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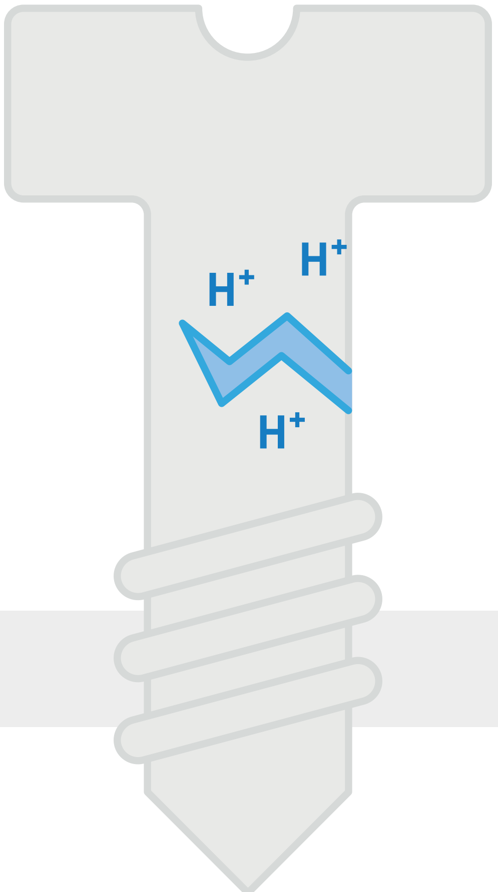

Hydrogen Embrittlement

White Paper

Hydrogen Embrittlement

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The recommendations and advices mentioned must be adequately checked by the reader in practical use and be approved as suitable for its application. Changes reserved.

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HYDROGEN EMBRITTLEMENT

Introduction

Hydrogen embrittlement is a serious matter which mechanically degrades a range of different structural materials. Despite it was reported first time more than hundred years ago (1875) and that the phenomenon has undergone intensive studies for decades many uncertainties still exist.

Hydrogen embrittlement can be divided into two types. One is the environmental type where hydrogen embrittlement failure is due to the supply of hydrogen from the environment, normally through corrosion. The second is hydrogen embrittlement failure due to the supply of hydrogen from processes during manufacture. This type is designated internal hydrogen embrittlement.

The complexity of hydrogen embrittlement fractures is way beyond normal fracture processes and not all metals and alloys are affected. Materials that are most vulnerable include high-strength steels, titanium and aluminum alloys. Entry of hydrogen into the metals and alloys is of course one important element of hydrogen embrittlement. This process alone is quite a complicated process and the rate of hydrogen entry depends on many variables. Sources of hydrogen can besides corrosion e.g. include the steelmaking process, break-down of unsuitable lubricants, heat treatment atmospheres, arc welding and also machining in wet environments. However, the vast majority of processing embrittlement risk appears to be electrochemical surface treatments such as acid cleaning and electroplating.

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HYDROGEN EMBRITTLEMENT

Basics of hydrogen embrittlement

Hydrogen embrittlement of fasteners is typically associated with carbon and alloy steels, but as mentioned before also other metals and alloys can be affected. The hardness of the fastener is an essential parameter. Previously, standards dealing with the phenomenon hydrogen embrittlement stated that the risk started with hardness above 320 HV. Recent research makes it clear that hardness exceeding 360 HV is the threshold beyond which further steps to manage hydrogen embrittlement risk are required.

The failure of a fastener caused by hydrogen embrittlement is a delayed, brittle failure. Fracture only happens after installation and only for fasteners exposed to tensile stresses (a rare exception to this is certain spring parts containing residual tensile stress from cold forming that might break without installation). The level of tensile stress in the fastener is a decisive parameter as the fastener will be more prone to hydrogen embrittlement failure at higher loads. However, fracture can happen even for fasteners exposed to tensile loads well below the tensile strength. The failure occurs at some time after the fastener is assembled. Typically a fastener is installed during assembly and found broken hours later or the next couple of days. It rarely happens seconds after assembly and normally not later than a few months later but when it happens, it's sudden, with no advance warning or visible signs. Failures occurring in service are often costly and sometimes even catastrophic.

Visual inspection of the fracture shows an area with no ductility, however another part might show a ductile fracture originating from the final breakage of the fastener where the remaining cross section area could no more resist the load. The brittle fracture reveals a very similar appearance to intergranular fractures resulting from other causes. Examinations by experienced materials engineers using scanning electron microscope are critical for the identification of hydrogen embrittlement in the failure analysis.

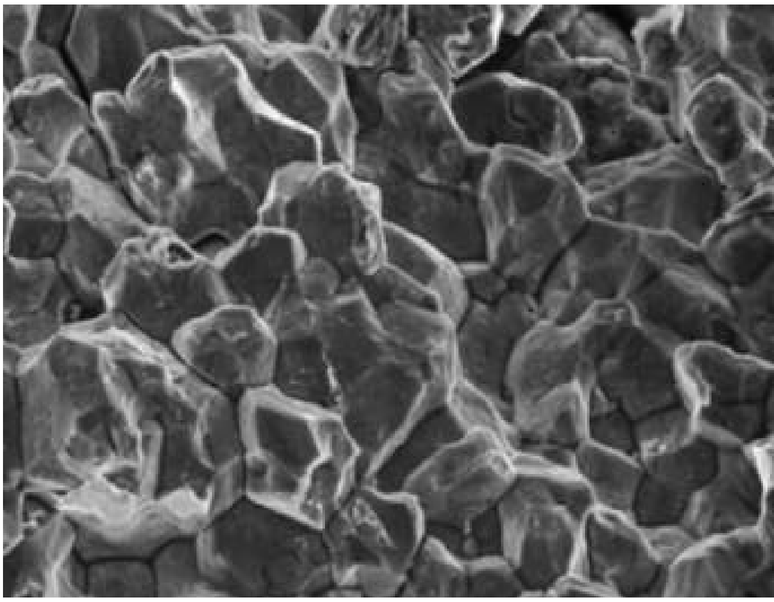

Figure 1: Intergranular fracture from caused by hydrogen embrittlement in bolt

The following processes will take place in case of hydrogen embrittlement:

1. Entry of hydrogen into the fastener
2. Diffusion of hydrogen to high tensile stress regions in the fastener
3. Hydrogen segregation to grain boundaries, inclusions, dislocations and other traps
4. Reach of critical value of hydrogen concentration
5. Crack development

Point 2 to 5 will continue until the fastener cannot resist the load and finally breaks.

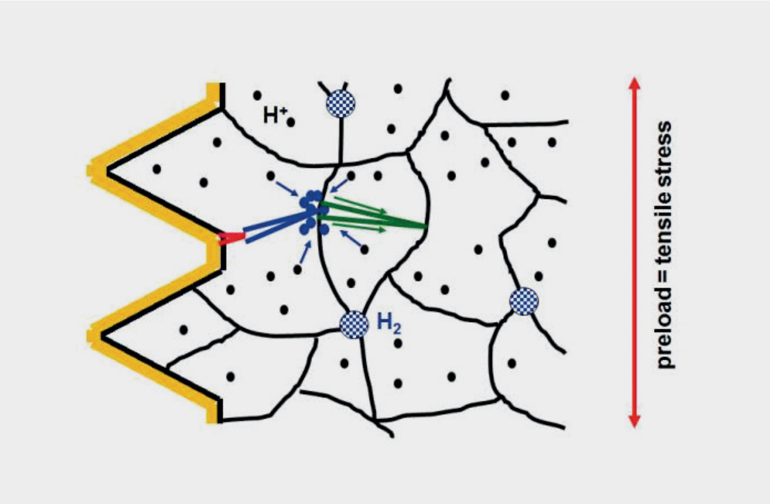

Figure 2: Crack development in a fastener

HYDROGEN EMBRITTLEMENT

Entry of hydrogen into the fastener

As mentioned already the hydrogen can originate from various sources. In most cases where hydrogen embrittlement failure is discovered in newly installed fasteners the biggest contributors are in the manufacturing process related to acid cleaning and subsequent electroplating.

Electrolytes used for plating has been optimized for higher efficiency over the years which has reduced the generation of hydrogen. There is, however, no guarantee that high efficiency will not lead to embrittlement.

Before electroplating can take place the fasteners needs an active surface and have to be chemically clean. Typically the cleaning process is alkaline degreasing followed by acid cleaning to remove heat treatment scales, rust and other oxide films. Alkaline and mechanical cleaning should be used for parts with very high strength but are slow and expensive processes.

Acid cleaning generates a considerable amount of nascent hydrogen (H) atoms which are formed on the surface of the fastener. Immersion time depends on the as-received surface condition and should be of minimum duration and always with usage of inhibitors. Some of the hydrogen atoms will join and form a H2 molecule which can be seen as bubbles in the acid. Some of the nascent hydrogen will be absorbed by the steel. The total quantity of hydrogen absorbed by the fastener is influenced by the time in acid cleaning and the chemistry of the acid.

Next step is the electroplating where the protecting material (e.g. Zn, Ni or Cr) in form as ions is deposited onto the fastener by a cathodic reaction in an electrolyte. Also this process generates hydrogen which can be absorbed by the fastener. ISO 4042 "Fasteners - Electroplated coatings" is the reference standard and provides guidance for avoidance of hydrogen embrittlement.

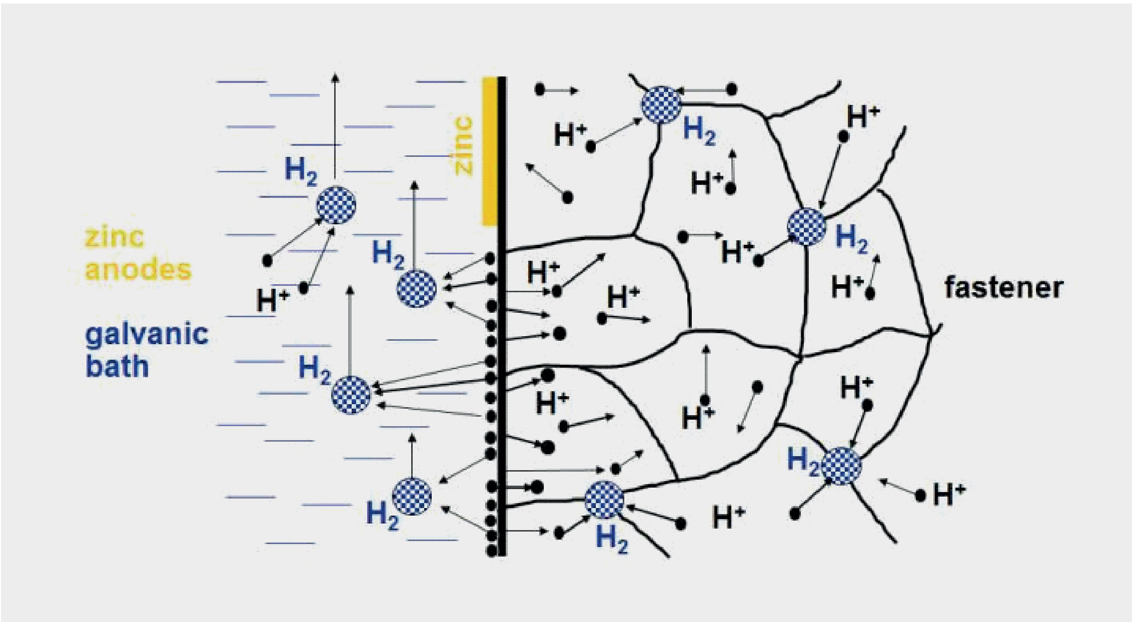

Figure 3: Electroplating

HYDROGEN EMBRITTLEMENT

Diffusion of hydrogen to high tensile stress regions in the fastener

Hydrogen dissolves in the steel fastener as hydrogen atoms (H). Absorbed hydrogen atoms are highly mobile and can diffuse within the fastener material over considerable distances. Inside the fastener the hydrogen atom will tend to segregate to regions of high tensile stresses and with time, the concentration of hydrogen will increase in these regions. If two adjacent atoms recombine to form molecular hydrogen (H2) in a trap, the applied stress required to cause movement becomes much greater and the molecule will be pinned at that point.

HYDROGEN EMBRITTLEMENT

Hydrogen segregation to grain boundaries, inclusions, dislocations and other traps

As mentioned fractures caused by hydrogen embrittlement are intergranular. Inside the fastener, hydrogen has a tendency to segregate to grain boundaries, inclusions, dislocations and other traps. With time as the hydrogen diffuse through the fastener segregation in these traps increases.

HYDROGEN EMBRITTLEMENT

Reach of critical value of hydrogen concentration

A higher hydrogen concentration results in lower critical stress at which failure may occur and a lower hydrogen concentration results in higher critical stress at which failure may occur. Mobile hydrogen atoms will segregate to surface flaws, inclusions, dislocations and other defects where tensile stresses are high and the consequence is that these regions will be weakened. When the combination of hydrogen concentration and amount of stress reaches the critical point fracture will occur and this process can go on until the fastener finally breaks. The initial crack will typically appear inside a grain and develop until it reaches the grain boundary. From this point on it will develop along the grain boundaries until final breakage of the fastener.

HYDROGEN EMBRITTLEMENT

Prevention and hydrogen relief

Hydrogen embrittlement is to a high degree unpredictable and all efforts to avoid it must be done during the design phase where the features of parts are decided and during the following manufacture.

Avoidance of manufacturing processes which allows hydrogen generation and hydrogen absorption into the fasteners will eliminate the risk of hydrogen embrittlement failures originating from manufacture. The environmental type caused by corrosion can be avoided by selecting an appropriate surface treatment which does not generate hydrogen during the plating process.

Among a range of possible solutions are:

- Mechanical zinc plating
- Dacromet
- Geomet
- Delta Protekt
- Xylan 1014/1400/1424
- Magni 565

Hydrogen embrittlement only occurs for high strength fasteners. If the application allows it, fasteners which do not require special measures should be selected when the manufacturing method cannot exclude hydrogen. ISO 4042 provides proper guidance.

Elimination of acid cleaning where possible, when not possible the time of immersion during acid pickling should be kept at a very minimum. The acid should always contain inhibitors. Where high strength fasteners are needed and the manufacturing process does not allow total elimination of hydrogen generation and absorption into the fastener, for example by acid cleaning and electroplating, it is critical to minimize the risk by a subsequent baking process called hydrogen relief.

The baking is specified by ISO 4042 at a temperature 190° C to 220° C up to 24 hours. Parts baked within four hours of plating is considered good practice for most fasteners as the hydrogen concentration immediately after acid cleaning and plating is high just below the steel surface. It is important to note that time at the given temperatures must be based on the fastener core temperature.

For fasteners with residual stresses time to baking is critical because residual stresses in the fasteners will cause the hydrogen near the surface to segregate to these stressed regions associated with surface defects, inclusions, dislocations and potentially cause embrittlement.

The intention of baking is to drive out as much hydrogen as possible and to redistribute the rest throughout the fastener. This will reduce the amount of mobile hydrogen which causes the embrittlement. Studies has shown that time of baking is crucial, the closer to 24 hours the better. Baking duration below 5-6 hours has shown to have very limited effect, in some cases even detrimental.

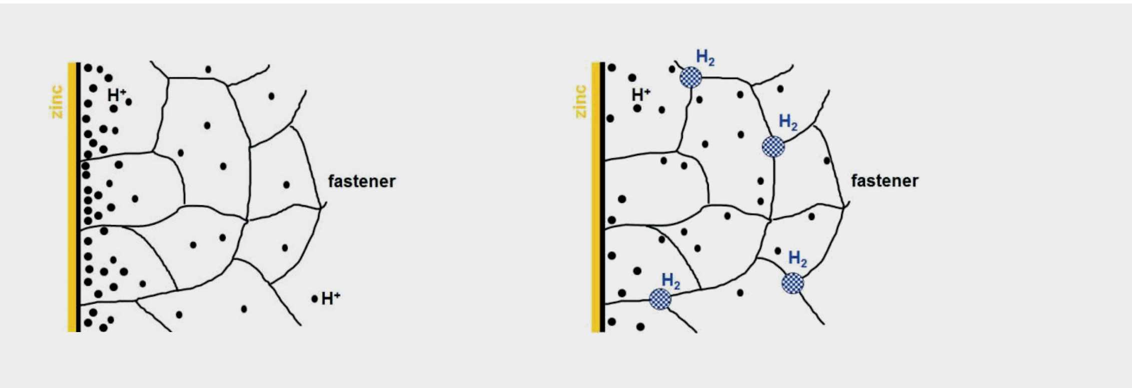

Figure 4: Hydrogen distribution before (left) and after baking (right)

HYDROGEN EMBRITTLEMENT

Procedure to inspect fasteners for hydrogen embrittlement

When embrittlement failures do occur all fasteners in a lot are rarely affected. In fact, usually only a few percent or less of the fasteners will show embrittlement when exposed to tensile loads. Inspection can be done but even a high number of tests might not catch affected parts despite the high efficiency of the test method itself.

Inspection of fasteners is defined by ISO 15330, "Preloading test for the detection of hydrogen embrittlement - Parallel bearing surface method". During the test the fasteners are subjected to tensile stress in the range of the yield point or the breaking torque. The stress or torque is held at least for 48 hours. It is crucial for the test that the fasteners are constantly exposed to tensile stresses and that seating (embedding) is limited to a minimum. After every 24 hours the fasteners are retightened to the initial stress or torque and at the same time checked if failure due to hydrogen embrittlement has occurred.

If all samples of fasteners from a lot have passed the test without breakage or visible cracks the lot can be released. Such tests are intended for in-process control in manufacture where they can be started within hours after hydrogen generating process steps. The test can of course be made at any point of time to detect potential risks, however after transportation and storage the hydrogen source might be environmental and concluding the reason can be difficult.

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