Hydrogen Embrittlement

An Overview from a Mechanical Fastenings Aspect

Current trends in fastener technology are towards high strength, light assemblies, and fewer fasteners in the overall construction. Coupled to this are the issues of friendly environmental policies, plus total reliability in every respect.

Against this background, understanding Hydrogen Embrittlement is still an issue on a global scale. Here we have presented the latest information (year 2000) that's available and can only advise that greater interest will ensure full understanding on the topic.

INTRODUCTION

If you search for information on hydrogen embrittlement you are inevitably directed to the directory subject matter – corrosion!

There are two types of hydrogen embrittlement; firstly the environmental type when it is hydrogen assisted failure due to the supply of hydrogen from the environment, i.e. through corrosion. The second is hydrogen embrittlement failure due to the processes during manufacture. We shall be addressing hydrogen embrittlement, as applicable to fasteners and the coating industries.

The significant increase in the specifying of coated finishes for safety critical and high strength fasteners requires an appreciation of the hazards when selecting a surface coating. Whilst limiting the potential problems of hydrogen embrittlement through strict process control, it’s now possible to consider new advanced coatings that will provide greater assurance for the engineer.

Not all applications will require these advanced coatings but they are referenced for information.

Whilst the subject in question is hydrogen embrittlement, we have taken the opportunity to cover related phenomena and to provide some reference position amongst the associated failure mechanisms in this topic sector. If in doubt, your supplier will be able to assist any technical issues related to surface coating and the occurrence of a failure.

WHAT IS HYDROGEN EMBRITTLEMENT?

When atomic hydrogen enters steel and certain other alloys, for example aluminium and titanium alloys, it can cause a loss in ductility or load carrying ability or cracking (usually as sub-microscopic cracks), or catastrophic brittle failures at applied stresses well below the yield strength or even the normal design strength for the alloys.

This phenomenon often occurs in alloys that show no significant loss in ductility, when measured by conventional tensile strengths, and is frequently referred to as hydrogen induced delayed brittle failure, hydrogen stress cracking or hydrogen embrittlement.

Hydrogen is the smallest atom possible and is the most abundant element in the universe. Two hydrogen atoms combine to form a molecule H2 which is a stable state. For hydrogen to do damage to steel, it must be in the atomic form and usually recently produced, called nascent hydrogen. As the atom is so small, it can enter the structure of steel.

The hydrogen can be introduced during heat treatment, as carbonising, cleaning, pickling, phosphating, electro-plating, autocatalytic processes and in the service environment as a result of cathodic protection reactions or corrosion reactions.

Hydrogen can also be introduced during fabrication, for example during roll forming, machining and drilling due to the breakdown of unsuitable lubricants as well as during welding or brazing operations.

Stress corrosion cracking, stress embrittlement, hydrogen embrittlement, and hydrogen assisted stress corrosion are failure mechanisms which are often viewed as being synonymous, and understandably so, because their cause and effect have similarities that outnumber their identifiable differences. Actually, only stress corrosion cracking and hydrogen assisted stress corrosion are corrosion related. However, this is an appropriate time to discuss the other two as well.

So often, with mechanical fasteners, when fatigue failures occur, hydrogen embrittlement is usually blamed. One must therefore examine carefully the situation in order to be certain which of the two has caused a failure.

All occur only in parts and components, which are stressed in tension. All cause failure, the actual breaking of the component into two or more pieces. The fracture is delayed. Sometimes it occurs within hours after the tensile load is applied; sometimes not for months, but seldom years. But when it happens, it's sudden, with no advance warning or any visible signs of imminence. Failures occurring in service are serious and costly, sometimes catastrophic.

HYDROGEN EMBRITTLEMENT – MECHANICAL FASTENERS

Hydrogen embrittlement is associated with fasteners made of carbon and alloy steels. It is only usually expected to be a risk for higher tensile fasteners with hardnesses above 320HV. It is caused by the absorption of atomic hydrogen into the fastener's surface during manufacture and processing, particularly during acid pickling and alkaline cleaning prior to plating, and then during actual electroplating.

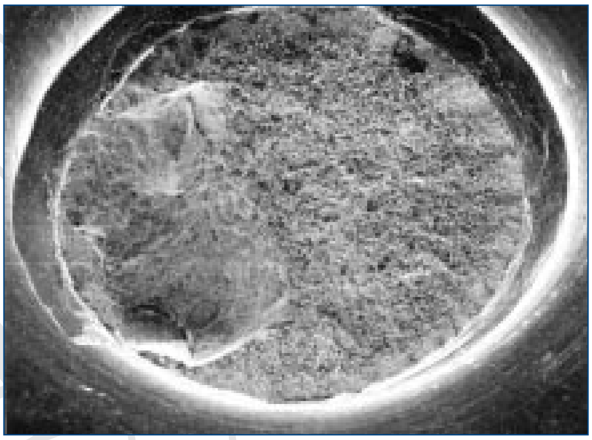
The deposited metallic coating entraps the hydrogen against the base metal. If the hydrogen is not relieved by a post-baking operation, when load or stress is applied the hydrogen gas migrates towards points of highest stress concentration. Pressure builds until the strength of the base metal is exceeded and minute ruptures occur.

Hydrogen is exceptionally mobile and quickly penetrates into any recently formed cracks, lesions or material surface discontinuities, which become high stress areas. Cracks will promulgate through the component surface, weakening the component due to the loss of cross-section area. The failure is usually completed by a ductile fracture. The *tougher* the material, the more it is capable of resisting the above phenomenon.

The susceptibility of any material to hydrogen embrittlement in a given test is directly related to the characteristics of its *trap* population. In this instance, *trap* population relates to the material microstructure, dislocations, carbides and other elements present in the structure. Such is the effect that interactions can be reversible or irreversible sources. Diffusion is controlled by the rate of escape of hydrogen from the *traps*; the nature and the density of the *traps* control the diffusion coefficients.

The greater the hydrogen concentration becomes, the lower the critical stress, or lower the hydrogen concentration, the higher the critical stress at which failure may occur.

Hydrogen embrittlement is non-corrosion related. It is interrelated to high hardness values of the component part. Products having Vickers hardness exceeding HV 320 require special care to reduce the risk of this phenomenon during the plating process or coating procedures. Some experts feel that hardness exceeding HV 390 is a threshold beyond which further steps to manage hydrogen embrittlement risk are required, often ensuring that acid is not used in the cleaning process, in our view, this would be prudent.



A typical hydrogen embrittlement fastener fracture.

When embrittlement failures do occur, they will usually only affect 2-3% of the components. The embrittling process is a random effect, and the de-embrittling process can be regarded similarly.

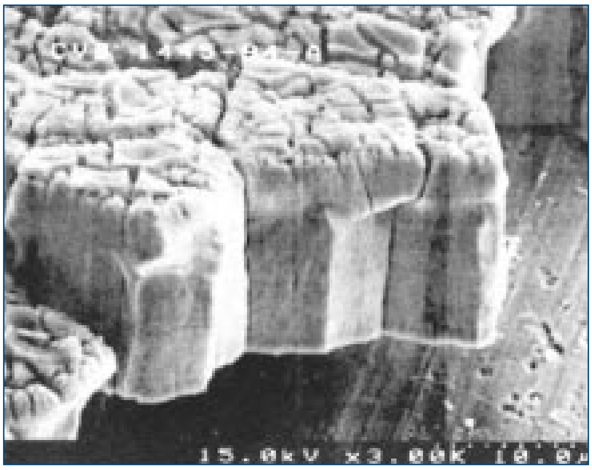
AVOIDANCE – HYDROGEN EMBRITTLEMENT RISK MANAGEMENT

Full, stringent and best practice process control is required, from raw material to end product, if one is to limit Hydrogen Embrittlement occurrence.

The amount of hydrogen that may be introduced in the manufacturing process is cumulative. The manufacturer should establish a series of checks to assure that all manufacturing sequences where hydrogen may be potentially introduced are optimised to reduce the production of hydrogen. Lubricants should be monitored to determine they are not used beyond the time period recommended by the lubricant manufacturer. A material history should be developed to establish which materials when fabricated and processed to a high hardness level are susceptible to embrittled failure. In any event, stress relieving will be required for high hardness parts to relieve built-in stress.

The vast majority of processing embrittlement risk appears to be attributed to electroplating process. Before electroplating can take place, parts have to be chemically clean with an active surface. The cleaning process is typically alkaline degreasing followed by acid pickling to remove heat treatment scale, rust and other oxide films. Acid pickling produces nascent hydrogen, so it is advisable, and often mandated in specifications, that this should be kept to a minimum time. Alternatives such as alkaline de-scaling, a slow and expensive process, or mechanical cleaning can be used, and often must be used for cleaning very high tensile components.

The other major source of hydrogen is from the actual electroplating solution. Up until a few years ago, the vast majority of plating baths employed cyanide as an electrolyte. Thus, zinc-cyanide solutions and cadmium-cyanide were commonplace. As plating solutions are depleted, the efficiency will drop with a corresponding increase in hydrogen release. The development of non-cyanide electrolytes has resulted in acid-zinc and acid-cadmium operating in the 95% or higher efficiency range. This has reduced the generation of hydrogen significantly.



A typical columnar structure.

There is, however, no guarantee that high efficiency gives no embrittlement. Low temperature heat treatment (baking) is required to reduce the risk.

The structure of the coating from an acid solution has a laminar structure, which, due to its lack of porosity, does not allow hydrogen to diffuse from the surface readily. The advantage of a columnar structure, which is given by an alkaline solution, as opposed to laminar, allows the hydrogen to diffuse through the coating.

Some plating specifications note this point and direct that only certain types of plating solutions should be used.

The electroplating efficiency of a solution varies with the electrical current density, and in barrel plating, the barrel loading, the rotational speed, contact efficiency, solution temperature, etc. can affect results. So barrel loading is important to reduce hydrogen embrittlement risk.

Thus, the manufacturer should work closely with the electro-plater to ensure risk reduction is achieved in prepared steps, for the plating process, and that process care and checks are in place to prevent over or under filling of plating barrels.

Hydrogen embrittlement mechanisms are thought to be diffusion controlled and thus the effects of time delay before bake are very important.

When high strength fasteners are involved, then no longer than one hour between plating to entry into the bake oven is often mandatory. The transfer time is important and governed by finishing specifications. Large bodies of evidence exist stating that delays exceeding 4 hours following plating are detrimental to the effectiveness of baking.

Depending upon product types, the baking time will vary from 2 hours for case hardened fasteners to 24 hours for very high tensile or safety critical fasteners.

Higher baking temperatures will increase diffusion rates and should improve de-embrittlement but there are risks of tempering back high tensile fasteners and also liquid metal embrittlement occurring, so baking temperatures of between 180°C and 220°C are usually recommended. Lower temperatures, and increased baking times, are required when this temperature affects the coating or the fastener material.

Reference documents to consider for the de-embrittlement processes and other useful applicable information are listed.

BS 7371 – Part 1:
1991 Coating of metal fasteners.

ISO 4042: 2000:
Fasteners electroplated coatings.

BS EN ISO 15330:
1999 Preloading test for the detection of hydrogen embrittlement.

BS EN ISO 20898-1:
1999 Mechanical properties of fasteners.

BS EN ISO 20898-2:
1994 Mechanical properties of fasteners.

Because residual and applied stresses are the drivers for hydrogen migration and interaction, it appears that higher strength (higher hardness) fasteners are more sensitive to any delays. The rapid transfer into the baking oven possibly reduces the opportunity for harmful hydrogen to begin its inward migration. It is the prevention of inward migration that will reduce the probability of embrittlement failure.

Table 1. The Coating Process – Preventative Actions to Reduce Risks.

Process	Details	Hydrogen Embrittlement Risk	Preventative Action
Degrease	Solvent		
	Alkali soak		
	Electro clean	Some	Only use anodically
De-rust or De-scale	Acid	High	Use inhibited short time
	Alkaline de-rusts	Low	Poor at de-rusting
	Abrasive clean	None	
Phosphate	Acid process	Medium	Bake – reduces with time
Electro-plating	Acid type	Medium	Bake
	Alkaline type	High	Bake

It is important to note that time at a given temperature should be based on the metal temperature (*core*) of the product being baked.

One great dilemma for the fastener industry is the problem of thread build up after plating. When the end product fails thread gauging, after de-embrittlement, can you rework the components or not?

The advice is to discuss the situation with supplier and customer and evaluate the risks. *Best is not to try.* But you may be faced with a dilemma and here one of the parties will have to assess the situation and make an appropriate decision based on the risk factor.

If work is *stripped* in an acid solution, extended baking times should be used immediately after the *stripping*, and prior to replating with further post plating de-embrittlement.

Furthermore, the movement by the international standards bodies is not to state baking times, and that the customer should specify his requirement, or the finisher should note best advice and favour longer times for safety.

Advice on preventative actions to reduce the risks within the coating process is detailed in Table 1.

Finally, record everything you do and retain the information for 10 years, or more.

PREDICTING HYDROGEN EMBRITTLEMENT?

Problems occur when least expected. Good house-keeping is the key driver.

Whist prediction is difficult, if the following rules are applied, then the risk should be minimised.

- Mechanically clean the products if possible.
- Mechanically plate high strength components.
- Avoid any embrittling process if possible.
- Use stringent baking control.

Component parts should be to good design practice.

Reviewing the following can reduce susceptibility to hydrogen embrittlement.

- Ensuring sufficient ductility even at very high strength levels.
- Limit content of detrimental elements, especially Sulphur and Phosphate.
- Remove phosphate before heat treatment of the component.
- Avoid the range of tempered martensite embrittlement or classical temper embrittlement.
- Take into account the influence of alloying elements.
- Endeavour to attain a material condition with homogeneous and fine dispersed irreversible traps.

Consider alternative surface coatings.

Some examples.

- Mechanical zinc plating.
- Dacromet.
- Delta Tone.
- Delta Seal.
- Xylan.

LEGAL REQUIREMENTS

The legal position, within the European Union, changed in 1997. Previous to this, a prospective claimant had to prove negligence. Even though, like the fastener industry, the surface finishing industry is bound by the requirements of ISO 9002 and QS 9000, where applicable, records are required for seven years minimum and the processor must be able to present a traceable record of events. This in itself does not absolve the supplier from any liability.

The position now is that the claimant only needs to prove the part was faulty and unfit for the use, or purpose, for which it was supplied in order to claim liability and recompense.

This should motivate responsible suppliers to look for risk free solutions to these problems. Cost restraints have perhaps acted to restrain such solutions? This could be false economy for the unlucky victims of failures due to hydrogen embrittlement.

The authors offer this information as best known practice and will not be held accountable for any liabilities that may result from the document.

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