FRACTOGRAPHY AND MECHANISM OF HYDROGEN CRACKING - THE FISHEYE CONCEPT

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ABSTRACT

Concerning the understanding of hydrogen cracking several concepts exist which describe various specific phenomena such as:

- **Hydrogen diffuses to cavities and produces pressure there.**
- **During plastic deformation hydrogen is adsorbed and dissociated on fresh surfaces.**
- **Hydrogen atoms can be transported by dislocations.**

Based on fractographic analysis of failures showing that local cracking starts from cavities and is due to slip-plane decohesion a model is proposed which comprises the above mentioned phenomena ("fisheye"-concept). A further step is added to explain slip band decohesion: Hydrogen atoms swept into the lattice by dislocations may again recombine in deformation-induced submicroscopic pores. Thus these pores will act as high-pressure bubbles impeding dislocation movement.

KEYWORDS

Hydrogen cracking, fractography, slip-plane decohesion, failures.

INTRODUCTION

Due to its small size the hydrogen atom can easily enter the metal lattice, where it has a great mobility. Under certain conditions hydrogen can initiate cracks. Atomic hydrogen can be supplied by different technical processes, which is the reason why this crack phenomenon has got several names. Even the relatively small amount of hydrogen produced during electroplating or local corrosion (pitting) is a danger for steels of strengths above 1000...1250 MPa ("hydrogen embrittlement", "delayed cracking" and "stress corrosion

cracking", respectively). In most of the cases the cracks grow intergranularly, along the primary austenite boundaries. For the cracking of steels of lower strengths larger amounts of hydrogen are needed, and the cracks spread transgranularly. Hydrogen cracking cannot occur at temperatures above 80... 100°C, which is why welders speak of "cold cracking".

As failure analysts the authors have become familiar with most types of hydrogen failures. Having spent some time in observing their fracture surfaces with the scanning electron microscope, they believe that they have noticed some common features. Respective details are given in the literature, but to the authors' knowledge they have not been associated with one another as discussed in this paper.

MECHANISM OF HYDROGEN CRACKING - THE "FISHEYE" CONCEPT

Initiation of cracking requires both the storage of hydrogen in cavities ("storage effect") and plastic deformation. This can be shown most clearly by the well-known "fisheyes" which are observed on the fracture surface of welding-bend samples, if welding is carried out under "moist" conditions. Due to their fine-structured and bright-glittering appearance they contrast with the surrounding ductile or brittle final fracture, which is shown in Figs. 1 and 2. This cracking turns out to be an unusual type of brittle fracture. Fisheyes are known to form as follows in regions where the yield strength is exceeded: The atomic hydrogen which could not leave the weld during solidification diffuses to inclusions, hot cracks or pores, recombines there to molecules and generates high pressures (Zapffe and Sims, 1941) thus producing an "inner load". If during bending plastic deformation takes place, new (active) surfaces are created in the cavity walls. Here the hydrogen molecules are adsorbed and dissociate to atoms (Hofmann and Rauls, 1965). By dislocations great quantities of atomic hydrogen are carried into the lattice, where a separation along slip planes (<110>-planes; Kikuta, Araki and Kuroda, 1978) is initiated, resulting in a characteristic small faceted crack structure (Fig. 3).

The procedure of picking up and transporting hydrogen by dislocations (Bastien and Azou, 1951) can be called "pumping" or, in a more general way, "tribosorption".

Now the question arises why the slip-planes are separated. Hydrogen is assumed to block up the movement of dislocations, but not in its atomic state; on the contrary, there is evidence that atomic hydrogen promotes gliding (Chu, Hsiao and Li, 1982). To prevent it, however, atomic hydrogen has to recombine before (see Bastien and Azou, 1951), for which it will find enough space in the slip planes. The places of recombination within slip planes are thought to be submicroscopic pores, which are either produced by interaction of dislocations according to the known mechanisms proposed by Zener and Stroh or Cottrell, or formed by vacancies. Vacancies (produced by cold forming) were observed to delay the effusion of hydrogen (Dahl, Lange and Hwang, 1979)

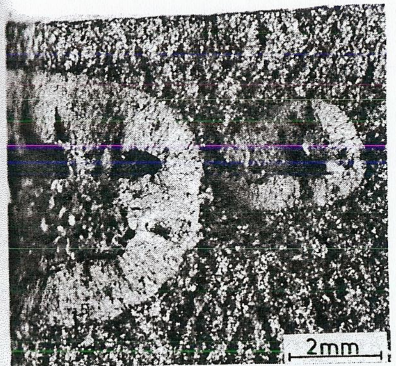

Fig. 1. Macro-fisheyes

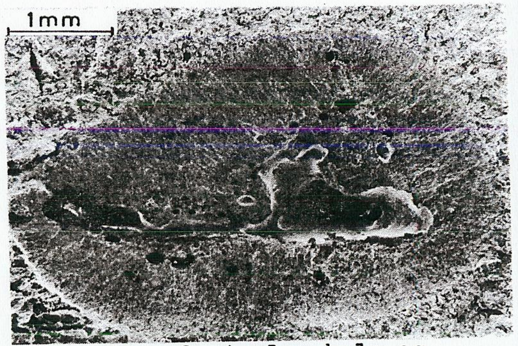

Fig. 2. A slag hole as fisheye center (detail from Fig. 1)

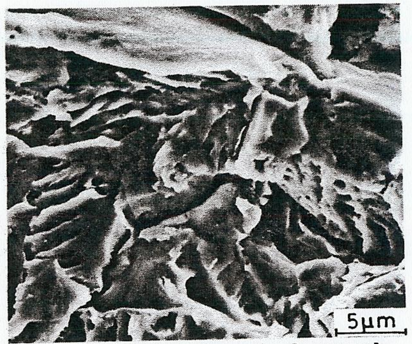

Fig. 3. Fine faceted crack structure in a fisheye

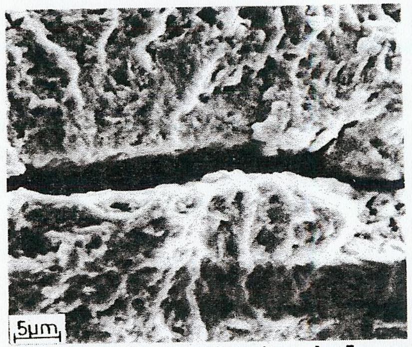

Fig. 4. An inclusion hole as local crack origin

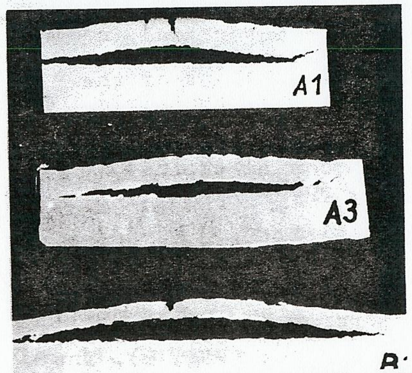

Fig. 5. Pressure vessel wall showing blisters

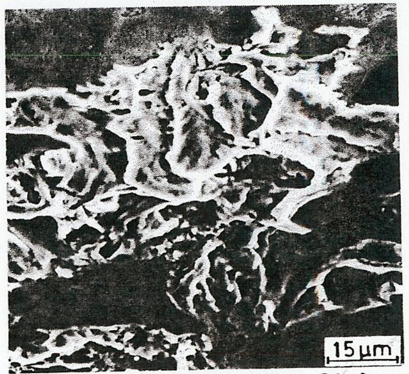

Fig. 6. An "inverse" fisheye in an opened blister

due to the fact that vacancies or vacancy clusters act as recombination sites, i.e. as pressure centres.

APPLICATION OF THE FISHEYE-CONCEPT

It certainly is somehow surprising that a pressure vessel of a petroleum refinery passes the water pressure test but bursts few days later during usual operation: Little H_2S in the medium was sufficient to charge the steel with hydrogen which was stored in the inclusion cavities. During the pressure test - by superimposing a high outer load on a low inner load - the yield strength was exceeded around cavities. Thus the fisheye effect occurred, and cracks were formed. After restarting the plant, the cracks were quickly growing due to the further acting influence of H_2S, until there was a leak. Fig. 4 shows that the holes of inclusions (oxides, sulfides), which were broadened by the enclosed hydrogen, are the centres of small fisheyes. The site where cracks are formed is the heat affected zone of a weld, which is hardened and therefore susceptible to hydrogen cracking.

Due to "full killing" (deoxidation with aluminium) in steels the sulfide inclusions are long and flat, reducing the plastic properties in through-thickness direction even for purely mechanical loading ("lamellar tearing"). For hydrogen the flat inclusions represent a relatively large effective storage area, resulting in a high "inner load". In the case of strong hydrogen charging, which occurs by the attack of wet H_2S or strong acids (pickling), the pressure can become so high that (promoted by the fact that the flat inclusion cavities act as notches) the fisheye mechanism will start without any outer load. This can result in visible bubbles ("blistering") as shown in Fig. 5 for a pressure vessel. Here the local density of inclusions - mainly iron oxides - was so high that "inverse" fisheye were formed: The cracks have not grown from a central inclusion into the surrounding metal, but from the surrounding inclusion in the metallic isle (Fig. 6). To initiate transverse cracks ("sulfide stress cracking") from the blisters (Fig. 7), similarly to the case discussed first, an outer load is needed, since here the effective storage area and therefore also the inner load are too small. But the amount of the outer load has to be only about a quarter of the yield strength in the extreme case (Pöpperling and Schwenk, 1980). By desulfurization to contents below 0.003 % blistering and sulfide stress cracking, respectively, can be avoided, because hydrogen does not find storage space and cannot produce an inner load.

An analogy to blistering are the "underbead cracks" often detected below fillet welds some hours after welding. The source of hydrogen is given by water in the electrode covering etc., which is thermally dissociated in the melt. While the weld cools hydrogen diffuses to the heat affected zone and is stored in the inclusion cavities (Fig. 8). The outer load necessary to initiate the fisheye effect is produced by shrinking.

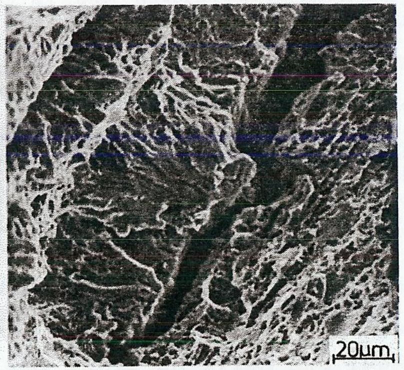

Fig. 7. A transverse crack emanating from a blister

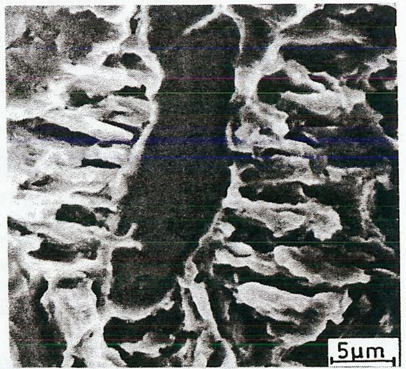

Fig. 8. An opened underbead crack: fisheye

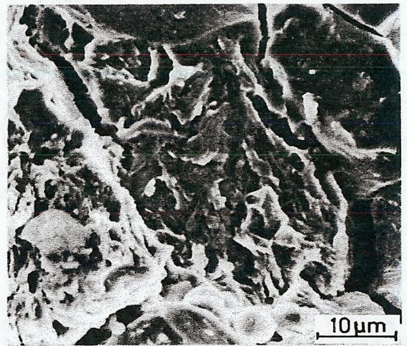

Fig. 9. A cracked grain boundary as local crack origin

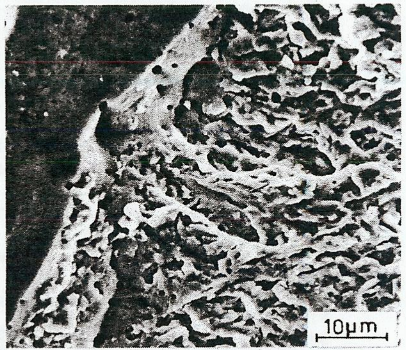

Fig. 10. Weld crack: grain boundary as crack origin

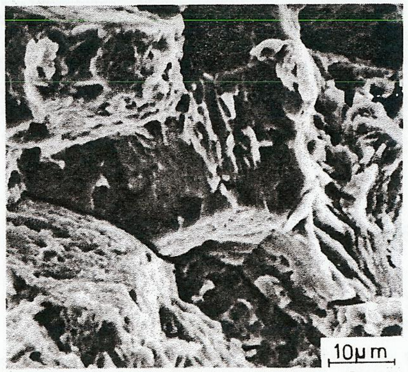

Fig. 11. Intergranular fracture beside a weld

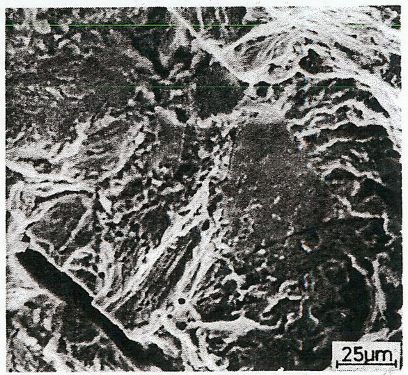

Fig. 12. Inclusion and grain boundary as crack origins

In the Introduction the cracks in high-strength steels were said to follow mostly the primary austenite boundaries. The question arises whether this can also be explained by the fisheye effect, or not. It should be noted here that the "primary" grain boundaries actually do not exist in the temperature range of hydrogen cracking (< 100°C). But to a certain extent they are marked by carbides, segregations (As, Sb, Sb, P) but mainly sulfides, which can be considered as "microinclusions" (Ø 10 nm) (Joshi, 1978) of a high density giving hydrogen place for recombination. If the pressure in these microcavities is high enough, the fisheye effect occurs in very minute regions with a transgranular crack path and with the intergranular path being only virtual. If the austenite boundaries are marked weakly, cracking occurs partly, or completely, in the usual transgranular way, and the steels are not so susceptible.

Grain boundaries already cracked, can serve as traps for diffusive hydrogen thus being the origin for usual transgranular cracks as shown in Fig. 9 for a high-strength bolt. This can also be observed, if cold cracking occurs in the welding deposit itself. As the usual inclusions are missing, hydrogen is stored in pores, at carbides or small sulfides on the austenite grain boundaries and cracking begins intergranularly (Fig. 10). In the heat-affected zone regions of intergranular cracking can be found (Fig. 11), presumably due to "overheating": During welding the sulfides partly are liquified. Under the action of restraint stresses the sulfide melt spreads along the boundaries of the growing grains and a fine sulfide dispersion is formed during cooling. The intergranular fracture is mainly observed at butt-welds, since - as Fig. 12 shows - the effective storage area of the inclusions is small in the load direction. Here the role played by inclusions is ambigous. First, for high charging they initiate cracking, second, for low charging hydrogen is sagged in them, which otherwise would concentrate on the fine cavities provided by grain boundary sulfides. It is therefore important to prevent overheating by "sulfide stabilization", i.e. if calcium or cerium are added to the melt, sulfides are formed with melting points higher than those of steels. Desulfurization without stabilization may promote hydrogen cracking, not only due to the missing "sag-effect" but also because overheating is more pronounced then. The latter has been studied extensively by Middleton (1981) for relaxation cracking where the grain boundary sulfides act as creep nuclei.

HYDROGEN CRACKING BY ETHYLENE

Cracks were detected in pipes for high-pressure ethylene. The fracture surfaces showed the features known for (static) hydrogen cracking. Two cases could be distinguished:

- if the strength of steel was about 1000 MPa, the fracture path was transgranular here with very small sulfide inclusions as local crack origins (Fig. 13)
- if the strength was far more than 1000 MPa, cracking occurred intergranularly (Fig. 14).

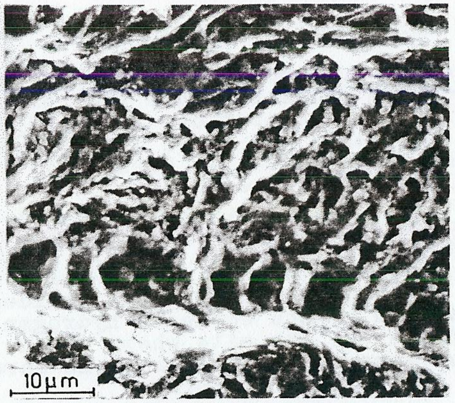

Fig. 13. Ethylene pipe: fisheyes ("ultraclean" steel)

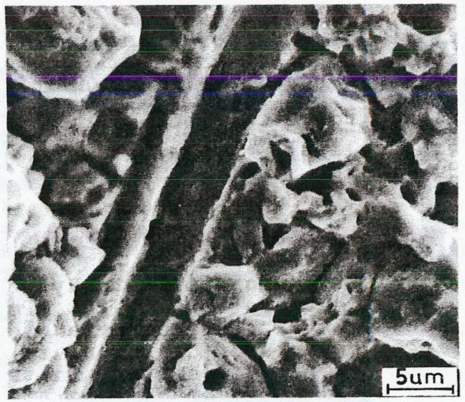

Fig. 14. Ethylene pipe: intergranular fracture

Obviously ethylene behaves like molecular hydrogen: On fresh metal surfaces - produced by the pulsating pressure in the slightly rough pipe wall - it dissociates and delivers atomic hydrogen. In one case the crack started from a defect caused by overheated forging (Fig. 15).

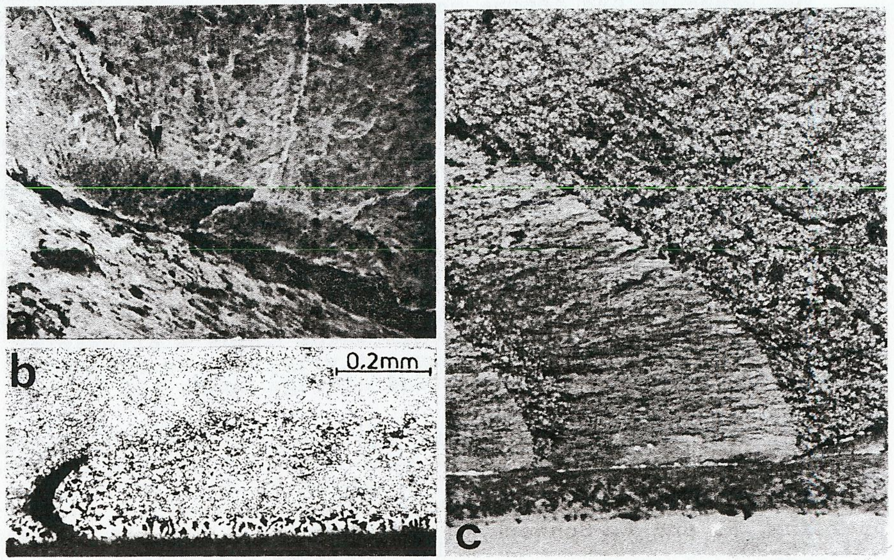

Fig. 15. Ethylene pipe
a), b) forging defect as crack origin
c) fibre-like structure of crack surface

MACROSCOPIC APPEARANCE OF HYDROGEN CRACKS

Hydrogen cracking, especially the transgranular one, has in common with the ductile (dimple) fracture that both are initiated at second phase particles. Since owing to the rolling process these are arranged in lines, the fracture surfaces have a fibre-like or lamellar appearance (Fig. 15). The difference lies in the trend of ductile fracture to propagate in the 45° plane relative to the load direction (shear lips) - while hydrogen fracture always lies in the 90° plane.

SUMMARY

Especially susceptible to hydrogen cracking are steels of strengths above 1000...1250 MPa; the cracks follow the grain boundaries of the primary austenite marked by segregations. Larger amounts of hydrogen are needed for cracking steels of lower strengths resulting in transgranular fracture. The prerequisites to cracking are storage of hydrogen in cavities (at inclusions, carbides, segregations) and plastic deformation.

The atomic hydrogen diffuses to cavities, recombines there and generates high pressure. Plastic deformation causes new surfaces in the cavity walls. There the hydrogen molecules are adsorbed and dissociated. Dislocations carry the hydrogen atoms into the lattice where due to a repeated recombination in deformation induced submicropores the hydrogen forms pressure bubbles.Latter produce innerload within the slip bands and impede gliding. In the present work the whole process is called fisheye effect (Möser 1982, 1983)

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