 40%塑性應變狀況

Fig. 8 Dislocation structures in mild steel a) annealed b) 10% plastic strain c) 40% plastic strain (courtesy J.D.G. Groom).

Further remarks concern the observations made on the Fe-3Si alloy, referred to in this paper. First, the "major" striations are spaced at 0.3μm, rather than ≥ 1μm. Second, the crack front is "jogged" on the 0.3-0.1μm scale Fig. 5. It should be noted that this Fe3Si alloy was not simply cooled from the as-cast state and then annealed, but was cold-rolled by 20% before annealing at 1200°C. It is conceivable that this procedure has given rise to an "in-grown" dislocation density slightly greater than that of annealed mild steels or other silicon-irons: *single crystal* silicon-iron grown by the strain-anneal technique has a critical strain of only approximately 3%. Second, "in-grown" dislocations will have, in general, a randomly "mixed" character, but, for 20% prestrain plus an anneal, some degree of texture may develop.

It is, therefore, plausible that a crack front, parallel to $[1\bar{1}0]$, advancing in a [110] direction might intercept a "row" of dislocations (in "partially-textured" array) of Burger's vectors, such that the crack front is "jogged", at appoximately regular (0.3-1.0μm) intervals. If such dislocations can also act as sources, they might "operate" before being intersected by the crack front, so that the front intercepts not a single dislocation but an array. Note that, in all these cases, a critical factor is the slow, "creepy" nature of hydrogen-induced quasi-cleavage. For "fast-cleavage", the crack runs so rapidly that there is no time for sources to operate and so no striations are seen: no crack front "jogs" of more than a few Burger's vectors would be anticipated. The general mechanism, as described above, relies heavily on the observation of the notch effect: the conclusion is that the process is tensile-stress controlled and hence a *cracking* process. The effect of hydrogen is to facilitate decohesion, rather than crack-tip dislocation emission. An alternative mechanism is based on crack-tip shielding.(11)

CONCLUSIONS

The paper has addressed issues concerning hydrogen-induced "quasi-cleavage" cracking in mild steel and silicon-iron. This is seen as a good model for behaviour of the high-chromium ferrite "alpha-phase" in duplex stainless steel and for cracking in other high-chromium ferritic steels. In addition to the observation of "macro" striations, of spacing 0.3-5μm, use of a variety of high-resolution techniques has revealed the presence of finer striations, of some 15-30nm spacing. A *rationale* for the crystallographic features of crack advance has been proposed. Results have been discussed to try to elucidate the micro-mechanisms of hydrogen-induced "quasi-cleavage" extension. The important feature appears to be the accumulation of hydrogen in the zone of high plastic strain (approximately 0.2δ–δ) ahead of the cavity-crack tip, such that cohesion is lowered to the extent that an increment of cavity-crack advance occurs. This increment is approximately 15-30nm which agrees with the spacing of fine striations and (local) dislocation plane-spacing. The more widely-spaced (1-5μm) striations are attributed to interactions with the "in-grown" dislocation (source) density which produces changes in tilt, twist or skew and hence modifies the details of the advancing cavity-crack front. The operation of such sources may be the cause of "detectable" acoustic emission and to the observation of "discontinuous" crack growth, using optical microscopty.

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REFERENCES

1. Tetelman A.S. and Johnston T.L. Phil Mag 11, 1965, pp. 389.
2. Chen X. and Gerberich W.W. Met Trans 22A, 1991, pp. 59-70.
3. Vehoff H. and Rothe W Acta Metall 31, 1983, pp. 1781.
4. Birnbaum H.K. and Sofronis P. Mater. Sci. Eng. A176, 1994, pp. 191.
5. Knott J.F. Proc. 5th Intl Conf. on "Effects of Hy-

drogen on Material Behavior" Wyoming, Sept 1994, ed. N.R. Moody and A.W. Thompson, in press.
6. Marrow T.J. and King J.E. Fatigue and Fracture Engng Mater Struct 17, 1994, pp. 761-771.
7. Marrow T.J. Cotterill P.J. and King J.E. Acta Metall Mater, 40, 1992, pp. 2059-2068.
8. Tong Y. and Knott J.F. Scripta Metall Mater. 25, 1991, pp. 1651-1656.
9. Chen X. Gerberich W.W. Scripta Metall. 22, 1988, pp. 1499.
10. Marrow T.J. Aindow M. and Knott J.F. Proc 5th Intl Conf. on "Effects of Hydrogen on Material Behaviour" Wyoming Sept 1994, ed N.R. Moody and A.W. Thompson, in press.
11. Marrow T.J. Aindow M. Prangnell.P. Roberts S.G. Strangwood M. and Knott J.F. 1995 submitted to Acta Metall Mater.
12. Garrett G.G. and Knott J.F. Acta Metall 23, 1975, pp. 841.
13. Pickard A.C. Ritchie R.O. and Knott J.F. Metals Technology, 9, 1975, pp. 253.
14. Higo Y. Pickard A.C. and Knott J.F. Materials Science, 15, 1981, pp. 223.
15. Sofronis P. and McMeeking R.M. J.Mech Phys. Solids, 37, 1989, pp. 317.