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Fasteners — Fundamentals of hydrogen embrittlement in steel fasteners

Fixations — Principes de la fragilisation par l'hydrogène pour les fixations en acier

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Foreword

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This document was prepared by Technical Committee ISO/TC 2 *Fasteners*, Subcommittee SC 14, *Surface coatings*.

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Introduction

High strength mechanical steel fasteners are broadly characterized by tensile strengths (R_m) above 1 000 MPa and are often used in critical applications such as in bridges, engines, aircraft, where a fastener failure can have catastrophic consequences. Preventing failures and managing the risk of hydrogen embrittlement (HE) is a fundamental consideration implicating the entire fastener supply chain, including: the steel mill, the fastener manufacturer, the coater, the application engineer, the joint designer, all the way to the end user. Hydrogen embrittlement has been studied for decades, yet the complex nature of HE phenomena and the many variables make the occurrence of fastener failures unpredictable. Researches are typically conducted under simplified and/or idealized conditions that cannot be effectively translated into *know-how* prescribed in fastener industry standards and practices. Circumstances are further complicated by specifications or standards that are sometimes inadequate and/or unnecessarily alarmist. Inconsistencies and even contradictions in fastener industry standards have led to much confusion and many preventable fastener failures. The fact that HE is very often mistakenly determined to be the *root cause* of failure as opposed to a *mechanism* of failure reflects the confusion.

Fasteners — Fundamentals of hydrogen embrittlement in steel fasteners

1 Scope

This document presents the latest knowledge related to hydrogen embrittlement, translated into *know-how* in a manner that is complete yet simple, and directly applicable to steel fasteners.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
hardness
resistance of a metal to plastic deformation, usually by indentation or penetration by a solid object (at the surface or in the core)

3.2
work hardening
increase of mechanical strength and *hardness* (3.1) when a metal is plastically deformed at ambient temperature (by rolling, drawing, stretching, sinking, heading, extrusion, etc.) also resulting in a decrease of ductility

3.3
heat treatment
process cycle (controlled heating, soaking and cooling) of a solid metal or alloy product, to obtain a controlled and homogeneous transformation of the material structure and/or to achieve desired physical or mechanical properties

Note 1 to entry: Quenching and tempering, annealing, case-hardening and stress relief are examples of heat treatment for fasteners.

3.4
quenching and tempering
QT
heat treatment (3.3) process of quench hardening comprising austenitizing and fast cooling, under conditions such that the austenite transforms more or less completely into martensite (and possibly into bainite), followed by a reheat to a specific temperature for a controlled period, then cooling, in order to achieve the required level of physical or mechanical properties

3.5
case-hardening
thermochemical treatment process consisting of carburizing or carbonitriding followed by quenching which induces an increase of *hardness* (3.1) in the surface of the fastener steel

Note 1 to entry: This process is used for tapping screws, thread forming screws, self-drilling screws, etc.

3.6
stress relief
heat treatment (3.3) process by which fasteners are heated to a predetermined and controlled temperature followed by a slow cooling, for the purpose of reducing residual stresses induced by *work hardening* (3.2)

3.7
baking
process of heating fasteners for a specified duration at a given temperature in order to minimize the risk of *internal hydrogen embrittlement* (3.15)

[SOURCE: ISO 1891-2:2014, 3.4.11, modified — "time" was replaced with "duration"]

3.8
crack
beginning of *fracture* (3.10) without complete separation

[SOURCE: ASTM F2078-15, modified — "line" was replaced with "beginning"]

3.9
failure
loss of the ability of a fastener to perform a specified function, which in some cases can lead to complete *fracture* (3.10)

3.10
fracture
break occurring when the plastic deformation in a fastener increases locally above its resistance limit, resulting in the separation of the fastener into two or more pieces, during testing or in service

3.11
fracture morphology
structure and aspect of the fractured surface

3.12
ductile
exhibiting a large amount of plastic deformation before *fracture* (3.10) with a resulting non-flat fracture surface showing fibrous ductile dimple morphology that is typically dull or matte

3.13
brittle
exhibiting little or no plastic deformation before *fracture* (3.10) with a resulting flat fracture surface showing brittle morphology that is typically shiny

Note 1 to entry: Brittle fracture along cleavage planes is known as transgranular fracture.

Note 2 to entry: Brittle fracture by separation at prior austenite grain boundaries is known as intergranular fracture.

3.14
hydrogen embrittlement
HE
permanent loss of ductility in a metal or alloy caused by atomic hydrogen in combination with load induced and/or residual tensile stress that can lead to *brittle* (3.13) *fracture* (3.10) after certain time[1]

Note 1 to entry: In the context of describing hydrogen embrittlement of high strength steel fasteners, the term "hydrogen" refers to atomic hydrogen and not molecular H_2 gas.

[SOURCE: ISO 1891-2:2014, 3.4.9, modified — Note 1 to entry has been added.]

3.15
internal hydrogen embrittlement
IHE
embrittlement caused by residual hydrogen from manufacturing processes, resulting in delayed brittle *failure* (3.9) of fasteners under load induced and/or residual tensile stress

[SOURCE: ISO 1891-2:2014, 3.4.10]

3.16
environmental hydrogen embrittlement
EHE
embrittlement caused by hydrogen absorbed as atomic hydrogen from a service environment, resulting in delayed brittle *failure* (3.9) of fasteners under tensile stress (i.e. load induced and/or residual tensile stress)

[SOURCE: ISO 1891-2:2014, 3.4.13]

3.17
hydrogen embrittlement threshold stress
critical stress below which *hydrogen embrittlement* (3.14) does not occur, which represents the degree of susceptibility of a steel for a given quantity of available hydrogen

3.18
stress corrosion cracking
SCC
category of *environmental hydrogen embrittlement* (3.16) where *failure* (3.9) occurs during service by cracking under the combined action of corrosion generated hydrogen and load induced tensile stress

[SOURCE: ISO 1891-2:2014, 3.4.14]

3.19
hydrogen diffusion
propagation of hydrogen and interaction with metallurgical features within the steel microstructure (microcracks, dislocations, precipitates, inclusions, grain boundaries, etc.) which constitute areas of traps into the fastener material: *non-reversible traps* (characterized by high bonding energies and low probability of hydrogen being released) and *reversible traps* (characterized by low bonding energies and hydrogen being released more readily)

3.20
hydrogen effusion
outward migration of hydrogen from the fastener material, occurring naturally at ambient temperature due to concentration gradient or as the result of a thermal driving force [e.g. *baking* (3.7)]

4 Symbols and abbreviated terms

EHE environmental hydrogen embrittlement

HAC hydrogen assisted cracking

HE hydrogen embrittlement

HELP hydrogen enhanced local plasticity

HIC hydrogen induced cracking

IHE internal hydrogen embrittlement

SCC stress corrosion cracking

5 General description of hydrogen embrittlement

Generally, hydrogen embrittlement is classified under two broad categories based on the source of hydrogen: internal hydrogen embrittlement (IHE) and environmental hydrogen embrittlement (EHE). IHE is caused by residual hydrogen from steelmaking and/or from processing steps such as pickling and electroplating. EHE is caused by hydrogen introduced into the metal from external sources while it is under stress, such as in-service fastener.

The term "stress corrosion cracking" (SCC) is used in relation to EHE that occurs when hydrogen is produced as a by-product of surface corrosion and is absorbed by the steel fastener. Cathodic hydrogen absorption is a subset of SCC. Cathodic hydrogen absorption occurs in the presence of metallic coatings such as zinc or cadmium that are designed to sacrificially corrode to protect a steel fastener from rusting. If the underlying steel becomes exposed, a reduction process on the exposed steel surface simultaneously results in the evolution of hydrogen in quantities that are significantly greater than in the case of uncoated steel.

The terms "de-embrittlement" and "re-embrittlement" are also used in the aerospace field but are technically incorrect because embrittlement is not reversible. De-embrittlement is misused to describe the effect of baking, and re-embrittlement is misused to describe the effect of hydrogen absorption during service or by use of maintenance cleaning fluids.

6 Hydrogen damage mechanism

High strength steel is broadly defined as having a tensile strength (R_m) above 1 000 MPa. When high strength steel is tensile stressed, as is the case with a high strength fastener that is under tensile load from tightening, the stress causes atomic hydrogen within the steel to diffuse (i.e. move) to the location of *greatest stress* (e.g. at the first engaged thread or at the fillet radius under the head of a bolt). As increasingly higher concentrations of hydrogen collect at this location, steel that is normally ductile gradually becomes brittle. Eventually, the concentration of stress and hydrogen in one location causes a hydrogen assisted (brittle) microcrack. The brittle microcrack continues to grow as hydrogen moves to follow the tip of the propagating crack, until the fastener is overloaded and finally fractures. This phenomenon is often called hydrogen assisted cracking (HAC) [or hydrogen induced cracking (HIC)]. The hydrogen damage mechanism as described causes the fastener to fail at stresses that are significantly lower than the basic strength of the fastener as determined by a standard tensile test[1][2].

Theoretical models that describe hydrogen damage mechanisms under idealized conditions have been proposed since the 1960s[2]. In the case of high strength steel, these models are based primarily on two complementary theories of *decohesion*[3] and *hydrogen enhanced local plasticity (HELP)*[4][5][6]. Given the complexity of HE phenomena, hydrogen damage models continue to evolve and be refined[7]. An in-depth review of the theories of hydrogen damage is outside the scope of this technical report. However, detailed information is given in the references listed in the Bibliography.

Hydrogen "traps" refer to metallurgical features within the steel microstructure such as grain boundaries, dislocations, precipitates, inclusions, etc., to which hydrogen atoms can become bonded[8]. Hydrogen thus "trapped" is no longer free to diffuse (i.e. move) to areas of high stress where it can participate in the mechanism of HAC. Traps are typically classified as *reversible* or *non-reversible* based on their bonding energies. Reversible traps are characterized by low bonding energies: in other words, hydrogen is more easily released from the trap. Non-reversible traps are characterized by high bonding energies: in other words, hydrogen requires a great deal of energy (e.g. from heat or stress field) to be released from the trap. Non-trapped hydrogen which is free to move in the metal lattice is called *mobile* hydrogen; it is also known as *interstitial* or *diffusible* hydrogen[9][10][11].

7 Fracture morphology

With quenched and tempered high strength steel fasteners, the fracture surface resulting from hydrogen assisted cracking (HAC) is typically characterized by *brittle intergranular* morphology which is caused by a crack growth path that follows the grain boundaries (see Figure 1). The morphology of a fracture surface varies based on the susceptibility of the material and the degree of embrittlement. Clearly defined grain facets (i.e. sharp and angular features) and/or a high proportion of brittle versus ductile features are indicative of high degree of embrittlement[12]. Figure 1 illustrates a fracture surface that is 100 % intergranular with very well-defined grain facets. Less susceptible materials can present fracture surfaces that contain a mix of intergranular and cleavage (i.e. trans-granular) morphologies.

With a tensile loaded fastener, a brittle hydrogen assisted crack typically grows up to a point where the reduced cross section of the fastener can no longer withstand the applied load. At this point, the fastener fractures rapidly (i.e. *fast fracture*). A normal fracture morphology corresponding to fast fracture is ductile, characterized by *ductile dimples*. Figure 2 illustrates a fracture surface where the brittle hydrogen assisted crack propagation ended (i.e. final crack tip) prior to final ductile fast fracture of the fastener.

Other forms of embrittlement failure are caused by phenomena not related to the presence of hydrogen such as temper embrittlement, quench embrittlement, quench crack, etc., that must be distinguished from hydrogen embrittlement failures. These other types of embrittlement can exhibit similar intergranular fracture surfaces but are principally distinguished from hydrogen embrittlement by the fact that they are *not time dependent*.

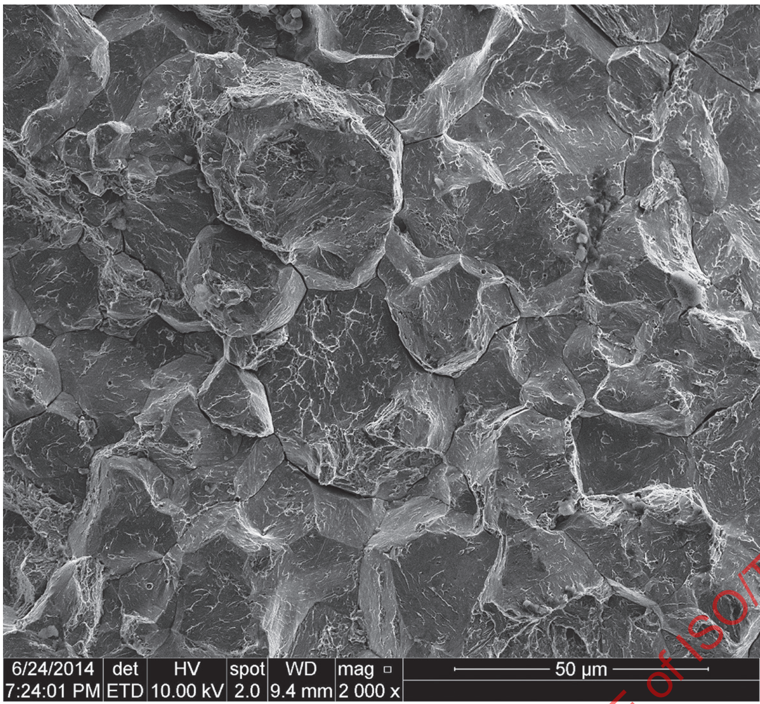


Figure 1 — Fracture surface showing 100 % well defined brittle intergranular morphology — Cr-Mo alloy steel (AISI 4135), quenched and tempered to 530 HV, zinc electroplated

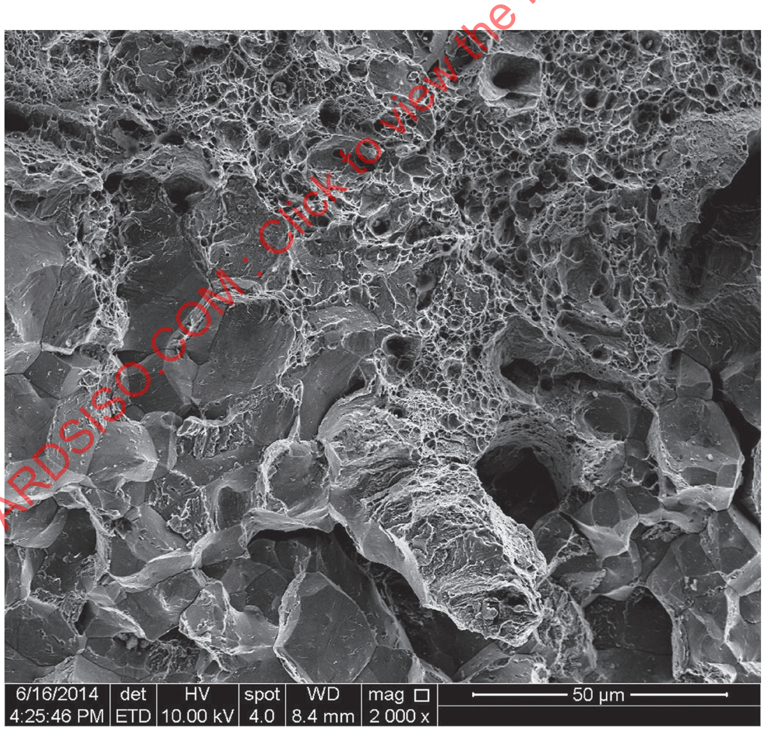
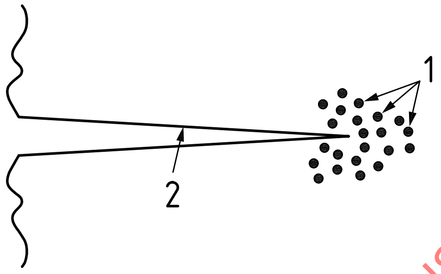


Figure 2 — Fracture surface showing both brittle intergranular morphology resulting from HAC and ductile dimple morphology indicative of final fracture — Cr-Mo alloy steel (AISI 4135) at 530 HV, zinc electroplated

8 Conditions at the tip of a crack

A microcrack can be initiated in a loaded fastener by several mechanisms that are not necessarily related to HAC (e.g. fatigue, overloading, grain boundary weakening by phosphorous segregation). However, once a crack is initiated by any mechanism including HAC, the conditions at the tip of the crack, notably the concentration of stress, are often much more severe than initial conditions[13]. The crack can propagate readily by a single or a combination of mechanisms that seek to reduce the stress at the tip of the crack. If it happens that a sufficient quantity of hydrogen is available to interact with the crack tip, then the propagation of the crack can be facilitated by HAC (see Figure 3). For example, even in low susceptibility materials, an existing crack under static or cyclic load exposed to a corrosive environment can propagate in part by stress corrosion cracking[14][15].



Key

1 atomic hydrogen

2 propagating crack

Figure 3 — An existing sharp crack surrounded by atomic hydrogen that can interact with the crack tip to cause hydrogen assisted crack propagation

In the case where HAC is the mechanism of an initial microcrack, the time to failure is significantly shortened as available hydrogen continues to interact with and follow the tip of the propagating crack. In such a scenario, HAC is the primary failure mechanism. A failure investigation needs to distinguish the scenario where HAC is the mechanism of an initial microcrack from a scenario where the mechanism of the initial crack is not related to HAC. The fracture surface presented by the latter scenario can nevertheless exhibit intergranular features if hydrogen becomes available to interact with the crack tip; in this case, HAC must be considered only as a secondary fracture mechanism.

9 Conditions for hydrogen embrittlement failure

9.1 Root cause and triggers for hydrogen embrittlement failure

Three elemental conditions must be present concurrently to cause hydrogen embrittlement failure (see Figure 4):

— **material condition** that is **susceptible** to hydrogen damage,

— **tensile stress** (typically from an externally applied load or residual stress), and

— **atomic hydrogen**.

If all three of these elements are present in *sufficient and overlapping quantities*, and given *time*, hydrogen damage results in crack initiation and growth until the occurrence of fracture. *Time to failure* can vary, depending on the severity of the conditions and the source of hydrogen. Stress and hydrogen are considered *triggers*, whereas material susceptibility is the fundamental requirement for HE to occur and is therefore associated with the *root cause*[16].

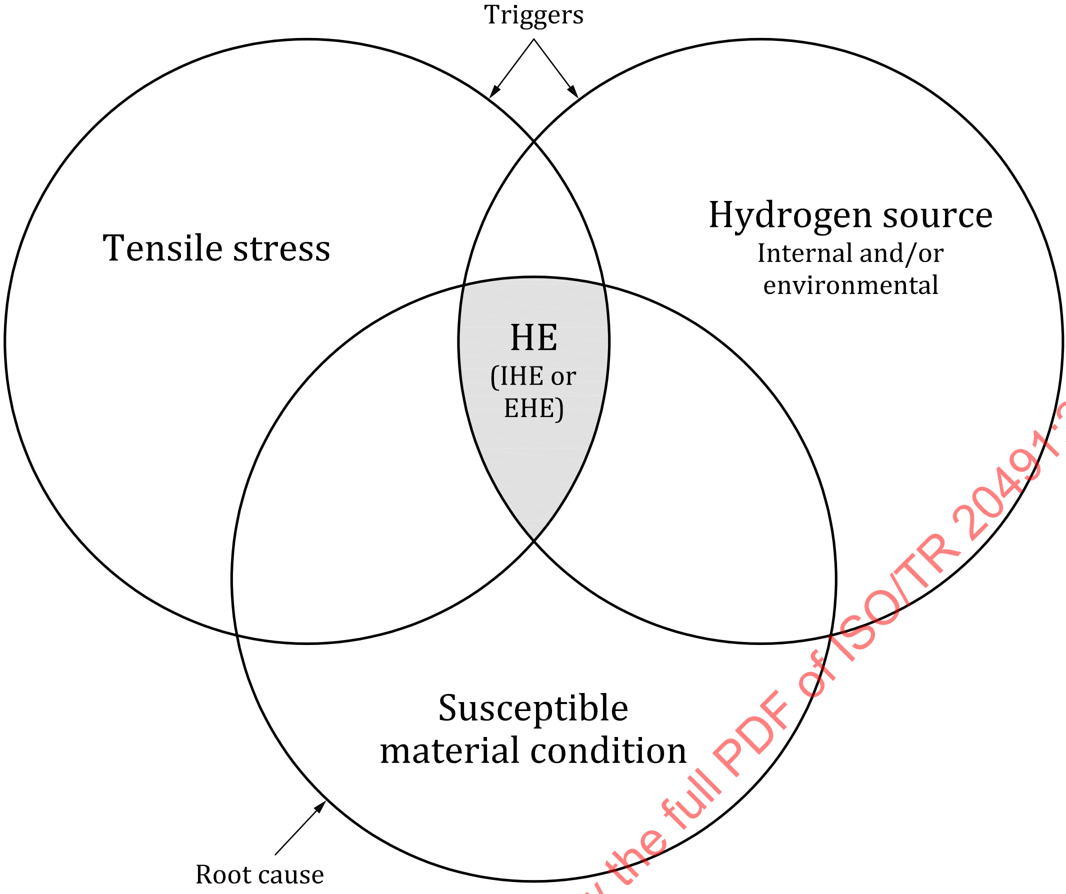


Figure 4 — Confluence of the three necessary conditions for *delayed* hydrogen embrittlement (HE) failure to occur

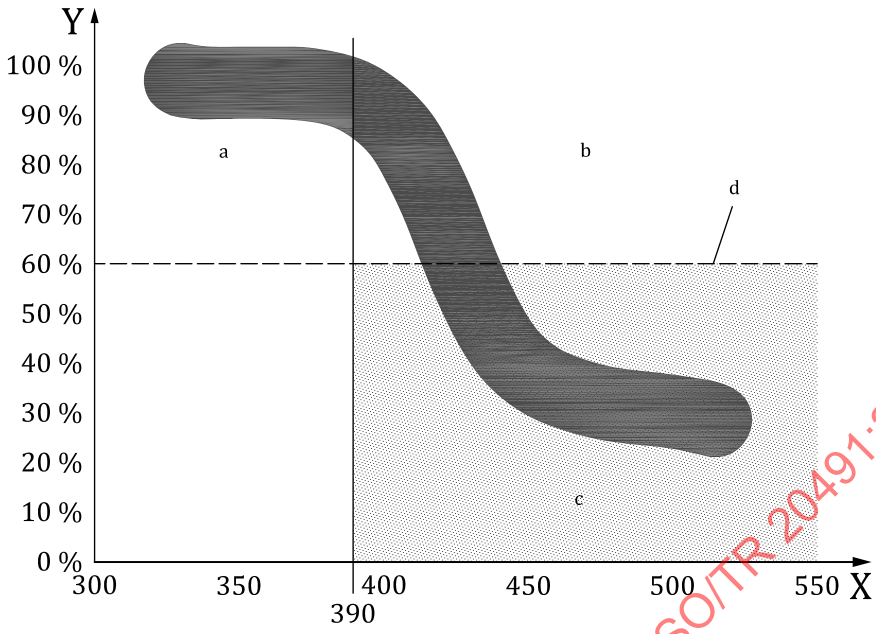
9.2 Material susceptibility

9.2.1 General

Susceptibility of a material to hydrogen damage (i.e. *material susceptibility*) is a function of the *material condition*, which is comprehensively described by the metallurgical structure and mechanical properties of a material such as steel. Examining material susceptibility is the fundamental basis for understanding hydrogen embrittlement phenomena.

Given that hydrogen embrittlement causes loss of ductility and, consequently, loss of strength, the foundation for studying and quantifying susceptibility of a material to hydrogen damage begins with mechanical testing. This testing measures the behaviour of the material under increasing stress, first without, and then with the addition of absorbed hydrogen. A detailed description of such a methodology is given in 9.2.2.

Material strength (i.e. tensile strength and/or hardness) has a first order effect on HE susceptibility of steel. As strength increases, steel becomes harder, less ductile, less tough and more susceptible to hydrogen damage. The susceptibility of steel fasteners increases significantly when the specified hardness is above 390 HV[17]. This increase in susceptibility is characterized by a ductile-brittle transition, whereby the material rapidly loses its ductility. The ductile-brittle transition can occur over a narrow range of increasing hardness[17]. See Figure 5.



Key

X hardness (HV)

Y normal scatter range - percent notch fracture strength ($NFS_{\%}$)

a Not susceptible.

b Ductile-brittle transition (transition begins as hardness is increased above 390 HV).

c Susceptible [high probability of failure by hydrogen embrittlement (HE)].

d Acceptance threshold for fasteners.

Figure 5 — Scatter range of a model HE threshold stress curve for zinc electroplated notched square bars tested in air under four-point bending load[36]

Up to hardness of 390 HV (left part of Figure 5), steel does not exhibit any loss of fracture strength: in other words, it is not embrittled.

Above 390 HV (right part of Figure 5), a ductile brittle transition occurs as hardness is increased. The start of the ductile-brittle transition is dependent on the microstructural characteristics of the specific steel alloy and the concentration of available hydrogen[36][12].

Steel fasteners with a specified hardness up to 390 HV, such as fasteners of property class 10.9 in accordance with ISO 898-1[6], have no significant susceptibility to hydrogen embrittlement failure. In other words, these steel fasteners can tolerate the presence of hydrogen without any delayed degradation of their mechanical strength. This assertion assumes that the fasteners are produced by using appropriately selected steel, well-controlled steel making and fastener manufacturing processes[12][17].

To minimize the risk of internal hydrogen embrittlement (IHE), ISO 4042[18] and ASTM F1941/F1941M[19], which are the recommended standards for electroplated fasteners, classify susceptible fasteners requiring *mandatory baking* as those having minimum specified hardness above 390 HV. The mandatory baking limit of 390 HV is based on both scientific research (see Figure 5) and longstanding fastener industry practice. These standard specifications also require appropriate process control measures and test methods as additional tools for minimizing the risk of IHE.

NOTE Some coating specifications have defined hardness limits for mandatory *baking* that are lower than 390 HV. However, these lower limits are not supported by data and were originally adopted as a matter of precaution.

To minimize the risk of environmental hydrogen embrittlement (EHE), ISO 898-1:2013, Table 2[20] contains a cautionary footnote warning about the risk of stress corrosion cracking for property class 12.9 fasteners for which the specified hardness range is 385 HV to 435 HV.

The scatter range shown in Figure 5 is caused by second order effects related to *alloy composition* and *microstructure* of quenched and tempered steel that affect hydrogen transport and trapping. Therefore, above 390 HV, for a given concentration of hydrogen, the critical hardness value above which the ductile-brittle transition begins can vary. Hardness alone is not enough to predict these second order effects. Measuring hardness, essentially quantifying local plasticity, is a quick and useful test to estimate strength. Hardness is achieved by the combined effects of composition and heat treatment that is specific to each steel alloy. In a tempered martensite structure, the same hardness can be achieved by different combinations of composition and heat treatment, resulting in slightly different microstructures, each characterized by slightly different stress-strain curves and slightly different hydrogen transport and trapping characteristics. The scatter range depicted in Figure 5 represents the normal range of susceptibility (i.e. lowest to highest susceptibility) as was determined from HE threshold stress measurements of 10 different steel alloys at 4 hardness levels[12].

9.2.2 Defects and other conditions causing abnormal material susceptibility

Beyond normal variations of metallurgical structure described above, *non-homogeneity* of the microstructure resulting from *poorly controlled heat treatment* and *high occurrence of non-metallic inclusions* can cause an unpredictable, but measurable, increase in HE susceptibility of steel[11][21][22]. Heat treatment is the single most consequential process to achieve the required metallurgical structure and physical properties of fasteners. Not surprisingly, the root cause of HE failures with fasteners that are not normally considered susceptible is often linked to improper heat treatment. Consequences of improper heat treatment include higher than expected hardness, unintended carburization and/or incomplete martensite transformation. Therefore, it is imperative that the heat treatment process produces fasteners that satisfy the explicit and implicit requirements specified in material standards, such as adequate though-hardening, homogeneity of micro-structure and non-carburization.

Poorly controlled and non-homogeneous microstructures are typically characterized by low toughness. Consequently, measurement of impact strength (e.g. in accordance with ISO 898-1)[20] can be a useful test to detect fasteners with aberrant microstructures.

Finally, when raw material is phosphate coated prior to cold forming, phosphorous diffusion at the surface of the finished fastener can occur during austenitizing, producing a phosphorous enriched white layer (δ-ferrite) and phosphorous segregation that can weaken the grain boundaries. With high strength fasteners, this phenomenon can result in brittle intergranular cracking at the surface of the fastener. The propensity to brittle intergranular cracking increases with increasing hardness. Although brittle intergranular cracking by this mechanism happens in absence of hydrogen, once a crack has been initiated, it can propagate with hydrogen assistance as described in Clause 8. Phosphorous diffusion is mitigated by washing the fasteners before quenching and tempering to remove phosphate located on the surface (i.e. de-phosphating). De-phosphating of property class 12.9 fasteners is mandatory in ISO 898-1[23][24][25].

9.2.3 Methodology for measuring HE threshold stress

The susceptibility of a material to hydrogen damage is characterized (i.e. measured) by its hydrogen embrittlement *threshold stress*. The chart shown in Figure 5 is based on measured HE threshold stress values that are expressed as a ratio of the baseline strength of the material. This ratio is known as *percent notch fracture strength* ($NFS_{\%}$). The more a sample is hydrogen embrittled, the lower its HE threshold stress, and the lower resulting $NFS_{\%}$ from the baseline strength of the sample (represented by 100 $NFS_{\%}$)[26][27].

The data represented in Figure 5 were developed by testing material specimens shaped as single edge notch square bars, illustrated in Figure 6. Dimensional specifications for the test specimens are given in ASTM F519 (type 1e geometry)[28]. The radius at the root of the notch is intended to simulate the thread of a fastener[12]. However, the square bar geometry is tailored for loading the specimen in

4-point bending, which generates higher stress than a test performed in tension using a notch round bar specimen. Figure 6 also shows a simplified schematic of the bending load frame.

In brief, the loading method consists of incrementally increasing the load applied to the specimen. This mode of loading is known as *incremental step loading* (ISL) and represents a modified form *slow strain rate loading* (SSRL). The test methodology is designed to measure the HE cracking threshold of the material, which is a measure of material susceptibility. The addition of hydrogen in the sample is achieved by prior charging, such as exposure to an electroplating process (IHE), or during the test in an environmental chamber where the sample is immersed in a 3,5 % mass fraction NaCl solution, and where a potentiostat is used to impose the cathodic potential. The imposed potential and the resulting current density control the quantity of hydrogen being introduced into the specimen[26].

The bending mode of applying load makes the test very severe and offers the benefit of increased sensitivity for measuring the effect of changing variables. For the given notch radius, the applied concentration of stress in bending is greater than stress generated in tension by a factor of 1,65[29]. Given the increased severity of the test method, results must be translated to determine if a fastener under normal service condition (i.e. loaded in tension), and exposed to similar hydrogen conditions, will suffer hydrogen embrittlement. The *acceptance threshold for fasteners* (illustrated as the dashed-line in Figure 5) is defined as the threshold above which a fastener under equal conditions (i.e. same material and hydrogen concentration), but loaded in tension instead of being loaded in bending, will not suffer hydrogen embrittlement. To determine the acceptance threshold for fasteners which are used in tension, 100 $NFS_{\%}$ in bending is multiplied by a factor of 1/1,65 to convert the bending stress condition to an equivalent tensile stress condition. By this conversion, 60 $NFS_{\%}$ in bending corresponds to the "no risk" acceptance threshold for fasteners made of the same material[29].

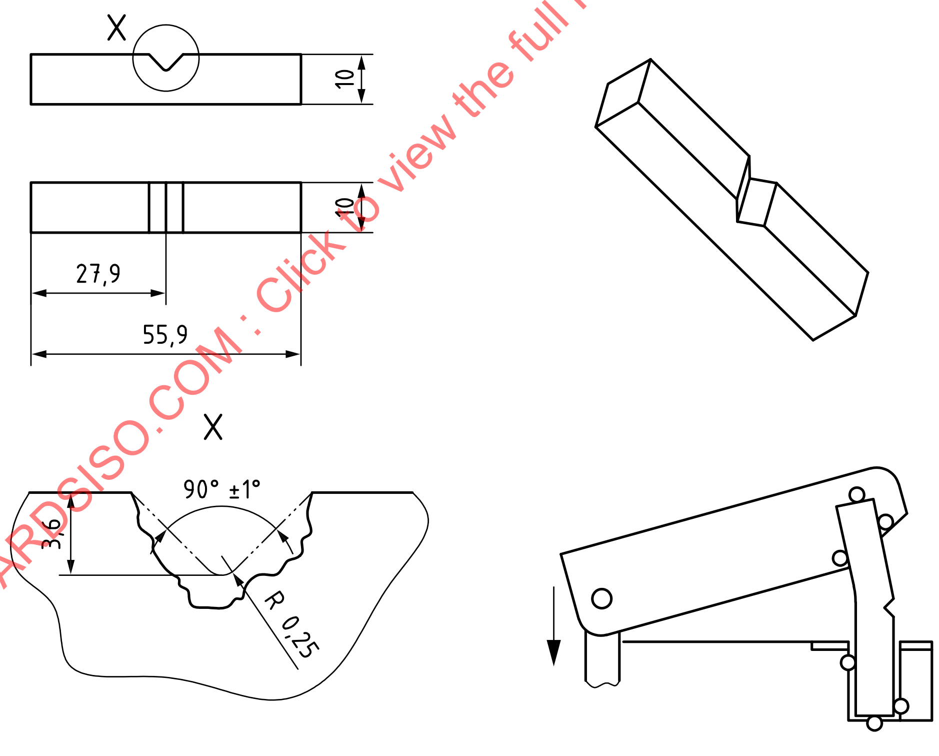


Figure 6 — Dimensional specifications of ASTM F519 (Type 1e) single notch bend square bar and schematic of loading frame showing the bending motion being applied to a test specimen

9.3 Tensile stress

Load induced stress is a normal service condition for fasteners. Tensile loaded fasteners such as bolts and screws are primarily subject to tensile stress and a varying amount of torsional stress during tightening. In some cases, fasteners can be subject to shear loads, typically in the unthreaded shank. In some rare but critical cases, fasteners can also be subject to unintended bending loads. Given time, tensile stress in the fastener can result in HE failure *provided it exceeds the HE threshold stress of the material*. Hydrogen embrittlement *threshold stress* is defined as the critical stress below which HE does NOT occur. As was described in 9.2.3, HE threshold stress is a measure of the degree of susceptibility of a material for a given quantity of available hydrogen. *Time to failure* is dependent on the amount by which the HE threshold stress is exceeded. Time to failure decreases with increasing stress.

The applied stress in a bolt or screw is a function of the loading conditions in the joint. These loading conditions are a combination of joint design (i.e. service loads) and installation preload of the fastener. Usually, bolts are installed to preloads ranging from 50 % to 100 % of the yield strength. For property class 10.9 fasteners which have no significant susceptibility to IHE, this amount of loading is below the HE threshold stress of the material. However, if these fasteners have hardness above the specified limit or other defects such as poor microstructure and low toughness (see 9.2.2), they can exhibit abnormally low HE threshold stress which is below the stress resulting from normal installation preload. Under these conditions, given the *same concentration of hydrogen* and *normal installation preload*, the probability of exceeding the HE threshold stress of the material becomes significantly greater, thus increasing the risk of hydrogen assisted cracking (HAC).

NOTE As with all failure mechanisms, HAC is normally initiated at the points of greatest concentration of stress:

— in the case of bolts and screws, this corresponds to the fillet radius under the head, the thread runout, or the root of the first engaged thread;

— in the case of nuts, the distribution of load in internal threads makes it significantly less likely that the HE threshold stress can be exceeded; consequently, HE failure of a nut, although possible, is extremely rare;

— in the case of non-flat washers, a significant tensile stress amount is present as the washer is compressed; it is not unusual for electroplated high-hardness elastic washers to fail due to HAC, unless they are adequately baked.

Unintended geometrical irregularities such as angles, sharp radii, unintended surface discontinuities or pits can arise from poor fastener design, poor manufacturing, over-pickling or corrosive service conditions. Notably, poor radii and thread laps at the thread root are highly localized concentrators of stress. These irregularities can often lead to unexpected crack initiation, thus exacerbating the stress condition, particularly for a material that is already susceptible to HE.

9.4 Atomic hydrogen

9.4.1 Sources of hydrogen

There are two possible sources of hydrogen: *internal* and *environmental.*

9.4.2 Internal hydrogen

Steel inherently retains a small amount of *residual* hydrogen as it is produced. Even with advanced vacuum degassing techniques, steel of standard quality contains hydrogen concentrations *roughly* in the order of 1 ppm. This residual hydrogen is not normally cause for concern because it is typically in a trapped state. Internal hydrogen can also be introduced into fasteners during their manufacturing processes. For example, during austenitizing or carburizing, hydrogen can be absorbed by the fasteners. However, it is subsequently "*baked out*" during tempering. In a steel fastener that has been properly quenched and tempered, any remaining residual hydrogen is typically trapped and innocuous[12][30].

NOTE 1 Secondary processes such as welding can also introduce hydrogen into the heat affected zone.

The relevant manufacturing processes to consider with respect to internal hydrogen embrittlement are primarily coating processes and related surface cleaning and preparation processes (e.g. pickling). The reasons these processes are critical is that they are the final manufacturing steps, and coating materials (e.g. zinc) act as a barrier to hydrogen effusion, i.e. the coating prevents or impedes hydrogen's natural tendency to diffuse out of the steel at room temperature[31].

Typical cleaning for electroplating comprises hot alkaline degreasing followed by electrolytic (i.e. anodic) alkaline cleaning and inhibited acid pickling. Acid pickling is a significant source of hydrogen in coating processes. Therefore, a suitable inhibitor and minimum cleaning cycle time should be used to minimize the risk of internal hydrogen embrittlement (IHE). For fasteners with hardness greater than 390 HV, such as property class 12.9 fasteners, special pre-treatments are advisable using non-acidic methods such as mechanical or alkaline cleaning.

Inhibitors reduce corrosive attack on the steel and the generation and/or absorption of hydrogen. Quenched and tempered steel fasteners should ideally be supplied with a surface that can be cleaned with a minimum immersion duration when acid pickling is used.

Cathodic cleaning is a source of hydrogen; it should be avoided for fasteners with hardness above 390 HV.

Electroplating processes generate hydrogen; however, the amount of hydrogen absorbed by the fasteners is not equal to the quantity of hydrogen generated by electrolysis. The amount of hydrogen which can be absorbed depends on the process type (e.g. alkaline zinc, acid zinc, zinc alloy) and process parameters (e.g. current density, electroplating duration, rack/barrel)[31]. The most important factor that influences the quantity of hydrogen that remains in a fastener is *permeability* of the coating to hydrogen diffusion[31][32]. The permeability of the coating determines if it allows hydrogen to diffuse into the steel during electroplating as the coating layer thickens, and later if the coating is an effective barrier that blocks hydrogen effusion, thus forcing it to remain in the fastener.

Studies have shown that there is no risk of IHE for phosphate coated property class 12.9 fasteners when left at ambient temperature for more than 24 hours, because phosphate coatings are very porous[23]. Similarly, studies have shown that the risk of IHE is significantly lower for aerospace LHE-Cd cadmium electroplating and certain zinc-nickel (Zn-Ni) electroplating processes containing 12 % to 16 % nickel[32]. The principal reason is that such coatings are more permeable than zinc (Zn) or zinc-iron (Zn-Fe) electroplated coatings.

Common industry practice is to *bake* the fasteners after the coating process to extract any diffusible hydrogen that was introduced in the course of such processes. For more information about baking, see Clause 15.

NOTE 2 Typically, IHE failure occurs within hours or days after installation of a fastener.

9.4.3 Environmental hydrogen

Environmental hydrogen is introduced in steel fasteners as a result of corrosion during service. Contact with water and corrosive substances can generate hydrogen that can be absorbed by fasteners. More critically, galvanic corrosion of a sacrificial cathodically protecting coating (e.g. Zn, Zn-Ni, Cd) generates hydrogen, which can then be absorbed by exposed steel surface areas of a fastener (i.e. cathode). This condition occurs when the coating is damaged, cracked, porous or partially consumed by corrosion. The quantity of hydrogen absorbed in this manner is orders of magnitude higher than under normal corrosion conditions (i.e. steel fastener without coating).

These conditions can lead to stress corrosion cracking (SCC), also called hydrogen assisted stress corrosion cracking (HaSCC) or hydrogen induced stress corrosion cracking (HiSCC).

From a failure analysis perspective, any amount of corrosion prior to failure of an in-service fastener can lead to EHE as the dominant failure mechanism, independently of the presence of internal hydrogen. With the passage of time, the localized contribution of corrosion generated hydrogen is cumulative, and the relative contribution of internal hydrogen becomes negligible.

NOTE Typically, EHE failures take much longer to occur than IHE failures. EHE failure can occur anywhere from weeks to years after installation of a fastener, as hydrogen is absorbed during corrosion processes.

10 Case-hardened fasteners

Case-hardened screws present additional challenges in that the surface is intentionally hardened to fulfil self-drilling, thread-forming and/or self-tapping functions. These types of screws vary greatly depending on the purpose for which they are supplied. They are used for joining wood, steel, galvanized steel, aluminium or combinations of these materials. Consequently, they can be supplied with core hardness ranging from 250 HV to 450 HV and surface hardness up to 600 HV. The combination of high surface hardness and core hardness can make case-hardened screw materials very susceptible to both IHE and EHE. Case-hardened screws are sometimes coated with zinc, zinc alloy or zinc rich organic coatings, but are very often coated by zinc electroplating. The availability of hydrogen provides ample triggers for HE to occur.

The possible sources of hydrogen are:

— internal hydrogen introduced during carburizing;

— internal hydrogen introduced during electroplating processes;

— corrosion generated environmental hydrogen, resulting from the sacrificial corrosion of cathodic protective coatings;

— corrosion generated environmental hydrogen, resulting from galvanic mismatches of materials being joined.

Most chemicals preservatives used in pressure treatment of lumber are copper-based and can significantly accelerate the corrosion of screws. This accelerated corrosion process begins with rapid corrosion of zinc or zinc rich coatings, followed by an equally rapid corrosion of the underlying steel. These complex galvanic couples further increase the rate of hydrogen generated by corrosion.

Fortunately, case-hardened screws do not often fail by hydrogen embrittlement because they are usually loaded below their HE threshold stress. However, even slight variations in hardness, loading conditions or corrosive environment can lead to relatively rapid failure (i.e. hours to days after installation). Case-hardened screws manufactured under poor process control conditions make prevention a challenge. It is therefore highly recommended to consider the know-how of the fastener manufacturer as well as the application and service environment.

From the perspective of preventing HE failure, the key product characteristics that must be controlled are: core hardness, case hardness and case depth.

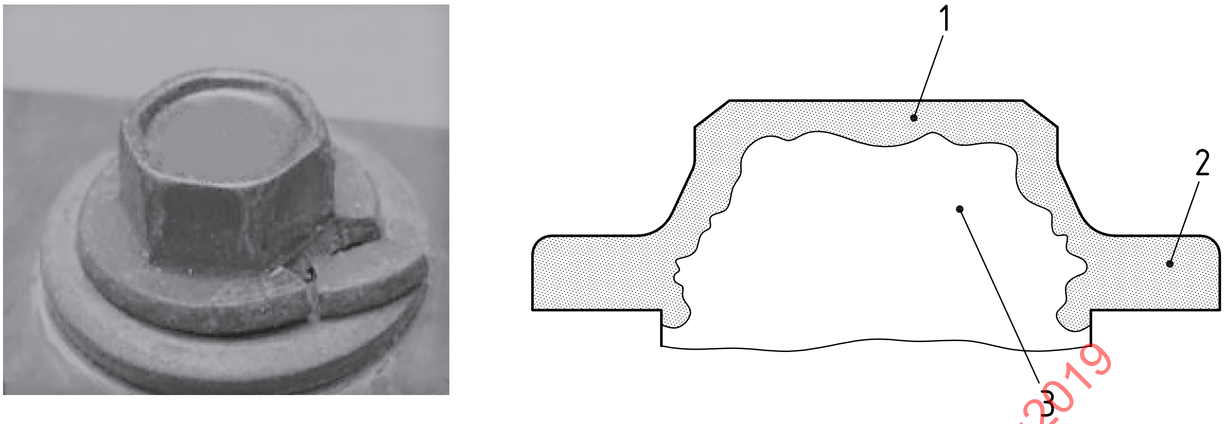
— Core hardness: experience has shown that core hardness is the most critical characteristic and should be kept below 370 HV.

— Surface hardness: surface hardness should be specified in accordance with the intended purpose of the screw; as with core hardness, surface hardness should be specified as a range (i.e. minimum and maximum values) and not only as a minimum requirement.

— Case depth: experience has shown that with increasing case depth, susceptibility to HE increases, therefore the maximum case depth needs to be limited (see e.g. ISO 2702 for self-tapping screws)[33].

Additional preventive measures include the selection of an appropriate coating. For example, although zinc electroplating is very economical and widely used, sometimes it is not appropriate for case hardened screws at a high hardness range. Alternative coatings include zinc flake coatings, zinc-nickel electroplating and organic coatings. Other precautions include specifying and overseeing the use of appropriate installation methods, for example the use of impact wrenches is usually not recommended.

A further consideration is the effect of the screw shape and geometry. Normally, a case-hardened layer is relatively uniform in terms of hardness and effective depth, regardless of its location on the screw. Below the depth of the case, a transition zone exists between the high hardness case and the lower hardness core. Thin sections, such as those in washer head geometries or head-to-shank transitions in screws with internal drives, sometimes do not provide enough thickness for a full transition to lower hardness. Consequently, thin sections are areas of elevated hardness that can be prone to HE failure, even if the body of the fastener is not likely to fail. Therefore, geometry and particularly the elimination of thin sections must be considered in the design and processing of case hardened screws, to minimize the risk of hydrogen embrittlement failures[34][35]. See an example of fractured fastener due to IHE in Figure 7.



Key

1 case depth on head (thick section)

2 flange with entire thickness having elevated hardness (thin section)

3 core (neutral hardened)

Figure 7 — Hydrogen embrittlement fracture of flange on a case-hardened screw (left) and case-hardening profile showing the flange (i.e. thin section) having been hardened through the entire thickness (right)

Finally, for some thread forming screws, e.g. according to ISO 7085[51][1)] or DIN 7500-1[52], used in applications where a defined preload is applied, it is possible that HE threshold stress is exceeded. Special care should be taken to minimize exposure to hydrogen, in order to prevent failure by IHE or EHE.

11 Hot dip galvanizing and thermal up-quenching

In the 1970s, failures of hot dip galvanized high strength fasteners attributed to stress corrosion cracking (SCC) prompted ASTM Committee F16 on Fasteners to prohibit hot dip galvanizing of ASTM A490[36] high-strength structural bolts used primarily in North America.

In Europe and elsewhere, hot dip galvanizing of structural bolts of property class 10.9 per ISO 898-1 has remained a standard practice. As additional precaution, guidelines and requirements addressing materials and processing, such as those included in ISO 10684, have been established to avoid or minimize the risk of IHE. In spite of these precautions, failures have occurred with hot dip galvanized fasteners that:

— were never exposed to acid prior to hot dip galvanizing,

— failed shortly after installation, and

— were not subject to environmental corrosion.

Even in the absence of conclusive evidence of exposure to hydrogen, either from processing or from the environment, these failures of hot dip galvanized high strength fasteners have been incorrectly attributed to IHE, allegedly by acid pickling, or to EHE, allegedly by in-service corrosion.

Although the hot dip galvanizing process itself does not introduce hydrogen, a recently revealed phenomenon resulting in an additional source of hydrogen can better explain the mechanism of such failures. It has been proved that a significant source of hydrogen is the freeing of trapped residual hydrogen by thermal shock (i.e. *up-quenching*) that occurs when the fasteners are immersed in molten zinc during hot dip galvanizing. The presence of a thick zinc coating prevents "released" hydrogen escaping, instead causing it to accumulate at grain boundaries[37]. The release of trapped hydrogen by

1) Withdrawn.

up-quenching is therefore a third and potentially the most significant source of hydrogen in addition to conventional internal and environmental sources.

This "newly discovered" source of **internal** hydrogen is likely to have played a primary role in triggering failures of hot dip galvanized high strength fasteners that are not adequately explained by conventional models of IHE or EHE. However, as was described earlier, hydrogen is a trigger and not the root cause of HE failure. The underlying fundamental condition for such a failure to occur must also exist. In other words, the material must be susceptible to hydrogen embrittlement. Hot dip galvanized fasteners with a specified hardness range of 240 HV to 390 HV are not susceptible to hydrogen embrittlement. This assertion is corroborated by the fact that high strength structural fasteners, including ISO 898-1 property class 10.9 bolts and ASTM A354 BD[38] bolts, are routinely and safely hot dip galvanized. On the other hand, incorrectly heat treated or otherwise defective fasteners can become significantly more susceptible (see 9.2.2). Therefore, the root cause of failures of hot dip galvanized high strength fasteners is invariably related to poor or non-conforming material condition, resulting in higher than normal HE susceptibility.

NOTE A dramatic example of such a case is the failure of anchor rods on the San Francisco-Oakland Bay Bridge in 2013. The root cause of these failures was attributed to defective material of one lot of ASTM A354 BD anchor rods[39].

12 Stress relief prior to electroplating

Stress relief prior to electroplating is not required or appropriate for fasteners that are quenched and tempered, because tempering effectively relieves residual stress.

On the other hand, residual tensile stress in fasteners that are work hardened after quenching and tempering and prior to electroplating can lead to the initiation of hydrogen assisted micro-cracks. HAC can only occur provided *all three* conditions for hydrogen embrittlement are met: notably that the material is susceptible, that there is sufficient hydrogen *and* that the residual stress resulting from work hardening exceeds the HE threshold stress of the steel. In such a case, it is beneficial to perform a stress relief operation prior to electroplating as a preventive measure.

Only operations that lead to significant plastic deformation resulting in residual tensile stresses such as cold forming, cold bending, cold straightening, and some drilling and welding operations can justify stress relief before electroplating. Standard secondary machining operations such as grinding, turning, tapping and milling are not problematic and do not require the fastener to be stress relieved.

The effectiveness of stress relief increases with increasing temperature and duration. However, standards state that the temperature must not impair the mechanical properties of the fasteners and more precisely that it must not exceed their tempering temperature. The selection of an appropriate temperature and duration for a stress relief operation is specific to each case and depends on an assessment by the fastener manufacturer of the likelihood that all three hydrogen embrittlement conditions are present. Achieving a well-founded and effective stress relief strategy should be based on data obtained by product inspection or testing. Any such method should also consider the fact that hydrogen embrittlement is time dependent.

NOTE The stress relief criteria recommended in ISO 9587[40] are too broad and not applicable for fasteners.

13 Fasteners thread rolled after heat treatment

There are several beneficial effects of thread rolling fasteners after heat treatment (i.e. after quenching and tempering). Cold rolling and the resulting compressive residual stresses improve fatigue performance. Studies have shown that thread rolling fasteners after heat treatment also decreases HE susceptibility[41][42]. This observation is explained by reduction of lattice space and increase of dislocation density (i.e. traps) in the critical thread root areas, thus resulting in a greater number of trap sites and reduced hydrogen mobility. Thread rolling after heat treatment can be an additional manufacturing strategy for limiting the risk of hydrogen embrittlement failure.

14 Hydrogen embrittlement test methods

Given the *time dependency* of hydrogen embrittlement, test methods designed to either detect or measure any loss of mechanical strength resulting from the effect of hydrogen need to incorporate a lengthy *time* component.

Typically, hydrogen embrittlement testing is performed by means of sustained load testing, which is a qualitative (pass/fail) method. Sustained load testing is intended as a post-production (e.g. after electroplating) quality assurance step for testing high strength fasteners that are susceptible to IHE. Sustained load testing consists of applying a specific static load for a fixed period of time ranging from 24 h to 200 h, depending on the specification. The qualitative nature of the sustained load test is such that a fastener will either pass or fail at the given point in time. The result does not reveal how close the fastener is to its point of failure. There are several methods for sustained load testing. The tests most often used for fasteners are specified in ISO 15330[43], DIN 50969-2[44], NASM 1312-5[45], and ASTM F606[46].

NOTE 1 Sustained load tests are suitable for production testing. Standard sustained load test specifications are not intended for testing parts after removal from service.

Quantitative alternatives to sustained load testing are slow strain rate (SSR) testing, as described e.g. in ISO 7539-7[47] and ASTM G129[48], or incremental step load (ISL) testing such as in ASTM F1624[26]. The basis for these tests is to apply a slowly increasing load until fracture of the sample. Given a slow enough loading rate, it is possible to measure the HE threshold stress for a given material under a given concentration of hydrogen.

NOTE 2 Analytical test methods described in ISO 7539-7, ASTM G129 and ASTM F1624 are not suitable for embrittlement testing of fasteners on a production scale due to the time and cost associated with performing the test. These quantitative test methods are better suited for analytical purposes including research and development.

15 Baking

The potentially damaging effects of hydrogen absorbed during surface cleaning or electroplating can usually be prevented by baking the fasteners after processing. Baking is a moderate heat treatment that has been shown to either extract hydrogen by effusion or to cause it to migrate to trap sites, thus making it immobile. As mobile/diffusible quantity of hydrogen is reduced, both time-to-failure and HE threshold stress increase. However, it should not be assumed that baking will completely eliminate IHE in all cases.

The key factors that influence baking effectiveness are:

— temperature,

— duration, and

— permeability of the coating.

In addition, increasing the rate of heating has been shown to improve the effectiveness of baking. These factors lead to a great deal of variability for determining appropriate baking conditions. For example, with susceptible fasteners (e.g. above 390 HV) that are zinc electroplated, 8 h to 10 h at 190 °C to 220 °C is a minimum recommended baking duration. However, depending on size and strength level/hardness of the fasteners, fasteners can require baking durations up to 24 hours to sufficiently reduce the quantity of mobile hydrogen. A common practice of baking fasteners above 390 HV for 4 hours is insufficient and can even lead to occasional failures.

NOTE 1 The practice of baking zinc electroplated fasteners for 4 hours at approximately 190 °C is inadequate for extracting hydrogen because zinc is an effective barrier to hydrogen diffusion. It has been shown that baking duration of 4 hours can even be detrimental. For baking to be effective and beneficial, significantly longer baking duration is needed.

On the other hand, parts such as property class 10.9 fasteners in accordance with ISO 898-1 do not need to be baked, yet they are often unnecessarily baked to ISO 2081[49] and ISO 9588[50]. Given our current understanding of baking effectiveness and material susceptibility, it is not the baking that prevents these fasteners from failing. Rather, property class 10.9 fasteners that are correctly manufactured to the material and metallurgical properties in accordance with ISO 898-1 are not susceptible to IHE.

NOTE 2 Baking criteria as specified in ISO 2081 and ISO 9588 are too broad and not applicable for fasteners.

The maximum temperature of heating in a baking process is limited by the following considerations:

— it should not exceed the temperature at which the fasteners were originally tempered;

— it should not impair the functional properties of the coating, and

— it should not negate the beneficial effect of compressive residual stress from thread rolling after heat treatment.

NOTE 3 Zinc electroplated fasteners are usually baked to maximum temperature of 200 °C to 220 °C. Cadmium electroplated fasteners are baked to maximum temperature of 190 °C to 200 °C.

The baking process is typically performed after electroplating, prior to application of a conversion coating and/or sealant or top coat. However, other sequences can be suitable depending on the specific properties of the coatings and finishes.

The time between electroplating and baking should be kept short as a matter of good practice. The intent of such practice is to maximize the extraction of mobile hydrogen, otherwise a portion of the mobile hydrogen can become reversibly trapped and more difficult to bake out. This phenomenon has been shown to be relevant for electroplated steel parts at hardness in the range of 500 HV and above[40][41]. The often-used approach of specifying an exact duration (e.g. 4 hours) is purely subjective and is intended as a practical operational time-frame, and also as a quality assurance mechanism for monitoring good practice. Time between coating and baking should not be used as a rigid criterion for acceptability of a fastener lot, and it definitely has not been used as the basis for assigning root cause to a fastener failure.

The electroplater needs to monitor and control the baking furnace conditions, including methods of loading, duration in the furnace and uniformity of temperature. Achieving a well-founded and effective baking strategy can be validated by empirical test data obtained from sustained load testing of production fasteners described above, and/or process qualification tests such as those specified in DIN 50969-2[44], ASTM F519[28], and ASTM F1940[27].

