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AESF Heritage: The 2002 Hydrogen Embrittlement Seminar:
1. Hydrogen Embrittlement

by
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ABSTRACT

A detailed overview of hydrogen embrittlement is presented beginning with elemental discussions of the scientific phenomenon, occurrence, metallurgical attributes, habits of various metals and alloys and basic solid-state physics. Hydrogen transport mechanisms, susceptibilities of various high strength alloys in use today, sources of hydrogen and a history of testing for the phenomena are presented. Design considerations for avoiding hydrogen embrittlement are offered, including the current state-of-the-industry flight safety philosophy. Avoidance and control of embrittlement are discussed including an overview of embrittlement relief (baking) parameters, effects of baking variables and methods to improve bake-out efficiencies. A 30-year summary review of aircraft embrittlement failures is presented. A discussion of procurement requirements, along with pre-existing metallurgical problems and their effects on subsequent embrittlement potentials are reviewed. Future areas of design engineering concerns are given. A final section details "Goofs in Plating - The legacy of Hydrogen Embrittlement". The most common "goof" scenarios are presented along with known industry damage recovery, salvage and part dispositions.

What Is hydrogen embrittlement?

Hydrogen embrittlement is physical damage to metallic alloys caused by atomic hydrogen. The damage is manifested as a reduction in ductility in the elastic range, causing a reduction in the yield and ultimate strength of the metal. The hydrogen damage can be immediate or delayed, that is, failures can occur before or after an embrittled part enters service. Embrittled parts have been known to crack or "pop on the shelf" before being assembled or even used.

Almost 75% of the known elements of the universe are metals - their usefulness to man is unparalleled. They are:
- Widely available
- Inherently ductile - able to take damage
- Strong
- Easy to manufacture by casting, forging, machining or powder form
- Useful to conduct heat and electricity

Hydrogen inhibits metal's ductility. The strength can be lowered if loss in ductility is severe. If a metal's ductility is lowered from embrittlement, then the usefulness of metals can disappear. Embrittled metals now behave like ceramics. A hydrogen embrittled part will not deliver the strength or performance called for by the design engineer. Premature failures can happen sometimes with catastrophic, deadly results. High strength martensitic steels are the most prone to embrittlement due to the high transformation stress of the martensite lattice structure. Other steels such as PH (precipitation hardening) grades can also be embrittled. Some austenitic grades such as the 18-8 (300 series, FCC lattice structure) can also be embrittled if work hardened into the martensitic phase. Titanium alloys can also be embrittled, but the phenomenon is different. Here hydrogen forms brittle ceramic type titanium hydrides on the grain boundaries. Aluminum alloys are not prone to embrittlement but are susceptible to hydrogen porosity damage. Nickel alloys are not prone to embrittlement; however, some super alloys such as MP35, etc. have been reported as susceptible.

How does hydrogen get in?

Hydrogen is the smallest size element. In ferrous materials, hydrogen travels interstitially within the lattice structure, or in between the iron atoms themselves. The permeability of hydrogen is tremendous. In electroplating, it enters at the surface of the steel as the plating process continues. Hydrogen moves by a process called diffusion, which obeys Fick's Law, *i.e.*, hydrogen will always travel from highest to lowest concentration areas or, during electroplating, from the surface of the steel inward. Several crystal (lattice) structures are possible for steels depending on carbon concentration, temperature and resulting phase changes taking place during / after heat treatment (Fig. 1). By far the steel crystal (lattice) structure most sensitive to embrittlement is the Martensitic Body Centered Tetragonal (BCT), the most highly internally stressed crystal structure in steel alloys. BCT is a BCC crystal structure with one axis longer, forming a tetragonal lattice.

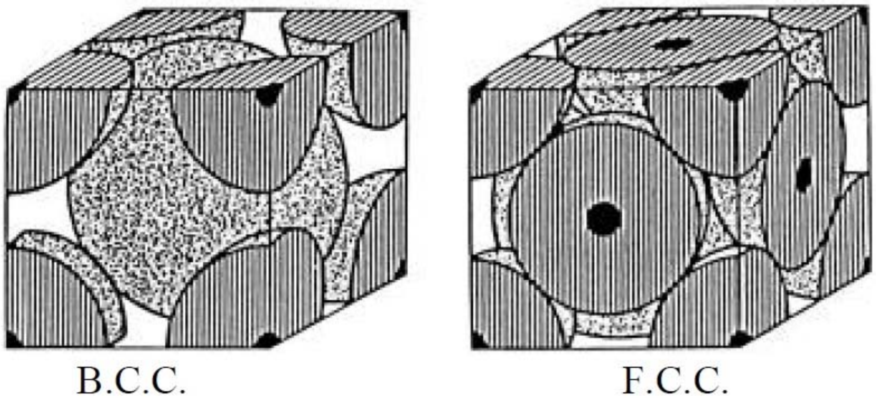

Figure 1 – Body-centered cubic and face-centered cubic crystal structures.

Metallurgically, hydrogen embrittlement is still being debated in the scientific community after almost 50 years. Two prevailing schools of thought are:
1) Atomic hydrogen combines to form molecular hydrogen on grain boundaries or areas of structural instability.
2) Atomic hydrogen acts as a surfactant allowing grain boundary slip into stacking faults, producing micro cracks along the grain boundaries.

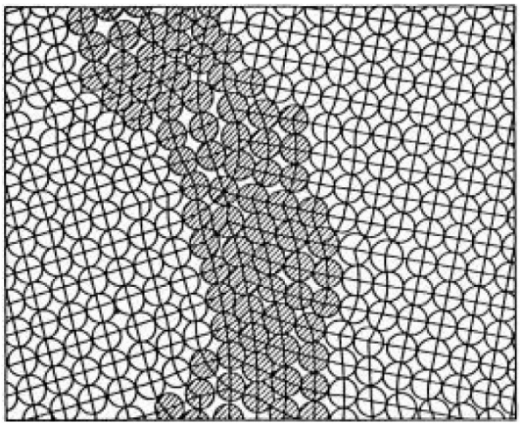

Figure 2 - Grain boundary between two crystals cross hatched atoms are grain boundaries

Crystal boundaries are regions of misfit or disorder between crystals. At slow strain rates, grain (crystal) boundaries lose their strength more rapidly than do the grains themselves, with the result that fractures can now be along the grain boundaries or inter-granular (Fig. 2). Indeed, the presence of atomic hydrogen lowers the critical resolved shear stress on the grain boundaries. In the 1940's both Bragg and Burgers introduced the idea that the grain boundaries between grains (crystals) are arrays of defects known as dislocations. Dislocation theory forms one of the foundations for hydrogen embrittlement theory today.

By far, high strength steels are the most susceptible to hydrogen embrittlement due to (a) martensitic transformation stresses and (b) usefulness of higher strength levels for weight reduction.

The susceptibility of steels to embrittlement goes up with strength:

High strength → Higher susceptibility *Conversely >* Low strength → Low susceptibility

Hydrogen can be introduced from many sources beginning at the initial steel making operation. It can be introduced at forging and casting operations, from grinding if performed in a moist environment, from contact with acids, especially reducing acids, and of course from electrolytic processing - **metallic plating**. Many acidic and oxidation reactions with steel will release hydrogen. The application of electrical current quickly accelerates the generation of hydrogen. Metal finishing can be a major contributor to hydrogen embrittlement due to the electrolytic nature of plating. Even the natural corrosion-oxidation of cadmium will generate hydrogen.

Testing for hydrogen embrittlement

For embrittlement to occur, hydrogen must exist and a driving force or stress must be present. The phenomenon is diffusion controlled. Hydrogen must enter the steel and must be forced to areas of metallurgical instability. If hydrogen levels are low, embrittlement may not occur. If the driving force is low, once again, embrittlement may not occur. Both are needed before embrittlement happens.

Hydrogen diffusion is time dependent. In similar fashion, time is critical for its testing. All valid embrittlement tests require extended time, usually from between 150-200 hours. Short duration tests can miss potential embrittlement! Besides the presence of actual hydrogen, embrittlement also requires a driving force or stress. For embrittlement testing, the stress is applied in the form of a long term external sustained load. Hydrogen embrittlement testing is oftentimes called sustained load testing. Internal residual stresses from cold work, grinding, shrink fits and high levels of heat treatment can also be the driving force for embrittlement. Residual stresses are the cause for “shelf popping” or part cracking while sitting on the storage shelf.

History of hydrogen embrittlement testing

About 45 years ago, the aircraft industry standardized embrittlement testing using very high strength notched steel samples. 4340 airmelt steel was chosen as the test sample alloy, heat treated to the highest condition of 260-280 ksi (Rc 51-53). A precision notch at the center of the samples is used, raising the stress intensity or Kt factor in the notch to 2.9-3.2. The notch will accelerate the test and tends to force any failure to a predictable, reproducible site. This test is sometimes referred to as a Draconian Test, the principle being to use an alloy very susceptible to embrittlement, heat treated to the highest level, and utilizing a notch for test acceleration. The philosophy is simple - that a plating process passing this test should produce parts free from embrittlement. Sustained load in tension has become the world standard, with a track record of millions of data points. Sustained load in tension has consistently provided protection and control over embrittlement for the aircraft and aerospace industry. The physics of sustained load testing are straightforward, with the test parameters being stress and time. Sustained load tests accelerate the detection of embrittlement by going immediately to 75% of Notched Ultimate Tensile Strength (NUTS) with extended dwell time. Sustained load testing provides the best opportunity to catch embrittlement that may be missed with bend tests or shortened “quickie” tests.

This testing philosophy is similar to aircraft wing tests. Wing structures can be tested at:

- Max flight level loads
- Max limit loads - (similar to embrittlement tests)
- Proof loads to failure

Most embrittlement tests are tensile tests or tests conducted under tension or pulling forces. Probably 90% of embrittlement tests are sustained load notched tensile tests. A notched sample held under tension creates a tri-axial state of stress, further enhancing the conditions for embrittlement to manifest itself. Embrittlement bend tests have been found to be less sensitive and less reproducible than notched tensile tests. This is based on the realization that bend samples inherently have three stress zones: *Tensile - Neutral - Compression*. Since cracks of any nature, including hydrogen embrittlement, only open under tension, only 50% of the notch cross section is available for embrittlement to manifest itself. Also, surface edge effects are far more pronounced with bend samples, with resulting data scatter. Chemical tests to determine hydrogen content have not been found useful in the past for several reasons:

- The accuracy of an atomic hydrogen test may produce more scatter than the mean, *i.e.*, 8 ppm ± 10 ppm.
- Very low hydrogen content can cause fracturing. Hydrogen embrittlement with hydrogen contents as low as 5 ppm has been documented.
- Easy escape of hydrogen from crack surfaces can result in no traceable hydrogen left.

Fracture investigations

Hydrogen embrittlement always produces intergranular cracking, or cracking along grain boundaries. If, during a scanning electron microscopy (SEM) scan, you cannot find intergranular cracking - you do not have hydrogen embrittlement. However, intergranular cracking can also be caused by (a) temper embrittlement, which is the precipitation of epsilon carbides along prior austenitic grain boundaries or (b) stress corrosion cracking (SCC).

Good SEM work can determine if either temper embrittlement or SCC are the root causes rather than hydrogen embrittlement. Temper embrittlement and SCC leave tell-tale clues (epsilon carbides and oxide films respectively) whereas hydrogen embrittlement will not. Many times, it is difficult to trace the cause of intergranular cracking. Multiple failure causes can be present along with multiple fracture modes, *i.e.*, dimple rupture or cleavage. Hydrogen embrittled parts usually exhibit only a small amount of intergranular cracking. The embrittled zone is simply the catalyst for additional fracture modes.

Embrittlement tests other than mechanical

The Lawrence or Porosity meter/gauge test method is sometimes used as an embrittlement test. This is only an embrittlement potential test. It tests the ability of a coating to pass hydrogen during a baking operation, hence the porosity gauge name. The Lawrence gauge relies on the principles that:

- A porous coating will efficiently bake out hydrogen.
- Assumes that a baked porous coating is not embrittling.
- Assumes that a porous coating has been baked. If baking has been missed, embrittlement can still be present.
- Currently used for cadmium plate only.

Design considerations and drawing callouts

Some steel alloys are more prone to embrittlement than others. Good marks can be given to alloys heat treated under 150 ksi tensile strength. Also, PH (precipitation hardening) grade stainless steels and high nickel steels have good track records. More embrittlement problems can be expected with the following: alloy steels over 150 ksi tensile strength, carburized steels, ball bearing alloys which are usually heat treated to over 300 ksi (Rc54 and up), spring steels and piano wire. Drawing callouts with the potential to highlight embrittlement problems are:

- Envelope plating, or complete coverage plating.
- Decorative Class 1 chromium plate on very high strength steel parts. This can be problematic as less porous copper and nickel strikes are present under the top chromium plate.
- Class 2 E Nickel called out for very high strength steels, (see comments on temper embrittlement).
- Thin dense chromium plating applied to ball bearings which allow only a 275°F embrittlement relief bake vs. the more desirable 375°F bake.
- Hard chromium plate applied to carburized surfaces (case hardened surfaces with strength levels up to Rc65).

Flight safety parts

Flight safety parts are parts whose failure would result:

- In a loss of structural integrity
- In a loss of control function
- In a transfer to a backup structure or control system

Flight safety parts normally are at least 100% inspected prior to release for assembly, buildup and flight. Hydrogen embrittlement must be treated as a process parameter capable of affecting flight safety. Statistical Process Control (SPC) has not in the past been allowed for flight safety process acceptance.

Avoidance and control of hydrogen embrittlement

Two powerful tools are available to the metal finisher: (a) lowering or eliminating hydrogen generation initially and (b) removing damaging hydrogen afterwards.

The first tool, that of lowering initial hydrogen generation, can be accomplished by staying away from reducing acids such as HCl, H_2SO_4, etc. Always maximize plating efficiency at the cathode. Use plating processes and bath chemistries that are more electrolytically efficient. Minimizing plating time and maximizing current density will reduce hydrogen damage. Use electroless processes whenever possible. Vapor deposited coatings are also finding favor for critical components where fears of hydrogen are strong.

The second tool, that of removing hydrogen, is called embrittlement relief or baking. This thermal process is accomplished in atmospheric air and is a diffusion-controlled process governed by Fick's Law. Fick's Law defines a relationship between concentration gradient, time and temperature. Temperature is exponential in the math calculations, therefore it is the most powerful part of Fick's Law. Never shortcut temperature! As an example, a normal baking cycle requirement is 375 ± 25°F. You will bake out twice the hydrogen at 400 vs. 350°F. A little extra temperature (energy) goes a long way during baking.

Never shortcut time. Time is a linear relationship in the math calculations of Fick's Law - double the bake time and you will double the hydrogen removed. Always quickly transfer the parts to the bake oven. Most plating specs have a 4-hour maximum delay from plating-rinse tank into the bake oven. Some aircraft primes call for shorter transfer times; Bell Helicopter at 1 hour max. and Fairchild Dornier with an immediate transfer (parts still dripping with rinse water). Quick transfers minimize potential for atomic hydrogen to recombine into molecular hydrogen. Molecular hydrogen can be more damaging as microcrack formation accelerates. Extended bake times are very useful. Some zinc processes need a 96 hour or longer bake time, a position first proposed by the U.S. Navy Air Systems Command 15 years ago. Thin dense chromium plate on ball bearings has been found to require at least a 96 hour bake cycle when baking at 275°F.

The power of baking

Almost 71% of documented aircraft embrittlement failures over the past 30 years have been attributed to baking operation errors, that being:

- Missed or omitted bake
- Extended delay from plate into the bake oven
- Insufficient baking temperature
- Short bake time

(Sources: National Transportation Safety Board, U.S. Naval Air Systems Command, U.S. Airforce Material Command, U.S. Army AVSCOM)

Acquisition problems - the purchasing department's role

Many times, contradictions appear when the purchase order calls for processing in conflict with the plating specification requirements. The results are that parts are being plated when they should not be. Possibly a wrong plating application has been stated, or the heat treat strength levels are too high for the plating method called for. Maybe post plating baking-hardening temperatures will damage prior shot peen cold work, etc. The results can be serious with service failures and product recalls. Many times, pre-existing problems conspire to doom good parts. Metal finishing is usually the last manufacturing operation before assembly of finished components. Any prior errors in heat treatment, shot peening or grinding can manifest themselves during plating. Accidental carburization, abusive grinding burns, cold work from straightening, or shot peening mistakes can spell disaster during plating, as any hydrogen generated will seek out those areas of metallurgical instability.

Future areas of concern

- Thin dense chromium plate: less porous than Class 2 Chromium - many times used on ball bearing steels
- Zinc Nickel: Less efficient plating than cadmium - with brighteners it is less porous
- Tin Zinc: Requires lower bake temp of 340°F, hence less efficient bake out
- IVD Aluminum: Larger galvanic couple compared to cad - possible corrosion induced hydrogen?
- Silver plate on bearings: Brightened silver acts like cadmium - many times plated on ball bearing steels

Goofs in plating! The legacy of hydrogen embrittlement

Webster's defines a *Goof* as "..to make an unusually foolish or careless mistake .." Common baking goofs are:

- Forgot to bake the parts
- Baked the parts for wrong times
- Baked the parts at the wrong temperature
- Bake oven went off line - power turned off or controller failures

What can be done? In reality, many times nothing can be done as irreversible damage has already occurred. Possibly micro-cracks have developed. Sometimes the complexity of parts will prohibit rework. Also, flight safety could be compromised - the risk of failure if the parts are used or reworked is too great. Good material review engineers earn their pay here! A good engineering response is to begin a recovery plan immediately - this means damage control. Act quickly by getting parts into the bake oven, or the bake oven back on line. Document what happened immediately, while the facts are fresh. Ongoing embrittlement stops increasing the moment the parts reach proper bake temperature. *However*, what about existing embrittlement damage, *i.e.*, possible cracks?

Continue the recovery plan by completing the **proper** bake cycle in its entirety - do not cut corners on either time or temperature. Notify your customer of what has happened. Propose a recovery plan after you have documented all the facts and possible options. Submit a material review request on the suspect parts with the complete data package. Don't make the material review engineer go out on a limb by having to guess the "who-what-when-where-why".

Potential part dispositions from material review could be:

- Use as is
- Bake the parts for an additional time at normal temperature
- Bake the parts for an additional time at an elevated temperature
- Strip and bake - then replate
- Test the actual parts (expensive and time consuming)
- Test standard notched samples that have seen the identical plating-baking goof; replicate the problem using test samples
- Scrap out the parts - the risk of failure and its consequences may be too great.

The worst baking goof we can think of is a carburized, induction hardened, or ball bearing steel baked at 375°F instead of the lower 275°F. Here irreversible metallurgical damage has occurred; that is, the parts have now been over tempered and must be re-heat treated. 99% of the time these parts are scrap.

Some comments on hydrogen embrittlement testing

Routine Process Control Tests: Routine process control tests are intended to control the process over time. The interval may be daily, weekly, monthly etc. Usually, standardized test samples and test loads are employed. The tests establish trends or patterns over time; however, they should not necessarily be used for lot buy off or actual part acceptance.

Lot Buy-Off Tests: These tests represent real parts processed via test samples accompanying parts. They may represent actual serialized flight safety parts or components. Actual embrittlement conditions, if present, may be represented. The samples used may be standardized samples or special unique test samples.

Rogue Samples? Rogue samples can be defined as samples that conform to manufacturing requirements but fail when others don't. They are usually caused by subtle differences in the Kt factor in the notch. Notched tensile samples should have a Kt (stress intensity factor) of 2.9 to 3.2. If any non-metallic inclusions align themselves in the notch region, or if the sample has geometric problems from machining, the Kt factor could go up - to a Kt factor of 5.0 or possibly higher. Is this now a fair and valid test? Other reasons for sporadic failures are current density differences during plating. Unless cylindrical anodes are used around the sample, current densities may not be the same at all areas in the notch. Hydrogen generation varies with current density, thus potential embrittlement can vary. This is one reason why bend samples have fallen from favor.

SUMMARY

- ✓ Hydrogen embrittlement is serious! Numerous aircraft accidents have been caused by embrittlement failures.
- ✓ Avoidance involves a thorough understanding of hydrogen generating reactions.
- ✓ Control involves both avoiding hydrogen generation, and hydrogen elimination normally referred to as embrittlement relief or baking.
- ✓ Vigilance is required for continued flight safety! The physics of embrittlement are omnipresent - one mistake is all it takes for disaster.