ECHNICAL
DATA

HYDROGEN EMBRITTLEMENT RISK MANAGEMENT

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1. Scope

This technical update provides a review of concepts to manage and minimize the risk of hydrogen embrittlement in electroplated screws. These concepts do not assure elimination of failure resulting from hydrogen embrittlement, but seek to manage that risk through minimization and setting forth those practices which have historically been thought to reduce probable embrittlement failure.

2. Background

It has long been recognized that interstitial alloying elements will, in small quantities, impact the mechanical behavior of metals. Elements considered to be interstitial are carbon, nitrogen, hydrogen, oxygen and boron. Hydrogen is widely recognized for its potential to severely embrittle steel and other metals as well.

As the atomic hydrogen enters the steel from which the fastener has been manufactured, it produces a loss of ductility or load carrying capability which could result in a sudden catastrophic failure at stresses below yield and even below the normal design strength for the fastener. This often takes place in fasteners which display no significant ductility loss when examined by tensile testing. Frequently this failure is attributed to hydrogen-induced delayed brittle failure, hydrogen stress cracking, or hydrogen embrittlement.

Professor Troiano at Case Western Reserve University, Cleveland, Ohio and Professors at the Ecole Centrale in France recognized that under the influence of a stress gradient, hydrogen atoms or the hydrogen protons will diffuse or migrate to regions of highest tensile stresses and then reduce the cohesive forces in the metal. Thus, in most hydrogen embrittlement failures in fasteners, the fillet or in some cases the thread runout or the threads near the bearing area, become the primary area of collection as hydrogen migrates to the area of highest stress. This migration, if to the fillet, is thought to produce a sudden catastrophic separation of the fastener head from its shank. The geometry of the fastener and its fit will influence the point of highest stress.

3. Contributing Factors

Hydrogen may be introduced to the fastener and/or its raw material during a broad variety of manufacturing operations and service environments. These include cleaning, pickling, phosphating, electroplating, autocatalytic processes, galvanic coupling, and localized joint corrosion. During fabrication, lubricant breakdowns are also thought to contribute, but little data exists to support or deny this and no known investigations have evaluated given lubricants. Research reveals that the basic fastener material itself may contain significant variables in this hydrogen introduction process. Variables in the raw material may relate to cleanliness, microstructural constituents and strength levels. Processing via heat treatment to higher hardness with increasing carbon to assure heat treating response further compounds this tendency.

Electroplating of fasteners which have a core hardness of Rockwell C40 or above is not recommended. These parts are highly susceptible to hydrogen embrittlement. Success with electroplating of these fasteners requires significant processing changes and well defined controls which are not widely available. Users should consult directly with an experienced metallurgist, preferably with extensive fastener experience, before considering this possibility which is not recommended for most commercial fasteners. Case hardened and carbonitrided screws usually have case hardnesses of Rockwell C42 or higher. The high hardness of the case makes these fasteners highly susceptible to embrittlement by hydrogen. Since the case is more brittle than the softer, more ductile core, the case is subject to cracking where the fastener is bent or when torsional stresses approach the maximum tightening torque as applied. A small degree of bending can multiply outer stresses by a factor of two or more. While the crack may not normally penetrate into the ductile core, the presence of hydrogen may lead to hydrogen assisted stress cracking, which could penetrate the core and cause failure.

Stress embrittlement, stress corrosion cracking, and hydrogen assisted stress corrosion failures differ from hydrogen embrittlement because they are all related to the service environment. These failures occur sometime after installation due to hydrogen being introduced by a chemical reaction induced by the service environment.

In a 1969 study by Battelle Columbus Laboratories, it was reported that steel exposed at a break in the zinc film would become the cathode of the electrochemical cell. This condition may promote the entry of atomic hydrogen into the metal. Thus, many failures of higher hardness/higher strength fasteners which have been zinc coated are not caused by trapped hydrogen being introduced during various stages of manufacturing and plating processes, but subsequent hydrogen introduced by in-service galvanic interaction. The susceptibility of a finished fastener to in-service hydrogen embrittlement is influenced by stress, environment, service time, actual fastener hardness, chemistry and coating used. For example, the Naval Sea Systems Command (NAVSEA) has historically objected to zinc substitutes for cadmium on higher hardness/higher strength fasteners. The objection to the substitution has been based on concerns relating to galvanic action between the plating and base metal and the fact that the driving potential of zinc is significantly greater than cadmium which facilitates a greater amount of current flowing between the anode (zinc or cadmium) and the cathode (steel) and thus increases the hydrogen generation at the cathode.

In the evaluation of a failure attributed to hydrogen embrittlement, it is extremely important to determine if the hydrogen contribution was introduced during the manufacturing and processing, or following installation. If, for example, the internal (manufacturing and plating processes) are wrongly identified as the cause, costly correction will result in no correction at all. The literature dealing with these topics is scattered and frequently contradictory. The engineer having any doubts should consult with an experienced metallurgist with failure analysis experience and most preferably, fastener manufacturing experience as well.

Thinner sections are more susceptible than heavier ones since, with higher surface to volume ratio, the amount of hydrogen absorbed per unit volume is greater and there is less chance to dissipate the high surface concentrations by internal diffusion. Thus, smaller diameter fasteners should be carefully managed.

4. Methods for Testing

Embrittlement testing or stress durability testing involves application of high preload which induces inordinately high stresses in the thread roots and head-to-shank fillet areas of screws and bolts and in notched specimens. These high stresses produce a favorable environment for the migration of embrittling hydrogen, if present, to these highly stressed areas precipitating failure. Test duration varies from about 24 hours to 200 hours depending on test specification.

Test loads of 75% to 90% of minimum ultimate tensile strength may be applied through four basic methods. These include the torque method, external loading method, elongation method and strain gage method. The torque method is the most economical and widely used and is required when an installation torque is specified to induce a preload. However, the torque method is difficult to control because of friction variation in the mating threads. In order for the torque method to be effective for controlling the test stress level, the torque-tension frictional components of the test joint must be understood. Selecting a torque based only on size and not accounting for finish, geometry, or strength level, will probably result in stresses over and under the desired test stress. Methods commonly used to deal with these variables include:

1. Testing at least ten sample parts to failure and calculating an average failure torque which is then factored to an appropriate lower torque for testing.
2. Torquing to yield using a special torque wrench.
3. Torque based on finish, thread type and hole size.

The external loading method involves the application of a longitudinal load for a prescribed time period and thus requires equipment other than tensile testing equipment. A strong body of evidence indicates this method to be one of the most discriminating in identification of hydrogen assisted failure.

Basic testing may utilize a flat plate or wedge plate. While experts dispute the relative merits of these plates, the wedge, while more expensive, increases the stress concentration at the fillet. Compensation is used by those supporting the flat plate testing method by using a higher tightening torque. The test plate hardness and surface finish may also affect the stress level during a given test, since the friction between the bearing surface of the fastener and the plate may vary and should be accounted for. Both the flat plate and wedge plate are included within procedures for standard tests. Various testing procedures are included in ASTM F606, ASTM F606M, SAE J81, SAE J78, MIL-STD 1312-5, MIL-STD 1312-14, ISO/DIS 10587 and ISO 4042.

5. Present Practice

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 optimized 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.

The vast majority of processing embrittlement risk appears to be attributed to electroplating. 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. Operating at about 60% efficiency level meant that they were releasing or liberating a high volume of hydrogen at the cathode. Today, the cathodic efficiency averages about 75%. As plating solutions are depleted, the efficiency will drop still lower with a corresponding increase in hydrogen release. The development of non-cyanide electrolytes has resulted in chloride-zinc and acid-cadmium operating in the 94% or higher efficiency range. This has reduced the generation of hydrogen significantly. The coatings so deposited, however, have a high density which makes it difficult to drive away any surface hydrogen. Thus, the manufacturer must work closely with the plater to assure risk reduction in preparation steps for plating and that attention and checks are in place to prevent over or under filling of plating barrels.

Large bodies of evidence exists stating that delays exceeding 4 hours following plating are detrimental to the effectiveness of baking. Evidence also exists that higher baking temperatures (425°F) improve baking effectiveness, particularly if the delay time has exceeded 4 hours. Additionally, high baking temperatures must be carefully evaluated to prevent liquid metal embrittlement. For example, cadmium has a high risk because it has a lower melting temperature than zinc. Hydrogen embrittlement mechanisms are thought to be diffusion controlled and thus the effects of time delay before bake are very important. 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 reduces the opportunity for nascent hydrogen to begin its inward migration. It is the prevention of inward migration which will reduce the probability of embrittlement failure. Current baking items at temperature vary from 4 to 8 hours in commercial applications and up to 23 hours or more for aerospace. Current tests indicate that delay time into the baking oven of up to 8 hours may be overcome by extending the bake time and the temperature of baking. Data seems to indicate that if delays exceeding 4 hours occur, a higher baking temperature (425°F) may produce significant embrittlement relief. It is important to note that time at a given temperature should be based on the core temperature of the product being baked. The respective oven design will have significant impact on the time required to reach this core temperature. The time and temperature should also be related to the fastener strength and its hardness. Delay time and time at temperature are economic issues and need the attention of all interested parties.

6. Interpretation of Test Results

The degree to which fasteners may be embrittled may vary over a range for a given lot. Degree of embrittlement is a function of the concentration of hydrogen ions found on each respective part within the lot which are free to migrate to areas of high stress. Examination of the barrel-plating process indicates that when hydrogen charging of fasteners does occur, it follows a normal distribution or bell-shaped curve common to statistical analysis. Platers cannot eliminate or easily control such a random hydrogen charging process. Thus, when baked at a given time and temperature, various degrees of free hydrogen may remain. Consequently, it is not generally possible to guarantee that lots of threaded fasteners produced are completely free of hydrogen embrittlement. On the contrary, the only self-evident result that may be depended upon is that representative samples from the lot which have been tested have indicated no embrittlement was present. Thus, to manage the risk, a statistical sampling plan is necessary.

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Checklist for Risk Management of Hydrogen Embrittlement

Item No.	Element for Management	Consideration Of. . .
1	Joint Material	– Compatibility with fastener materials.
2	Application Environment	– Exposure to moisture or other hydrogen combinations. – Stress levels in the installed fastener. – Surface condition of the applied coating.
3	Special Customer Requirements	– Do these impact other checklist items?
4	Product Design	– Sharp transitions or points of high stress as fillet design and thread runout.
5	Raw Material Selection • Cleanliness • Constituents	– History of material susceptibility. – Heat evaluations. – Did incoming material meet specifications and was this verified?
6	Cleaning Prior to Pickling	– Check PH which is a measure of the concentration of the cleaning solution. – Check for conductivity of cleaning solution efficiency.
7	Pickling Acid Concentration	– Frequent additions to avoid large variation in concentration. – Control of temperature. – Use of inhibitors: do they interfere with adhesion? – Have alternate descaling methods including alkaline permanganate or dry abrasive blasting been considered?
8	Phosphating	– Items 5 thru 7 must be controlled.
9	Electroplating • Cyanide • Noncyanide • Efficiency	– Cyanide has low cathodic efficiency, zinc chloride and acid cadmium have higher cathodic efficiencies. – Balance current density with surface area of parts to be plated to minimize hydrogen evolution. – Brightener additions should be related to ampere-hours in bath and monitored. Control plating bath temperatures to reduce brightener consumption. Chillers are used to control bath temperatures.
10	Heat Treatment	– Control atmosphere in furnace to minimize oxide formation and carburization of surface.
11	Baking	– Did baking delays occur following plating? – Time at temperature and methods for control. – Does baking capacity relate to plating capacity? – Was a recording thermocouple present in each 64 sq. ft. of heating zone?
12	Evaluation of Finished Fastener	– Which of the test methods discussed in Para. 4 have been applied? – Are sample sizes appropriate for given lot sizes to have a statistically valid sample?

Hydrogen Embrittlement
References and Recommended Reading

1. *Hydrogen Embrittlement.* R. L. Sproat and J. J. Laurilliard. Fasteners, Spring 1966, Vol. 21, No. 1.

2. *The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals.* Alexander R. Troiano. Thirty-fourth Edward deMille Campbell Memorial Lecture, November 4, 1959 at the Forty-First Annual Convention of the American Society for Metals.

3. ASTM B849-94, Standard Specification for Pretreatments of Iron or Steel for Reducing Risk of Hydrogen Embrittlement. ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

4. ISO/DIS 10587, Metallic and Other Inorganic Coatings - Test for Residual Embrittlement in Metallic Coated, Externally Threaded Articles, Fasteners and Rods - Inclined Wedge Method.

5. *Evaluation of Aerospace Stress Durability Test Methods.* Harry S. Gibson, Jr., Proceedings of the First International Technology Transfer Conference, Denver, Colorado, May 17-19, 1995.

6. *Hydrogen Embrittlement in Automotive Fastener Applications.* Brenda S. Kloberdanz and Eric D. McCarty. Proceedings of The First International Technology Transfer Conference, Denver, Colorado, May 17-19, 1995.

7. *Time and Temperature Effects on the Embrittlement Relief of High-Strength Steel.* W. Craig William. Proceedings of The First International Technology Transfer Conference, Denver, Colorado, May 17-19, 1995.