ZINC MATTERS

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PLACING HYDROGEN EMBRITTLEMENT OF FASTENERS IN PERSPECTIVE

What is problematic in identifying the presence of hydrogen embrittlement (HE)?

Failures from possible hydrogen embrittlement in steel are notoriously difficult to prove post failure for the following reasons[(1)]:

1a. Measuring the total *hydrogen concentration* in the steel to prove the presence of HE is often meaningless as hydrogen trapping occurs at carbides, grain boundaries etc, and it is really the so-called *diffusible hydrogen* that needs to be measured, i.e. that hydrogen that can move to a crack tip and enhance its propagation;

1b. Even if the diffusible hydrogen content is measured, the "danger level" of such hydrogen is not a fixed value as its effect varies with the strength of the steel. For a high strength steel, levels as low as 1 or 2 ppm may already be effective in initiating HE while for a low strength steel many tens of ppms may still be acceptable;

1c. Once hydrogen atoms have "done their damage" they can even move out of the steel, yet the damage remains there (as "flaking" or "fish eyes") and may later culminate as a long delayed failure;

1d. A SEM fractograph of the original fracture face is also not necessarily conclusive as a seemingly ductile dimple fracture is often present after HE. The observations from fractographs of a HE steel that often (but not always) shows intergranular fracture are also not necessarily characteristic of HE as a number of other metallurgical mechanisms also lead to intergranular fractures.

The currently accepted model for understanding hydrogen embrittlement of steels

The current most accepted mechanism of HE failures is the so-called HELP model[(1)], i.e. Hydrogen Enhanced Local Plasticity, in which the hydrogen atoms diffuse towards the high stress concentration area at the tip of a crack where they actually enhance the plasticity during crack advancement but thereby quickly exhaust the ductility of the steel in that area, forcing the crack to move a step forwards to "fresh" material where the process repeats itself. This brings about that the stop-start of the crack tip leaves so-called "tear ridges" on the cleavage planes on a slow fractured surface in contrast to clear cleavage planes for the same steel but fractured in a fast impact where the crack tip "runs away" from the diffusing hydrogen atoms.

The delay of failure by hydrogen embrittlement

Delayed failures in HE steel components often occur sometime after processing the component although the delay times are usually measured in hours or days and seldom are longer as diffusion of hydrogen (the smallest of all atoms) in ferritic steel is relatively fast and movement of the hydrogen atoms to the crack tip is relatively fast, even at room temperature.

Source of hydrogen for hydrogen embrittlement

If HE is suspected one needs to consider from where the hydrogen may have come? If there is no credible source of hydrogen then HE is not likely to be present. Hydrogen may arise from moisture on scrap steel or master alloys fed during melting of the steel or during electroplating or pickling of a final product. It is for this very reason that vacuum degassing is generally employed in the melting and casting of High Strength Low Alloy (HSLA) steels and electroplating and pickling of the same steels is avoided for critical components.

Loss of hydrogen during heat treatment

Ferritic steel actually has a very low solubility for hydrogen and any hydrogen contained within the steel will tend to diffuse out of the component if allowed to. This forms the basis for the so-called *diffusion anneal* of steel components that are suspected to be embrittled by hydrogen.

The design of such a diffusion anneal is a standard calculation[(1)] which takes into account the distance L from the centre to the surface of the component where the hydrogen will escape, the time t at temperature T and the diffusion rate D for hydrogen at the temperature of the anneal. The latter parameter needs to take into account that "trapping" of hydrogen atoms takes place at carbides, grain boundaries, dislocations etc. that results in a "lower than usual" diffusion rate and use is, therefore, made of experimentally determined "effective" diffusion rates.

Fasteners seldom suffer HE from an initial hydrogen introduced in the melting and casting process as the typical solution anneal, quenching and tempering for high strength bolts effectively act as a "diffusion anneal". Calculations for M30, M24 and M20 bolts during the solution treatment (the steel is austenitic then) and the subsequent tempering process (the steel is ferritic then) have shown the following *(see Table 1)* typical hydrogen retention percentages.

The overall hydrogen retention factor means, for M20 bolts as an example, that if the hydrogen content in the steel was say 2 ppm before the heat

Bolt size	Solution treatment: 880°C for 1 hour		Tempering treatment: 425°C for 45 min		Overall Hydrogen retention factor: % from the original
	$D\gamma/H$ cm^2/s	Retention factor %	$D\alpha/H$ cm^2/s	Retention factor %	
M30	1.3x10-5	90	1x10-4	35	32
M24	1.3x10-5	73	1x10-4	28	20
M20	1.3x10-5	47	1x10-4	13	6

Table 1: Calculated retention factors of any initial hydrogen in the steel during a typical solution anneal, quenching and tempering cycle.

treatment, that only 0.06 x 2 ppm will remain after the heat treatment, i.e. only 0.12 ppm will remain. For M24 and M30 bolts the retention factors are naturally somewhat higher from the longer diffusion paths from the centre of the bolt to the surface.

It is for the above reason that short term pickling of fasteners is even allowed in some standards provided that the pickling time is less than the galvanizing time at temperature where some hydrogen pickup from the pickling is removed again during galvanizing.

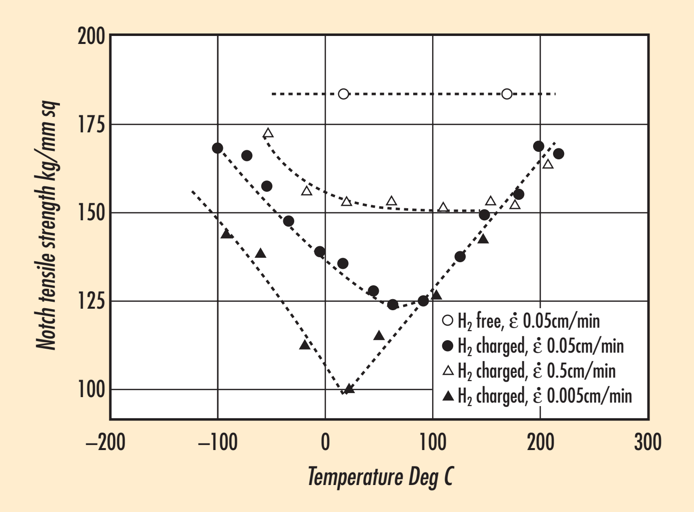


Figure 1: The notched tensile strength of steel AISI 4340 as a function of test temperature for three strain rates of testing[(8)].

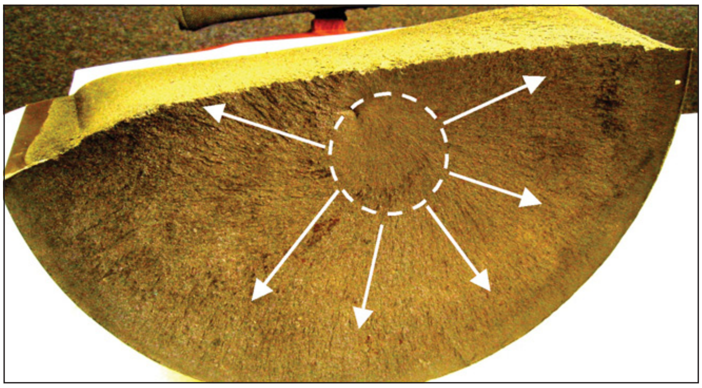
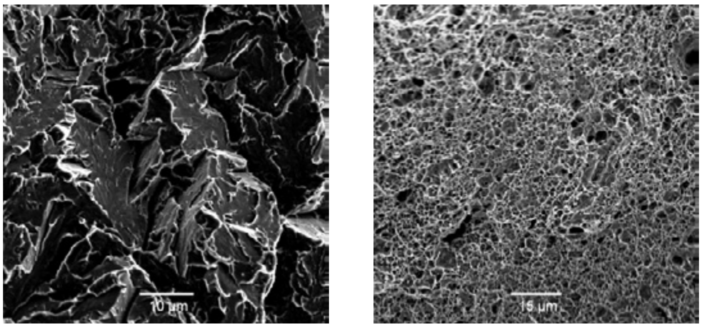


Figure 2: Macro-photographs of the failure by HE initiated at a "fish eye" of a 360 mm shaft manufactured from a low alloy Cr-Ni-Mo-V quenched and tempered steel[(9)].



Figures 3 (left) - 4 (right): SEM fractographs of both cleavage and dimple fracture areas from the same freshly impact broken sample of a quenched and tempered low alloy Cr-Ni-Mo-V steel that was known to contain Hydrogen in excessive quantities.The white arrows show a few of the large number of secondary microcracks[(9)].

Where high strength fasteners, however, appear to show effects of HE, the source of hydrogen generally is not from the original melting and casting process but most likely arises from the environment in which the fastener operates or from surface treatment processes of the fasteners such as pickling and/or electroplating. In such a case, HE-induced fracture will, therefore, not be initiated from the centre or core of the fastener but rather at its outer surface, most likely within the stress concentrated area of the threads.

Testing for hydrogen embrittlement

A number of standards exist to test for HE in steel[(2 to 7)] with slow bending or slow strain rate testing and stepped loading tests relatively common. Both of these classes of tests rely on the principle that hydrogen atoms, given enough time, will preferentially move to the high stress concentration at the tip of an advancing crack and thereby affect the ductility of the steel in that area, allowing the crack to advance one more step. These tests, however, also have some limitations:

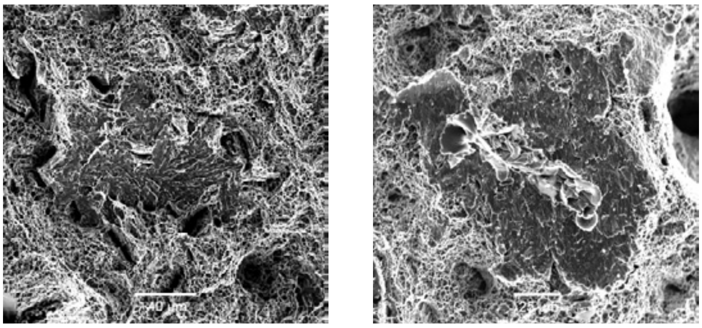
Step loading

In the step loaded test a critical stress / crack combination will be reached at some point during the regular increase in the stress level (typically on a daily basis), leading to HE-induced fast fracture. The weakness with this type of test is that it cannot distinguish between a pre-existing crack that will also become critical at a certain critical stress in the absence of hydrogen according to classical Fracture Mechanics and a crack induced by HE. This type of test is, therefore, well suited to indicate the presence of HE in those cases where no pre-existing cracks can be guaranteed but will fall short if any pre-existing cracks were present.

Slow strain rate tests

The SSR test for HE is based on the widely accepted HELP mechanism, i.e. strain a tensile test specimen in which HE is suspected, at a very slow strain rate (typically 10^{-5} to 1^{-6} s^{-1}) until fracture. The very slow crack propagation rate allows the hydrogen atoms to diffuse to the crack tip where they enhance the local plasticity but also quickly exhaust the local ductility, thereby extending the crack tip to a new area to which the hydrogen atoms will diffuse once more, thereby repeating the process. This brings about that the stop-start of the crack tip leaves so-called "tear ridges" on the cleavage planes on a slow fractured surface in contrast to clear cleavage planes for the same steel but fractured in a fast impact.

Temperature also plays an important role in the hydrogen embrittlement of steels with embrittlement most severe near room temperature and less severe at lower and higher temperatures. This temperature effect is shown in the *Figure 1* for an AISI 4340 steel (Fe – 0.4%C – 0.8%Cr – 1.8%Ni – 0.25%Mo).



Figures 5 (left) - 6 (right): Slow SSR tested fractographs of the same 360mm shaft as in Figures 3 - 4. Note the "patches" of cleavage fracture areas amidst dimple fractured areas in the center of both figures with both of them showing clear "tear ridges"[(10)] *seen as the fine lines on the cleavage planes*[(8)].

It is for this reason that the SSR test is also conveniently done at room temperature.

Note the significantly lowered notch tensile strength for the quenched and tempered low alloy steel AISI 4340 if tested at a cross head speed of only 0.005cm/min compared to less severely affected notch tensile strengths at higher strain rates, both with hydrogen charged specimens.

Signatures for a hydrogen embrittlement fracture

A number of indirect signatures exist for identifying fractures from HE present in the steel:

2a. The fracture usually starts at a so-called "fish eye" which is mostly deep within or even near to the centre of the component where the hydrogen concentration will be the highest after any heat treatment. Fracture is, therefore, unlikely to start at or near to the surface where little or no hydrogen will be present after heat treatment.

2b. HE may show either dimple or cleavage fractographs but very often shows secondary cracks leading from the primary fracture face inwards.

2c. The fractographs from a Slow Strain Rate (SSR) test compared to a fast fractured one, show two signatures, i.e. a mixture of dimple and cleavage fractures and "tear ridges" on the cleavage planes.

Compare the "clean" cleavage planes in *Figures 3 - 4* of a fast fractured specimen with the cleavage planes full of "tear ridges" of a SSR tested one in *Figures 5 - 6,* both from the same 360mm Cr – Ni – Mo – V shaft.

2d. Finally, SSR testing will also reveal a low Z (Reduction in Area) if compared to a normal tensile tested sample, as shown in *Figure 7* taken from the Standard for slow strain rate testing for HE susceptibility: ASTM G129(2).

Summary

From all of the above background, it is evident that care should be taken not to arrive at any firm conclusion on the possible presence of HE based on only one or even two observations "that fit the picture" while ignoring the rest but that a "global" perspective needs to be taken, typically by a decision tree as proposed below for hydrogen present in the steel from its melting and casting:

3a. *Is there an identified possible source of hydrogen for contaminating the steel?* If yes, then consider HE;

3b. *Was there a "fish eye" present in the fracture face where the original fracture in the "field" was initiated and did the fracture start near to the centre of the component?* (This is particularly so for delayed failures running into months and not necessarily so for typical delay times of only a few hours) If yes. Then suspect HE;

3c. *Is there a marked reduction in the SSR's Z-value (Reduction in Area)?* If yes, HE is suspected;

3d. *Does the SSR tested fracture face contain a mixture of dimple and cleavage fracture?* If yes, then strongly suspect HE;

3e. *Do the cleavage planes of the SSR tested specimen contain evidence of so-called "tear ridges" whereas the fast fractured ones have "clean" cleavage planes?* If yes, HE is proven.

For the case where the source of hydrogen is from the operating environment or from surface processing (pickling and/or electroplating) and not from the melting and casting of the steel, the above decision tree is still applicable with the exception of Step 3b while steps 3d and 3e should be ideally located at or near to the surface of the fastener where the hydrogen may be present.

References

1. *"Hydrogen Embrittlement", WE Stumpf, Chapter 17 of the advanced post graduate course NHB 700 on the Heat Treatment of Steels, University of Pretoria.*
2. *Standard ASTM G129 (2006): "Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking".*
3. *Standard ASTM F519 (2008) "Standard test method for Mechanical Hydrogen Embrittlement: Evaluation of Plating/Coating Processes and Service Environments".*
4. *Standard ASTM F1624 (2009): "Standard Test method for Measurement of Hydrogen Embrittlement Threshold in Steel by the Incremental Step Loading Technique".*
5. *BS EN 2831 (1993): "Hydrogen Embrittlement of Steels: Test by Slow Bending".*
6. *BS EN 2832 (1993): "Hydrogen Embrittlement of Steels: Notched Specimen Test".*
7. *ISO 15530 (1999): "Fasteners: Pre-loading test for the detection of hydrogen embrittlement by the parallel bearing method".*
8. *BA Graville, RG Baker and F Watkinson, British Welding Journal: 14 (1967) p337.*
9. *Case Study: WE Stumpf, (2008).*
10. *Metals Handbook, Vol 12 Publ ASM (US), p293-307*

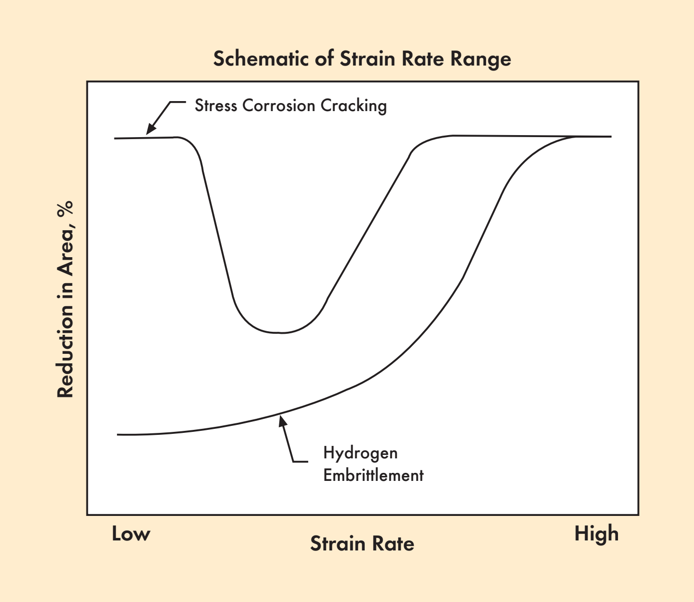


Figure 7: ASTM G129: Effect of SSR testing on the Reduction in Area for a HE specimen(2).