

OVERVIEW OF HYDROGEN EMBRITTLEMENT IN FASTENERS

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ABSTRACT

This paper focused the overview of hydrogen embrittlement in fasteners. Embrittlement is a phenomenon that causes loss of ductility in a material, thus making it brittle. 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. Generally in the bolt, fracture is occurred where stress is lesser as compares to yield stress. Embrittlement is occurred where there was no evidence of mechanical deformation. In most of cases hydrogen embrittlement causes fasteners failures in high hardness and high strength fasteners that are electroplated. The hydrogen embrittlement failures observes as a brittle break The bolts, which microstructure was typically that of hardened and tempered steel, had been zinc electroplated and it is well known that hydrogen release concurs with zinc deposition. Moreover, the diffusion and accumulation of the hydrogen in metals is favoured by cold working, as is the case of the head to shank transition region.

KEYWORDS: Embrittlement, Failure Analysis, Hydrogen Phenomenon in Metals

INTRODUCTION

Hydrogen embrittlement of fasteners is a major factor in the choice of material or coating for such components. Hydrogen embrittlement may be a serious concern with high strength fasteners made of carbon and alloy steels for which it can be caused by the absorption of atomic hydrogen into the fastener's surface during manufacture and processing. The introduction of atomic hydrogen is particularly possible during acid pickling and alkaline cleaning prior to plating, and then during actual electroplating.

The metallic coating subsequently plated on the fastener entraps atomic hydrogen in the base metal and if the hydrogen is not relieved by a post-baking operation the hydrogen atoms may migrate towards points of highest stress concentration when load or stress is applied. 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 susceptibility of any material to hydrogen embrittlement in a given test is directly related to the characteristics of its trap population related to the material microstructure, dislocations, carbides and other elements present in the structure. 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. 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.

A stress relieving anneal should be considered for fasteners which have been work hardened during fabrication and are to be electroplated. Instances have been reported of fasteners failing by hydrogen embrittlement after many years in service with the cracks associated with corroded thread roots, providing thus an indication of the role of corrosion as a possible source of the hydrogen necessary to promote hydrogen embrittlement

Hydrogen embrittlement is a time consumed process which results in drastically decrease in toughness of solid metal due to presence of atomic hydrogen. Hydrogen embrittlement is a well-known phenomenon in which a metal is weakened by the incorporation of hydrogen in or below its surface, e.g. during plating or etching.

Hydrogen diffuses easily into the metal crystalline structure either as atoms or protons. Non-metallic inclusions such as sulphides, as well as phosphorus, favour hydrogen desorption, acting as catalysts. Hydrogen embrittlement can be classified into two types firstly the environmental type when it is hydrogen assisted failure due to the supply of hydrogen from the environment like corrosion. The second is hydrogen embrittlement failure due to the processes during manufacturing operation. We shall be addressing hydrogen embrittlement, as applicable to fasteners and the coating industries. Zinc electroplated steel fasteners are widely used for assembling threaded joints, since zinc is anodic to steel and offers both good protection to atmospheric corrosion and good appearance, even when applied in thin films in order to obey the dimensional tolerances imposed to fasteners.

What is Hydrogen Embrittlement

Hydrogen embrittlement is also known as hydrogen induced cracking or hydrogen attack. In the universe the smallest atom is hydrogen and it is most abundant. Two hydrogen atoms combine to form a molecule H_2 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. Hydrogen can be introduced during heat treatment, pickling, cleaning, electroplating phosphating 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.

How Hydrogen Gets in

Hydrogen embrittlement can be described as absorption of hydrogen ions, which will later combine to form hydrogen molecules, trapped within grain boundaries promoting enhanced de-cohesion of the steel, primarily as an intergranular phenomenon. It is generally agreed that hydrogen, in atomic form, will enter and diffuse through a metal surface whether at elevated temperatures. Once absorbed, dissolved hydrogen may be present either as atomic or molecular hydrogen or in combined molecular form (e.g., methane). Since these molecules are too large to diffuse through the metal, pressure builds at crystallographic defects like dislocations and vacancies or discontinuities like voids, inclusion/matrix interfaces causing minute cracks to form.

How Hydrogen Gets Out?

Hydrogen absorption need not be a permanent condition. If cracking does not occur and the environmental conditions are changed so that no hydrogen is generated on the surface of the metal, the hydrogen can re-diffuse out of the steel, and ductility is restored.

Performing an embrittlement relief, or hydrogen bake out cycle (the term “bake-out” involves both diffusion within the metal and outgassing) is a powerful method in eliminating hydrogen before damage can occur. Some of the key variables include temperature, time at temperature, and concentration gradient (atom movement).

For example, electroplating provides a source of hydrogen during the cleaning and pickling cycles, but by far the most significant source is cathodic inefficiency. A simple hydrogen bake out cycle can be performed to reduce the risk of hydrogen damage.

Common Characteristics & Type of Hydrogen Embrittlement Failure



Figure 1: Typical Fastener Failure by Hydrogen Embrittlement

- Fasteners must be core hardened to at least Rockwell C32.
- The parts must have come into contact with acid at some point in their processing.
- The failures must occur some time after installation, usually between one and twenty four hours.
- Parts must have a nonporous finish (usually electroplated). The most common finish associated with hydrogen embrittlement failures in screws and bolts is electroplated zinc.
- The parts must be under stress when failure occurs.
- If any of these factors are not present, the chances of the failure being confirmed as hydrogen embrittlement are unlikely.
- Unhardened fasteners or those of Grade 5 or Property Class 8.8 or lower do NOT fail due to hydrogen embrittlement. Fasteners with phosphate and oil do NOT fail due to hydrogen embrittlement.
- Parts that are cleaned by mechanical processes instead of acid are highly unlikely to fail due to hydrogen embrittlement. Failures that occur while parts are being installed are NOT due to hydrogen embrittlement.

Factors That Influence Hydrogen Embrittlement on Parts

The severity and mode of the hydrogen damage depends on:

- Source of hydrogen—external (gaseous)/internal (dissolved).
- Exposure time.
- Temperature and pressure.
- Presence of solutions or solvents that may undergo some reaction with metals (e.g., acidic solutions).
- Type of alloy and its production method.

- Amount of discontinuities in the metal.
- Treatment of exposed surfaces (barrier layers, e.g., oxide layers as hydrogen permeation barrier on metals).
- Final treatment of the metal surface (e.g., galvanic nickel plating).
- Method of heat treatment. Level of residual and applied stresses.

Methods of Checking Hydrogen Embrittlement

When metals are subjected to pickling processes, the metals are dissolved by the acids and hydrogen is generated. The hydrogen is also generated during electrolytic de-greasing, electrolytic pickling, and electro-plating. This hydrogen is occluded (absorbed) by the base metal, especially steel alloys and makes the steel brittle. Parts with hydrogen embrittlement can break after being subjected to loadings. There are several methods to check hydrogen embrittlement. Here, we'll look at the delta method to see how much hydrogen embrittlement there is on plated steel.

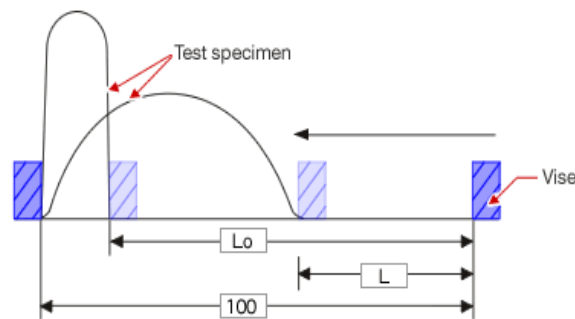


Figure 2: Method of Checking Hydrogen Embrittlement

For the test specimen: material; SK5 (C0.85%), shape; 9mm x 100mm x 0.8mm thick, hardened at 850 deg. C, tempered at 450 deg. C is used. The test is performed by placing the flat test specimen between the jaws of the vise, and slowly closing the jaws at a constant speed to bend the test specimen. If any hydrogen occlusion is present in the test specimen, the hydrogen will migrate diffusively towards the area of tensile stress concentration, and the specimen becomes brittle and likely to break in comparison to a specimen with no hydrogen occlusion. As seen, the Delta Gage method can numerically establish the hydrogen embrittlement rates with easy operations, excellent for factory floors where the plating processes take place.

Parts are Considered to be at Risk if They Have

- A tensile strength > 1050MPa, 1000N/mm² or
- 65 tons/sq. in. (T class Imperial fasteners and above)
- A hardness > 320 v.p.n. (10.9 grade fasteners or above)
- Reduce any time in acid media to a minimum.
- Bake parts as soon as possible after
- Processing in an oven at temperatures between 190-210°C.
- As susceptibility increases with higher strength, time at temperature needs to increase to reduce the risk.

USUAL REQUIREMENTS TO LIMIT HYDROGEN EMBRITTLEMENT		
Parts heat treated or cold worked to a surface hardness of	TENSILE STRENGTH OF PART	
	320HV to 390HV	390HV and above
Fasteners property classes:	9.9, 10.9	12.9 and above
Process Requirements Clean parts to remove phosphate coating prior to hardening heat treatment	Advisory	Mandatory
Use special wet cleaning methods	Advisory	Forbidden
Use abrasive cleaning methods	-	Mandatory
Electroplate	Allowed	Only allowed under special circumstances
Use non-electroplated coatings	Advised	Very strongly advised. Mandatory with Auto. Manufacturers.
Baking times (at 180-210°C) if electroplated	4-12 hours	12-24 hours (or longer)

Note: Phosphating can cause hydrogen embrittlement but it is generally considered that this disappears if the components are not used for 48 hours after processing otherwise a de-embrittlement baking of a minimum of 12 hours at 115°C is recommended.

Figure 3: Requirements to Limit Hydrogen Embrittlement

Prevention of Hydrogen Embrittlement

Steps that can be taken to avoid hydrogen embrittlement include reducing hydrogen exposure and susceptibility, baking after plating (mandatory and as soon as practical) and using test methods to determine if a material is suspect. Other options that could help in avoiding hydrogen embrittlement include the use of lower strength steels (not always viable), the avoidance of acid cleaning, the utilization of low hydrogen plating techniques and the reduction of residual and applied stress.

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

Figure 4: Preventive Actions to Reduce Hydrogen Embrittlement

CONCLUSIONS

Hydrogen embrittlement remained as the only probable cause of the failure observed. Unlike stress corrosion cracking and quenching cracks, cracks caused by hydrogen embrittlement usually do not branch neither show oxidized surfaces. Typical features of hydrogen embrittlement were observed on the fracture surfaces of both bolts. Bolts had been zinc electroplated, which is one way to introduce hydrogen into metals, and baking treatment.

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