Chapter 15
Fractography with the SEM (Failure Analysis)

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terms:
SEM = scanning electron microscope, TEM = transmission electron microscope

Griffith-equation: $\delta = \left( \frac{2E \times \gamma_s}{\pi \times a} \right)^{1/2}$

with $\delta$ being fracture stress, $E$ Young's modulus, $a$ the crack length and $\gamma_s$ the surface energy.

15.1 Introduction

It is known that any part of a structure can withstand a load only to a certain value, then it will deform and/or break. When the deformation can be seen with the naked eye – as necking or extensive shear lips – it is termed a yielding or ductile fracture, at the opposite extreme a brittle fracture occurs with a broad transition existing between these two extremes.

In general, a constructional material should be as strong as possible but also ductile to withstand a sudden overload (impact). These properties are usually exclusive; this is largely the situation in materials science.

The strength measured under uniaxial tension – the normal procedure – yields only a limited criterion for thick-walled constructional parts or for parts containing notches or cracks. To overcome this deficiency the criterion „fracture toughness“ was developed.

The fracture strength and even more the fracture toughness is lowered, when

– the part is loaded repeatedly (fatigue)
– the loading occurs under high temperatures (creep)
– the part has to serve in a corrosive medium which may also supply hydrogen
– the part contains hydrogen from the manufacturing process
– the part is in contact with certain liquid or vaporized metals.

In the case of fatigue, for instance, the fracture toughness is reduced to 1 … 3% [1] called „threshold value“, under the influence of hydrogen to 7 … 30%. Therefore, it is evident that pure overload fracture (fast fracture) rarely constitutes the primary cause of failure, even in its most feared form namely as brittle fracture, but it occurs as final step after a (stable) crack has grown by one of the above-mentioned reasons during service.

The pre-existing cracks from which such stable cracks often start are generally formed during manufacture, induced by working or shrinking stresses. The underlying reason can be the melting and vaporizing of sulfide inclusions and carbides („hot cracking“) or the uptake of hydrogen during melting, casting and welding („cold cracking“).
The main task for the expert is to define the nature of such a failure. As the first step the expert has to consider the fracture surface with the naked eye, then with a simple magnifier. In doing so, he is practising macrofractography as the oldest method of investigation of materials (see [2, 3]). If possible, a light microscope (stereomicroscope) should also be used, but the light microscope is known for its extremely low depth of field, whereas the fracture surfaces have a more (fast fracture) or less (fatigue fracture) rough structure limiting the useful magnification to not more than 20 times in general.

The whole range of magnification of the light microscope can only be used with very flat samples. Therefore, metallographic sections must be prepared by grinding, polishing and etching as the second step in a conventional investigation. Then, the internal structure of the specimen can be revealed. It can be recognized whether the form of the crack exhibits some correlation with any irregularities in the structure, i.e. heat-affected zones. Further, it is of interest, whether the cracks have propagated either through the grains, or along them, or whether the cracks have branched. The latter observations can be considered as indirect fractography. In many cases an unambiguous result cannot be obtained by this method.

Nevertheless, two examples should be mentioned here showing that the light microscope can also be used for imaging details of fracture surfaces. Already in the early 18th century Reaumur sketched dendrites at magnifications greater than 100 times (see [3]), obviously by changing the focus. In the forties of our century C. A. Zapffe [3 to 5] with the aid of a special adjustment device was very successful in this respect, which made him the real founder of microfractography. But in his work he was mistaken in a characteristic manner: On the one hand, Zapffe, as an engineer, was interested in hydrogen cracking, especially as it occurs after welding or rolling and is visible as „fisheyes“ and „flakes“ [4], which due to their bright-glittering appearance contrast with the surrounding fast fracture. On the other hand, by means of hydrogen cracking Zapffe believed he could prove the so-called mosaic theory, which suggested that the crystallites of metals are built up of submicroscopic blocks (Smekal). Zapffe assumed that the atomic hydrogen recombines in the „rifts“ between the blocks producing pressure, which results in a triaxial stress state in the single blocks as the cause of embrittlement [5].

The special glittering of fisheyes and flakes is due to an extremely fine-faceted (transgranular) crack structure at the microscopic level as it will be shown later. These small facets, however, are less detectable with the light microscope. Zapffe noticed that large mirror-like facets could be obtained when hydrogenized samples were broken by impact. These large facets enabled Zapffe to make sharp fractographs and therefore he confined his work to such artificially produced fractures [5]. However, what he imaged was not the structure of hydrogen cracking but that of normal brittle fracture – hydrogen cracking cannot operate at the high-velocity loading given by impact.

Simultaneously with Zapffe's work the first steps were undertaken to apply the newly developed TEM to fractography mainly because of its greater depth of field [6, 3]. But only replicas could be investigated, so the use of TEM was restricted. Only with the introduction of the SEM did it become possible to investigate fracture surfaces directly without restriction [3, 7 to 10].

In failure cases the fracture surfaces are more or less oxidized; so it is necessary to clean them for examination. The author successfully used a solution published by Dahlberg [11]: 1.5 m1 conc. HCl, 2 m1 2-butin-1.4-diole as inhibitor, 25 m1 distilled water (ultrasonic bath).

In the following sections of this chapter the various kinds of fracture are described.
Generally, the features of the fracture mechanisms are exemplified for steel, because steel is the most commonly used metal. Like iron, unalloyed or low-alloyed steel has two modifications of the lattice. At high temperatures (above 720 ... 910 °C), the lattice is face-centred cubic (f.c.c.), below that temperature it is body-centred cubic (b.c.c.). For low carbon contents the b.c.c. structure also exists just below the melting point. The f.c.c. modification is termed austenite, the b.c.c. modification ferrite, and in the case of hardening the latter is called martensite. The ferrite existing at highest temperatures is denoted as δ-ferrite.

By stronger alloying with nickel, or more seldom with manganese, both having only a f.c.c. lattice, steel remains austenitic, even down to lowest temperatures. This austenite exhibits high ductility which is typical of all f.c.c. metals, e.g. gold, copper and lead. Ferritic steel embrittles at lower temperatures, especially in the case of three-axial stress states or high-velocity loading.

15.2 Fast Fracture

a) Ductile fracture

At the microscopic level, ductile fracture is characterized by a dimple structure (Fig. 15.1a): The cavities arisen from inclusions or coarser precipitates are enlarged and during further yielding the material between them is necked and sheared. To a first approximation the depth of these dimples can be considered as a measure of the ductility.

When the inclusions are large and flat, which is the case for sulfides and oxides in ordinary rolled steels, the ductility will be low perpendicular to the rolling plane (short transverse direction) resulting in „lamellar tearing“. The flat grooves filled with inclusions are separated by rupture zones with fine dimples (Fig. 15.1b).

As a special case, structureless regions can be found e.g. in cold-worked austenitic manganese steel used for the end rings of generators (Fig. 15.1c). The yielding of such steel has a strong tendency to be localized. Coarse slip bands are then formed [12] providing the crack path.

b) Brittle fracture

In general, brittle fracture propagates through the grains (transgranular). In the case of high strength, i.e. hardened and tempered steels, sometimes the crack follows the grain boundaries (intergranular fracture). The cracked boundaries are those of the austenite, which forms the high-temperature phase of steel as mentioned above. During cooling these grain boundaries disappear when the austenite is transformed to ferrite or martensite. What actually delivers the crack path is only a „shell of dirt“ as will be discussed later.

Cleavage fracture

In cleavage, separation occurs along a well-defined crystallographic plane given in b.c.c. metals by one of the (100) planes. F.c.c. metals do not cleave under normal conditions.
The crack nuclei are formed at sites where the glide processes are impeded, like for example at precipitates (Fig. 15.2a) or grain boundaries. Because the grains have different orientations with respect to each other, the crack generally divides into terrace-like steps when crossing a grain boundary (Fig. 15.2b). The newly created different crack planes join together during further crack propagation producing a characteristic river-like pattern. The flatness of cleavage facets suggests the idea that only the two atomic planes forming the fracture surfaces are involved in the crack process. But in cleavage a plastic zone is also formed at the front of a running crack. This plastic zone consumes the main part of the work of fracture. Depending on the lateral extent of the plastic zone the material near the crack planes is plastically deformed.
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Fig. 15.2.
Transgranular brittle fracture (cleavage)
a) high alloyed Cr-steel: carbide precipitation as crack origin;
b) cast steel: river pattern, cracking started from a grain boundary;
c) two-phase CrNi-Steel: isolated cracking of single grains, no river pattern;
d) hardened low alloyed steel; fine faceted cleavage

In two-phase austenitic-ferritic CrNi-steels (25% Cr, 5% Ni) the austenite can be transformed into δ-ferrite near the fusion line during welding. During the subsequent cooling a re-transformation of this δ-ferrite occurs only partially resulting in the formation of thin shells of austenitic microcrystals along the grain boundaries. Because of the pre-dominating ferritic state, the steel now embrittles with decreasing temperatures just like other ferritic steels, but not so rapidly. During cracking, the ferrite grains are cleaved in the usual way along the \( \{100\} \) planes. When reaching the grain boundaries the crack stops due to the existence of regions of ductile austenite there. A new crack nucleus has to be formed in the neighbouring grain. Thus the grains crack in isolation from each other and the grain
boundary regions are separated only after a certain yielding. Accordingly no river pattern is formed (Fig. 15.2c).

In hardened and tempered steels the martensite also cleaves along the \(\{100\}\) planes. Due to the strong differences in the orientations of single martensite blocks the crossing of grain boundaries by a crack is hindered analogously to the case of two-phase steel mentioned above, i.e. shear processes must occur to unite the cleavage facets, thus the river pattern is scarcely visible (Fig. 15.2d).

**Intergranular fracture**

In general, no traces of any deformation processes can be found on the cracked grain boundaries. In the case shown in Fig. 15.3a the steel was carburized as the first step in the so-called case-hardening process. As is known, diffusion occurs preferentially along grain boundaries. During rapid cooling (quenching) the austenite is transformed to martensite. As a consequence of the carburizing, the former austenite grain boundaries now represent regions of oversaturation of carbon. During tempering, the carbon is bound in carbide, arranged as carbide shells which impede the gliding and thus provide the crack path. In case-hardening, the intergranular embrittlement can be avoided if hardening is not performed directly from the heat of the carburization process (as often done for economic reasons) but after a reheating. Finer grains are formed by the twofold phase transformation (normalization). However, the main reason for avoiding the embrittlement is that carbon diffusion can proceed in a satisfactory way from the former austenite grain boundary into the matrix.

A more important problem is the so-called temper embrittlement that often occurs in large forgings because they cool down very slowly. Thus the usual covering of the austenite grains by sulfides (see the section on „hot cracking and overheating“), which is undercritical in ordinary cases, can be increased by diffusing atoms of arsenic, antimony, phosphorus etc. during cooling in the temperature range of 575 to 350 °C.

When steel is annealed just below the melting point it can be „burnt“, i.e. oxygen enters the steel deeply leading to internal oxidation. The penetration of oxygen occurs preferentially along the grain boundaries similar to the case of carburization which can become visible by the peeling-off of grain boundary shells (Fig. 15.3b).

In the temper embrittlement mentioned above, the segregates at the grain boundaries are re-dissolved at higher temperatures. Therefore, by a reheating above 600 °C and fast cooling, the embrittlement is removed [10]. An exception to such dissolving behaviour is exhibited by the sulfides. This is the reason for the „relaxation cracking“ in creep resisting steels: During welding, the grain boundaries in the region near the fusion line are enriched by sulfides in a very fine dispersion („overheating“). When annealing for stress relief, the sulfide dispersion coagulates forming particles of about 0.1 ... 0.5 µm in diameter. The generation of these particles should not be critical, however, it is accompanied by a second process [13 to 16]:

Creep-resisting steels are more or less alloyed with chromium, molybdenum and possibly vanadium or niobium to form thermally stable carbides. These carbides are dissolved in the above-mentioned critical region during welding and precipitate high-dispersively when annealing occurs. Surprisingly, in all such cases a small zone along the grain boundaries remains free of precipitates. Therefore, these zones have a very low creep resistance. The
Fig. 15.3
Intergranular brittle fracture
a) case hardening: cracking of grain boundaries due to carburization;
b) internal oxidation: peeled-off grain boundary shells;
c) relaxation cracking: grain boundaries covered with fine dimples;
d) detail from c) microsulfides in the dimples

Gliding necessary for stress relief is thus restricted to these precipitation-free zones, which at the same time are additionally weakened by the coagulating sulfides. The sulfides act as creep nuclei and voids are formed [17], joining together and producing cracks. Due to this process the fracture surface shows correspondingly fine dimples covering the grain boundaries (Fig. 15.3c). In the dimples the sulfides are only weakly visible because of their small dimensions (Fig. 15.3d). The total creep deformation will not exceed 0.2 ... 0.3% i.e., the fracture is brittle with respect to the macroscopic scale in contradiction to its microscopically ductile character.
The same microscopic structure can be found sometimes for austenitic steels, brass, aluminium and nickel alloys. It is always connected with the phenomenon of precipitation-free zones.

15.3 Fatigue

Most of the part of machines, cars, airplanes etc. are loaded in an alternating manner which can occur cyclically (e.g. a crankshaft) or more randomly (e.g. a car as a whole, depending on road conditions).

Fig. 15.4
Fatigue
a) hip prosthesis (CrNiMo-steel): striations mark the steps of the patient immediately before fracture;
b) a pipe that failed after 40 load pulses: dimples on a striation wall (detail);
c) Ni-alloy: cleavage-like fracture initiated at an inclusion;
d) blade of a peak-load gas-turbine (FeNi-alloy): island of dimples on the grain boundaries due to creep
In general, the propagation of fatigue cracks is strongly restricted to the plane of normal stress and is therefore less dependent upon features of the material. At high stress intensities, striations arranged in bands can be found marking the crack growth during each load cycle (Fig. 15.4a). With decreasing stress intensities the striations will disappear and only a weak band structure remains indicating the direction of crack propagation. At very high load pulses as given for instance by a sequence of impacts, the striations can become visible to the naked eye and show a dimple structure in the SEM (Fig. 15.4b). In parts produced from nickel or cobalt alloys fatigue cracks propagate along crystallographic planes which results in a cleavage-fracture-like appearance as shown in Fig. 15.4c for an exhaust-driven turbo-supercharger. Peak-load gas-turbines are exposed to an extremely low-frequency loading ($10^{-4}$ Hz) under the influence of high temperatures favouring creep and hot gas corrosion, both acting especially in the grain boundaries. This leads to a complete intergranular fracture and a strong increase of the crack-growth per load cycle [18]. Islands of dimples visible on the grain boundaries (Fig. 15.4d) indicate creep processes.

At room temperature a partly intergranular fracture can be induced by atomic hydrogen which is generated from the surrounding water steam by deformation processes of the metal surfaces (cf. the following section).

15.4 Fracture induced by a medium

Such „medium-induced“ fractures constitute a wide field yielding many surprises. Most of them can be attributed to hydrogen.

a) Hydrogen cracking

Hydrogen, as the lightest element, has also the smallest atomic diameter, nearly 0.1 nm. As a consequence, atomic hydrogen easily enters the metal lattice, where it has a great mobility. This is especially true for the ferritic steels. In the more closely packed f.c.c. lattice of austenitic (CrNi) steels the diffusion coefficient is nearly four orders of magnitude smaller than in ferritic steels which results in a lower susceptibility to hydrogen cracking in the temperature range below 80 °C.

Ferritic steels of higher strength (and therefore of a higher brittleness) are particularly sensitive in this respect. For instance, the relatively small amount of hydrogen penetrating the steel during electroplating became a problem in the aircraft industry after the Second World War. The reason was the production of jet planes, which required threaded steel parts (screws) with strengths higher than the 1250 MPa, which had been sufficient previously [19].

In such high-strength steels the cracks propagate preferably along the austenite grain boundaries. This fact is obviously the pre-supposition of the theories of Troiano [20, 21] and Oriani [22] most cited in this field. They suggest that the cohesion forces between the atoms are reduced by hydrogen. This implies a reduction of the specific surface energy being the „elastic“ term ($\gamma_s$) of the effective fracture energy ($\gamma_{ef}$) in the Griffith-Orowan-equation (see „terms“, cf. also Chapter 14 of this book):

$$\gamma_{ef} = \gamma_s + \gamma_{pl}$$
However, high-strength steels containing hydrogen are much more ductile than glass, for example. For the latter the plastic term ($\gamma_{pl}$) of the fracture energy is nearly five times greater than the elastic term, for hydrogenated steels it is at least a hundred times greater. Hence the theories mentioned are not appropriate.

Therefore, a model of hydrogen cracking was developed by the present author [23 to 25] called here Tribosorption-Fisheye-Concept, which essentially comprises the three following theories and some further observations which have attracted less attention up to now:

1. Atomic hydrogen diffuses into cavities, recombines there forming molecules which produce pressure (Bardenheuer and Thanheiser [26], Zapffe [5]).

![Fig. 15.5](image)

Radiography of CrNi-steel penetrated by hydrogen (tritium) [32]

a) pure diffusion:

b) tribosorption along slip-bands during deformation at a notch
2. During plastic deformation hydrogen molecules are adsorbed and dissociated on freshly produced surfaces (Rauls and Hofmann [27]).

3. Hydrogen atoms can be transported by dislocations and recombine in micro-voids which are created during deformation (Bastien and Azou [28]).

Hydrogen atoms attached to moving dislocations are transported much faster than in the case of pure diffusion. In contrast to static conditions, hydrogen can be strongly absorbed by the material during plastic deformation under tension and correspondingly desorbed under compression. This can be confirmed by the following facts:

Fifty years ago, Bardenheuer and Ploum [29] showed that hydrogenized steel wires lost a great deal of hydrogen during torsion or bending. Again Zapffe [30] compressed hydrogenized samples of Armco iron immersed in oil and noticed an ejection of gas bubbles at slip-bands and Neumann-bands. Later on these experiments were repeated by Erdmann-Jesnitzer [31] on Armco iron under more defined conditions. The extensive hydrogen adsorption occurred with the onset of stronger yielding, at compression grades of 1 to 3%. Thus, hydrogen can be squeezed out of iron like as out of a sponge. On the other hand, a strong hydrogen absorption under plastic tension was revealed radiographically by Louthan et al. [32] in austenitic CrNi-steel (Fig. 15.5). The phenomena described cannot be explained on the basis of a conventional understanding of sorption and diffusion.

For characterizing these phenomena as being mechanically activated the term „TRIBO(DE)SORPTION“ suggested in the field of tribochemistry [33, 34] was chosen.

A strong tribosorption of hydrogen was observed, when silicon carbide [34] and graphite [35] were activated mechanically by crushing in hydrogen atmosphere. Moreover, the tribosorbed hydrogen reacted with the basic material yielding hydrocarbons e.g. methane and acetylene.

During the wearing of steel, a tribosorption of hydrogen occurs already in air [36] due to its water content. Methane was also produced during wear under hydrogen atmosphere by the reaction of the tribosorbed hydrogen with carbides of the steel [36].

In industrial practice, a critical uptake of hydrogen may occur during grinding from the coolant as detected by Das [37], and also during excessive turning according to the experience of the author.

Transgranular hydrogen cracking

Low-strength steels have a lower susceptibility to hydrogen cracking than high-strength steels. Therefore greater amounts of hydrogen must be stored locally and a higher degree of deformation is also necessary. Both factors lead to a special crack appearance most clearly visible in the case of the above-mentioned fisheyes; this term is therefore used as the second one in denoting our concept. Fisheyes are known to welders from the bend or tension test. Two such typical structures are shown in Fig. 15.6a, where bright-glittering fracture zones around larger defects (lack of fusion) can be seen contrasting distinctly with respect to surrounding brittle fracture.

The generation process of fisheyes can be described as follows: During welding a strong uptake of water vapour can occur in the melt due to the water content of the electrode covering or the welding flux or the shieldgas. The water reacts with iron to form iron oxide and hydrogen. That part of the hydrogen which cannot leave the weld deposit during solidification and cooling diffuses into pores and other cavities where it recombines and produces pressure. The hydrogen effuses through the more or less oxidized walls of
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Fig. 15.6
Fisheyes
a) fracture surface of a weld-bend sample showing two fisheyes;
b) fine-faceted crack structure, the cracking was initiated at the wall of a pore

these defects only slowly. When the cavity walls are plastically deformed during bending or tension, their oxide layers will rupture and hydrogen is tribosorbed into the slip-bands. These bands are then oversaturated and thus they will be cracked, resulting in the characteristic small-faceted crack structure shown in Fig. 15.6b. Such fracture facets were identified by Kikuta, Araki and Kuroda [38] as \( \{110\} \) slip-planes. Now the question arises, what is the reason of such a slip-plane cracking? Like a normal precipitate, hydrogen has to inhibit gliding and therefore it has to recombine again. The recombination sites are assumed to be submicroscopic voids (vacancies as the smallest voids) produced by interaction between dislocations according to the known mechanisms proposed by Zener and Stroh or Cottrell. These micro-voids, filled with molecular hydrogen, should act as pressurizing bubbles [23 to 25]. If hydrogen cannot find micro-voids for recombination it must remain atomic and it then acts in the opposite manner, i.e. in promoting ductility, which can be understood from investigations in single crystalline whiskers carried out by Lunarska and Wokulski [39].

The main problem in the welding of higher-strength structural steels (strength about 500 ... 600 MPa) are the so-called underbead cracks caused by hydrogen below fillet welds (e.g. [25, 40]). The hydrogen diffusing from the weld metal into the heat-affected zone of the basic material is accumulated at inclusions. As shown already in Fig. 15.1b for ordinary steel, the inclusions have a strongly flattened form in the rolling plane. Hydrogen as pressurized gas produces a relatively high „internal load“ perpendicular to the flat side of the inclusions. Furthermore, the yielding of the metal is concentrated at the sharp edges of the inclusion cavities. Here, the amount of deformation necessary for initiating a critical hydrogen tribosorption can be reached easily as a consequence of the superposition of internal load and the shrink stress acting as external load. Hence the inclusions serve as crack nuclei, visible in Fig. 15.7. There is no essential difference to the macroscopic fisheyes described above, therefore this characteristic detail can be termed „mini-fisheye“ and the whole process is called „fisheye effect“ [23 to 25]. Underbead cracks served as
initial sites for fatigue cracks in the known accident of the oil platform A. L. Kielland [41, 40].

At welds, hydrogen cracking is promoted by the fact that the heat-affected zones are hardened, therefore on a local scale the steel must be considered as a high-strength one. Here cracking can also occur in subsequent service; this is a problem especially for pipes or pressure vessels exposed to natural gas or petroleum because those raw materials contain more or less H₂S. Hydrogen sulfide not only attacks steels strongly by providing atomic hydrogen, but it also acts as „recombination poison“ allowing high quantities of hydrogen to enter the steel.

If the content of H₂S is very high in the gas or oil, now described as „sour“, the pipes and pressure vessels will be endangered also in the absence of hardened regions in the steel. In contrast to high-strength steels in which, in spite of their higher susceptibility, hydrogen cracking cannot start without any external load under technical conditions such a cracking is possible for low-strength steels. This pure „internal-load cracking“ is confined to the rolling plane and is termed blistering and in some cases these blisters can attain considerable dimensions.

A view of an opened blister is given in Fig. 15.8a. The local density of inclusions – mainly iron oxides – was so high in this case that inverse fisheyes were formed: The cracks were not grown from a central inclusion in the surrounding metal – as usually – but started from the surrounding inclusion in the metallic island [25, 42]. To initiate transverse cracks („sulfide stress cracking“) from the blisters (Fig. 15.8b) – the most important real
danger – an external load is necessary, but the effective pressure area becomes so large by the growing blisters that the amount of external load in the extreme case (H₂S in acid solution) [43] has to be only a quarter of the yield strength. By making the inclusions spherical („shape control“) sulphide stress cracking and blistering as its initial phase can be avoided [44, 45] since there are no internal notches now.

**Intergranular hydrogen cracking**

In steels with strengths higher than 1000 … 1250 MPa hydrogen induced cracks follow mostly the former austenite grain boundaries and the question arises whether this can also be explained by the fisheye effect. In connection with normal brittle fracture it was mentioned that the austenite grain boundaries exist in the lower temperature region only as „shells of dirt“. This dirt seems to consist firstly of very finely distributed sulfides and secondly, in hardened and tempered steels (due to their higher content of carbon) of small carbide particles. Such micro-inclusions should provide places for hydrogen recombination. When the pressure is high enough, the fisheye effect may occur in very small regions with a transgranular crack path where the intergranular path is only virtual [25]. Grain boundaries already cracked serve as traps for further diffusing hydrogen atoms, and therefore they are the origin for the usual transgranular cracks, as shown in Fig. 15.9a for a high-strength steel screw. Such screws, which were hot-dip galvanized, broke 1 … 12 hours after mounting. In this case the hydrogen was brought in by an unusually long-duration pickling.

A partial intergranular cracking can often be observed if the cracking occurs in the weld deposit itself. This is surprising so far as the weld deposit is generally not hardened, but obviously the grain boundaries are extremely marked by microsulfides explaining also the partly intergranular fracture of flakes in large forgings.

A special case of hydrogen cracking is the so-called stress corrosion cracking of high-strength steels which is illustrated by the following example: Screw springs in a water-
hydraulic device were protected against corrosion by a layer of tar-epoxy. Soon the layer ruptured resulting in localized corrosion and intergranular cracks started from the corresponding corrosion grooves. No traces of corrosion were visible on the grain boundaries with the exception of a small region around the corrosion grooves (cf. Fig. 15.9b). This suggests that the hydrogen was not generated by corrosion but arose more directly from the water by a tribosorption process.

b) „Stress Corrosion Cracking“

In the foregoing case (broken screw springs) the term „stress corrosion cracking“ was used but it is generally agreed that this kind of cracking is actually related to hydrogen.

The term mentioned is also used for a group of crack phenomena characterized by the fact that no pure metals but only alloys are involved and that the „attacking“ medium has to contain specific ions. This phenomenon became firstly known to the British soldiers in India as the so-called season cracking. Their cartridge cases made from cold-worked brass cracked during the monsoon time under the influence of (wet) ammonia coming from the dung of the horses. At present the main problem lies in the susceptibility of stainless austenitic CrNi-steels to chlorides since such steels are used to a large extent in chemical and nuclear-power plants. For this case in general a transgranular crack path with a specific fan structure can be observed (cf. Fig. 15.10a) similar to the above-mentioned cleavage fracture of ferritic steels.

Stress corrosion cracking is widely understood as a dissolution process which is expressed in the German term „Spannungsrissskorrosion“ and also in the Russian term „korrosija pod naprjashenijem“. Otherwise, the English term „stress corrosion cracking“ emphasizes the meaning of cracking in this process, which seems to be more adequate as shown below. From this linguistic phenomenon it becomes evident that unambiguous hints to hydrogen as the driving cracking force can be found only in the English literature [46 to 48].
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The change in the opinion of Scully as a former outstanding representative of the dissolution theory [49, 50] is of special interest here: At the end of the seventies, for the first time, detailed fractographic investigations of hydrogen-charged austenitic CrNi-steels were published [51, 52]. No essential difference in the fractographic features between hydrogen cracking and stress corrosion cracking was detectable. Therefore, Scully now [53] acknowledges that hydrogen may be responsible for the transgranular crack mode. Nevertheless, he still believes in dissolution processes with respect to the rarer intergranular crack mode. Figure 15.10b is an instructive example showing a fracture fan which starts from an inclusion cavity similar to the case of fisheyes.

For comparison, in Fig. 15.10c a fractograph is shown taken from a failure case, in which a CrNi-steel-“skirt” of a pressure vessel failed unambiguously under the influence of hydrogen gas. The similarity of the crack structure to that of stress corrosion cracking is evident.

An interesting contradiction in this connection should be discussed here: In ferritic steels hydrogen has its highest effectivity for initiating fracture at approximately room temperature.
with an upper limit at 80...130 °C. If this limit is exceeded, the hydrogen atoms probably are too mobile to be tribosorbed in slip-bands. Therefore, they cannot form pressurizing bubbles. Otherwise, in austenitic CrNi-steels stress corrosion cracking usually acts at temperatures higher than the given limit [54]. However, this can be explained by the relatively low diffusivity of hydrogen in austenitic steel. Hence, higher temperatures are necessary to reach a critical velocity of diffusion and a corresponding accumulation of hydrogen in cavities. For instance, Holzworth [55] has found that foils of austenitic steel embrittle faster and more strongly if they are electrolytically hydrogenized at 100 °C instead at room temperature.

Concerning the role of chlorides, the following assumptions can be suggested: The corrosion resistance of these steels is due to the formation of an oxide layer as a result of a chemisorption of oxygen. On the other hand, this oxygen prevents the adsorption of hydrogen but can itself be displaced by chlorides being also able to form a certain kind of passive layer [56, 57]. The displacement of oxygen should occur preferably at sites where the existing oxide layer is destroyed by slip-band formation. Chloride ions will be chemisorbed instead of oxygen. The chlorides otherwise enable free entrance for hydrogen, that means, chlorides act as a „door holder“ for hydrogen. Here again the question arises whether hydrogen is produced primarily by dissolution or by tribosorption processes.

c) Hot Cracking and Overheating

The so-called hot cracking is usually induced by sulfides, more seldom by carbides and oxides. Cracking can also occur influenced by molten or vaporized metals; but this is not confined to higher temperatures depending on the kind of the attacking metal.

Here preferably the case of cracking by sulfides should be considered, especially its subcritical stage, i.e. overheating: The reason for the generation of inclusions is that sulphur, like oxygen, is scarcely soluble in the iron lattice, even at the highest temperatures; otherwise, it reacts chemically with the iron producing a sulfide (FeS) and a special eutectic (Fe, FeS). The latter has a melting point of only 985 °C and initiates cracking in the temperature region between 1000 °C and 800 °C during rolling, forging or welding, i.e. the temperature range of cracking is generally below the melting temperature of the sulfide eutectic. This phenomenon was also observed for cracking of steels by cadmium [58] and lead [59]. Therefore it can be assumed that the crack activity is only due to the vapour phase of the attacking media.

For increasing the melting point of sulfides, the steels are alloyed with manganese but, nevertheless, the melting point usually remains below that of steel. This implies a high vapour pressure of sulfides in the upper temperature region (cf. Fig. 15.11). As a consequence, a process which was already described for hydrogen will be initiated under the action of shrinking or working deformations: TRIBOSORPTION. To enable this process to take place the sulfide molecules must be dissociated and then the sulfur atoms are pumped into the metallic matrix. Atomic sulphur is enriched in the grain boundaries, as at higher temperatures gliding occurs preferably along them. The accumulation process is followed by a new formation of sulfide vapour. By forming pressurizing bubbles (according to the hydrogen cracking model) gliding can be inhibited but cracking will occur only as an extreme case [60]. During cooling, the sulfide vapour crystallizes forming micro-inclusions. The overheating process occurs preferably during welding. At cooling down slowly or annealing at 600 ... 700 °C the finely dispersed sulfide particles coagulate and can serve as creep nuclei as discussed for stress relief cracking, see Fig. 15.3d.
The author assumes that the tribosorption of sulphur operates also at ordinary hot working. As a result the sulfide particles will serve as primary markers for the austenite grain boundaries where other diffusing elements including hydrogen can be accumulated at lower temperatures. This assumption corresponds to investigations of Joshi [61] on high-strength steels cracked under the influence of hydrogen. By using AES-SEM he found intergranular films of sulfides of thickness up to 15 nm.

Conversely, sulphur and oxygen can be driven out of the steel – like hydrogen – by compressing (triboDEsorption). This procedure was already known to the ancient smiths who were not able to melt the iron ore, but had to reduce it in the solid state; they then purified the iron by forging (pressing) out the sulfides and oxides [60].

15.5 Summary

Fractography with SEM has proved to be an excellent method of analyzing failures. Depending on the experience of the investigator, a high degree of certainty can be reached in a relatively short time reducing the former trial-and-error character of this field. Moreover, fractography delivers information about the microstructure, which can scarcely be obtained by light microscopy. This „fracture metallography“ is useful especially for estimating the size of the primary austenite grains and the size, the kind and the distribution of flat, small or finely dispersed inclusions and precipitates. Fractography with
SEM has revealed new insights into fracture mechanisms. In the present paper this results in the assumption that the medium-induced fracture of different kinds is based on the same fast-transport phenomenon introduced here as Tribosorption

15.6 References

15. Fractography with the SEM


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