MECHANISM OF ENVIRONMENT-INDUCED CRACKING

Martin Moeser


ABSTRACT

Some media such as hydrogen, sulfides and carbides but also metals are known to be able to embrittle metals. The present paper tries to elucidate this medium-induced cracking (environmental cracking). In regions of current flow (slip bands) a fast transport of foreign atoms may occur along the dislocations in certain temperature ranges. This leads to supersaturation at sites where gliding is stopped. In form of pressure bubbles, as short-time precipitates, the medium inhibits further gliding. For hot cracking and relaxation cracking, the precipitation of the attacking medium (carbide or sulfide) along the grain boundaries represents the frozen-in state of the process of embrittlement.

INTRODUCTION

Some media such as hydrogen, sulfides and carbides but also metals are known to be able to embrittle and to crack steel and other metallic materials. The existing concepts used to explain these phenomena are mainly based on the classical form of the Griffith-equation.

\[ \sigma = \sqrt{\frac{2E \times \gamma_s}{\pi \times a}} \]

with E being Young's modulus, a the crack length and \( \gamma_s \) the surface energy. The medium should reduce the surface energy and therefore promote cracking. In this connection, the TROIANO-ORIANI-theory [1] should be mentioned for hydrogen cracking and the REHBINDER-effect for liquid-metal embrittlement.

However, relative to the total fracture work, the surface energy is very small. Therefore, Orowan extended the Griffith equation by introducing the real fracture energy (\( \gamma_{eff} \)) as the sum of the surface energy (\( \gamma_{sl} \)) and the work of plastic deformation (\( \gamma_{pl} \)).
In hydrogen cracking of steel, for instance, the fracture work is at least a hundred times greater than the surface energy. Accordingly, the reduction of the work of plastic deformation has to be explained rather than that of the surface energy. The latter should be confined to describe the action of wetting agents.

THE TRIBOSORPTION CONCEPT

For metals, an embrittlement is usually caused by the formation of very fine precipitates impeding the movement of dislocations. The question arises in which way a foreign medium can produce the same effect.

The medium has to enter the matrix. As medium-induced cracking may reach considerable velocities, normal diffusion can be excluded as a transport mechanism; instead, a certain kind of pumping should occur. Solely atoms but not molecules can certainly penetrate the metal lattice. Whenever the medium is a compound, the molecules have to be dissociated a priori. Embrittling media, which exist in the solid state at room temperature, have their main activities in the range of their melting point or slightly below it, i.e. partially in the solid state. The latter fact points out that solely the vapour phase is responsible for the embrittlement. An embrittling effect is caused by those elements which are almost unsoluble in the matrix. But the reverse case occurs in regions of current flow (slip bands), i.e. where the solubility is high. The reason may due the fact that moving dislocations are small regions of very high temperatures, thus being able to carry foreign atoms.

When the movement of dislocations is locally stopped the solubility of the foreign atoms drops resulting in a strong supersaturation. Now, the foreign atoms tend to agglomerate and to rebuild the compound (recombination) as far as former compounds (hydrogen, sulfides, carbides) are concerned. The places of agglomeration (accumulation) and recombination should be provided by voids induced by the reaction of dislocations carrying the foreign atoms. The media accumulating in voids should remain in the gaseous state to form pressure bubbles as a kind of short-time precipitates inhibiting further gliding. The process of embrittlement is schematically summarized in Fig. 1:
When the process takes place at very high temperatures („hot cracking”), a fine dispersion of the attacking medium may be observed at the grain boundaries, since they are the places of gliding. This is particularly valid for regions only embrittled but not yet cracked. The so-called stress corrosion cracking is considered to be usually caused by hydrogen. Due to its mechanical activation the process of fast uptake and transport of foreign atoms is termed TRIBOSORPTION [2, 3].

The conclusions quoted here have mainly been drawn from failure analyses, some examples of which will be presented.

HYDROGEN CRACKING

An impressive fracture surface structure known to the welders is the so-called fisheye structure. Two of such structures are shown in Fig. 2a. Fisheyes are generated during the tensile or bending tests when welding is performed with moist electrodes etc. The crack zone is located around a larger defect in which hydrogen had accumulated. Due to their glittering appearance, fisheyes contrast with the surrounding brittle or ductile final fracture.
In general, fisheyes are detected on a microscopic scale, only. The mini-fisheye shown in Fig. 2b was found beneath a weld.

![Fisheyes](image1)

**Fig. 2**  
Fisheyes  
a) fracture surface of a welded-bent sample showing two fisheyes  
b) mini-fisheye beneath a weld: a flat inclusion hole served as the crack centre.

The fracture facets of hydrogen cracks are much smaller than those of normal cleavage. Kikuta, Araki and Kuroda [4] identified them as \{110\}-planes whereas cleavage follows the \{100\}-planes.

A strong hydrogen absorption under plastic tension as the basic process of cracking was revealed radiographically by Louthan et al. [5] in austenitic CrNi steel, Fig. 3.

![Radiography](image2)

**Fig. 3**  
Radiography of CrNi-steel penetrated by hydrogen (tritium) [5]  
a) pure diffusion (sample unloaded)  
b) tribosorption along slip-bands during deformation at a notch
HOT CRACKING OF NICKEL-ALLOYS

Rotors of exhaustion turbo-superchargers are produced of a nickel alloy by casting. As carbon is nearly unsoluble in nickel, it is enriched in the melt during solidification, forming coarse (primary) carbides (see Figs. 4a, b). In order to attain a higher ductility, the parts are solution-annealed at a relatively high temperature. During subsequent air cooling extensive cracking occurred. The cracks were opened for fractographic investigations. A region of intergranular brittleness was found ahead of the cracks. In this region the primary carbides have disappeared, leaving cavities behind (Fig. 4c). The carbides now form a fine dispersion along the grain boundaries. Such particles are shown in Fig. 4d. The particles are surrounded by matrix walls (dimple walls). Thus, the carbide melt is unlikely to be dispersed simply by flowing along the grain boundaries.

Fig. 4  Hot cracking of a nickel-alloy
a) and b) regular state: dimples with a large primary carbide
c) embrittled zone ahead of a hot-crack: grain boundary covered with fine dimples; a hole shows the former place of a primary carbide
d) fine carbide in the dimples: carbide dispersion
As the process of cracking partly remained subcritical, the distribution stage of the embrittling medium was frozen in.

**HOT CRACKING OF STEEL**

In structural steel sulfides are known to be responsible for hot cracking. Usually, the sulfide inclusions are large and flattened (Fig. 5a).

In the present example cracks were found in the heat-affected zone of a weld. Here again an embrittled („overheated”) region was detected in front of the cracks. Cracking occurred also intergranularly. As shown in Fig. 5b, the grain boundaries are covered with a dispersion of sulfides. Fan-like structures („sulfide flowers”) can be identified.

![Fig. 5 Hot cracking of structural steel](image)

a) regular state: flat sulfide inclusions  
b) embrittled zone with intergranular dimple fracture: sulfide dispersion

The grain boundaries were formed in the primary austenite, which does not exist at room temperature, i.e. these boundaries are only shells of impurities.
RELAXATION CRACKING

Relaxation cracking is known to occur in the heat-affected zone of welded pipes and vessels made of low-alloyed steel when they are annealed for stress-relief. An example is shown here of a hot-steam pipe having burst along the longitudinal weld some days after starting the plant. This kind of cracking is generally considered to be due to a precipitation hardening but also to overheating. Cracking occurred intergranularly; the grain boundaries show an extremely fine dispersion of sulfides (Fig.6).

Finally, a historic procedure should be mentioned in connection with deformation-induced fast mass transport. The old metallurgists were not able to melt the iron ore but they had to reduce it in the solid state. Afterwards, they purified the steel blooms by forging out the sulfides. Thus, metals may be said to behave like a sponge.

REFERENCES