Hydrogen Embrittlement
Its effect on Structural Bolting Assemblies

Introduction

Hydrogen embrittlement is a mode of failure that can affect high strength structural steel bolts. It is a reduction in the ductility of steel due to absorbed hydrogen making the steel less able to support the imposed stresses which can lead to the development of micro cracking and eventually failure.

This mode of failure is not well understood by engineers and specifiers, as all too often high strength steel bolts are specified without considering the implications of hydrogen embrittlement. This technical note describes hydrogen embrittlement and explains the three factors that need to be present to trigger this mode of failure and how this can be avoided.

Hydrogen Embrittlement

For a Hydrogen embrittlement failure to occur three factors must be present, the bolt must have a high tensile strength, there must be an applied tensile stress or load and the bolt must have absorbed atomic hydrogen.

The presence of a protective surface coating may be a factor in providing a source of hydrogen; however, hydrogen embrittlement can and does occur with self-colour (uncoated) bolting assemblies.

Hydrogen embrittlement results in the sudden and catastrophic failure of a high tensile carbon or low alloy steel bolting assembly under a tensile load (i.e., preload). The failure normally occurs sometime after the bolt has been tightened; the delay can vary from hours to months, even years depending on the source of the hydrogen.

Classical Theory of Hydrogen Embrittlement

The classical theory of hydrogen embrittlement indicates that as the tensile strength of the bolt material exceeds 1000 N/mm^2, the effect of absorbed atomic hydrogen becomes critical and the risk of hydrogen embrittlement increases.

When such a bolt is tightened, the effect of the tensile stress, generated within the lattice structure is to cause the absorbed hydrogen to move and collect at low energy sites in the lattice, such as dislocations. (Dislocations are imperfections or defects in the lattice structure of a metal).

As the hydrogen collects, the atomic hydrogen combines to form molecules of hydrogen. The volume occupied by a single hydrogen molecule is significantly greater than that of the two component hydrogen atoms. The increased volume generates high levels of stress within the steel structure which eventually causes micro cracks to develop, followed by bolt failure.

What are High Tensile Steel Bolts?

For the purposes of hydrogen embrittlement, a high tensile steel bolt is property class 10.9 or any that have a tensile strength range that exceeds 1000 N/mm^2; as defined by the bolt mechanical property standard BS EN ISO 898-1[(1)]. However, lower property classes such as 4.8, 5.8 and 6.8 where the mechanical properties are developed by 'cold working' can be at risk if the bolts are not stress relieved; especially when the head form is produced by cold heating.

In general, as the tensile strength of a fastener is increased so the susceptibility to hydrogen embrittlement increases. This can be related to the lower ductility and plasticity of steel, as the tensile strength increases; so, it is less able to adapt to and absorb the stresses, generated by the absorbed hydrogen, imposed on the structure of the steel.

The stresses imposed on the bolting assembly, generally caused by tightening, provides the energy to cause changes in the lattice structure of the steel and allows movement of the atomic hydrogen.

Over time with the higher property class assemblies as the stresses in the steel lattice build-up, due to their lower ductility, micro-cracks appear in the structure and crack propagation commences and continues until the reduced cross section will no longer support the applied tensile load.

With property class 8.8 and below, when the micro-cracks develop there is normally sufficient ductility in the steel that it will absorb the higher stress by plastic deformation and the crack propagation will stop.

Causes of Hydrogen Embrittlement

There are two principal sources of atomic hydrogen, these are internal hydrogen embrittlement (IHE) mainly from the various processes, such as surface coating, during manufacture and environmental hydrogen embrittlement (EHE), otherwise known as ‘hydrogen induced stress corrosion cracking’, resulting from corrosion of the bolting assembly after installation.

Internal Hydrogen Embrittlement (IHE)

Studies in the 1980s, by BSC Swinden Laboratories, into the adsorption of hydrogen during the production of fasteners have shown that the main sources of atomic hydrogen with IHE are from certain types of heat treatment and surface coating.

Heat Treatment – with controlled atmosphere furnaces, the endothermic gas used to prevent heavy oxidation and decarburization, of the steel fasteners, is a mixture which includes molecular hydrogen and carbon monoxide; this will not cause hydrogen embrittlement. However, with cold formed fasteners, generally sizes M16 – M30, the steel used to produce them is often phosphate coated to aid production and reduce wear on the cold forming tooling. If such fasteners are heat treated in a furnace with a strongly reducing atmosphere, the phosphate will be protected from oxidation and can diffuse into the surface of the steel. The iron / phosphorus layer formed can significantly increase the risk of hydrogen embrittlement, if later the fasteners are acid cleaned or electroplated. BS EN ISO 898-1:2013 Table 2-Steels specifically warns of the need to remove any phosphate residues prior to the heat treatment of property class 12.9 fasteners.

Other heat treatment processes, such as carbo-nitriding, involve the breakdown of ammonia gas which does result in the production of atomic hydrogen and the risk of hydrogen embrittlement. However, such processes are rarely, if ever used, with structural bolting.

Surface coating – the main sources of atomic hydrogen are from acid cleaning, when used with all types of surface coating, and electroplating. These processes generate atomic hydrogen at the surface of the steel as a result of a simple chemical reaction or as part of an electrolytic cell; because the hydrogen is generated at the steel surface its absorption into the material of the bolt occurs easily.

Such hydrogen can be removed or at least reduced by a simple low temperature baking process (~ 200^{o}C), the length of time at temperature increasing as the tensile strength increases. The ability to remove, or render safe, atomic hydrogen is also dependent on the coating thickness; as it increases so the de-embrittlement time at temperature must be increased. Some sources suggest that a Zinc coating thickness of 8–10 μm is approaching the practical limit for the removal of hydrogen; thick (+60 μm) hot dip galvanized coatings with a mixture of Zinc and Zinc-Iron alloys cannot be de-embrittled. Hot dip galvanized fasteners that have been acid cleaned must be de-embrittled before galvanizing.

The de-embrittlement process must be commenced within a maximum period of one hour. Delaying the process carries the risk that the material will develop micro cracks in the structure of the steel; this can occur without the bolt being assembled and tightened. The defects formed in this way will result in bolt failure during use; such defects are irreversible.

Once hydrogen has been absorbed into a high tensile steel bolt, even after de-embrittlement has been carried out, there is no absolute guarantee that hydrogen embrittlement will not occur. This fact is acknowledged in the more recent revisions of specifications for electroplating of bolts BS EN ISO 4042 (2) and BS 7371-1(3).

Other surface coating systems that are more generally used for long term protection of structural bolting assemblies do not involve the generation of any form of hydrogen during the coating process; these include Hot Dip Galvanizing, Sherardizing, Greenkote and Mechanical Galvanizing. However, the use of acid pre-cleaning should always be avoided for all these processes, but especially with Hot Dip Galvanizing, mechanical cleaning being used instead. The use of mechanical cleaning with Hot Dip Galvanizing is a requirement of the BCSA model specification (4) for all 10.9 bolting assemblies.

Environmental Hydrogen Embrittlement (EHE)

Environmental hydrogen embrittlement (EHE), otherwise known as 'hydrogen induced stress corrosion cracking' occurs when a high tensile steel bolting assembly with an applied tensile load is subject to corrosion and a chemical reaction occurs that releases atomic hydrogen at the surface of the fastener.

For the corrosive reaction, including galvanic corrosion with a protective coating, to take place an electrolyte is required usually water or moisture; if rain water contamination with atmospheric pollutants Sulphur Dioxide or Carbon Dioxide may have occurred, this will accelerate the rate of corrosion.

For the corrosive reaction to become critical it is necessary for the bolting assembly to be in contact with the electrolyte for a significant length of time, not simply 'rained' on then dried out; bolting assemblies sitting in an electrolyte would be at a significant risk of failure. This means the design of the bolting connections must ensure that the assemblies are not in an area where the electrolyte can collect and be immersed in the electrolyte; the clearance holes for the bolting assemblies, in the structural members, make 'pockets' where the electrolyte can collect. The thread tolerances required for the bolt and nut to assemble result in a gap that is ideal for 'crevice' corrosion to occur. Additionally, the profile of load distribution on the assembled bolt and nut threads ensures that the area of maximum stress would be in contact with the electrolyte. Other factors that increase the rate of the corrosive reaction include the composition of the electrolyte and possible breakdown of any surface coating.

The corrosive reaction takes a significant time to generate sufficient atomic hydrogen to cause failure, in many cases years. Over time the hydrogen 'charging' by the corrosive reaction will far exceed the amount of any hydrogen introduced into the fastener by the processes used in manufacture; any fastener with a tensile strength greater than 1000 N/mm^2 is at risk.

Externally used preloaded bolting assemblies, with surface coatings such as hot dip galvanizing, that are fully exposed and ‘rained’ on then dried will not result in environmental hydrogen embrittlement as they corrode. The surface corrosion mechanism involves the exposed zinc being converted to a layer of zinc carbonate; this layer continues to grow in thickness until it is impervious. Contaminated rain (mainly SO_2) falling on the bolting assembly gradually converts the carbonate to a mixture zinc sulphate and zinc sulphide; these unfortunately are water soluble and they dissolve away for the whole process to be repeated.

These reactions generate little if any atomic hydrogen and the thick hot dip galvanized coating would prevent any absorption.

Such hot dip galvanized preloaded 10.9 bolting assemblies have been used in Germany for more than 50 years without significant failures.

Environmental hydrogen embrittlement can occur with steel components that have no surface coating; where the corrosive reaction for environmental hydrogen embrittlement occurs the presence of a surface coating can delay the time before failure occurs.

Recent changes in thinking on Hydrogen Embrittlement

The latest revision of BS EN ISO 4042, published in 2018, deals with the question of hydrogen embrittlement based on the ISO technical report ISO/TR20491[(5)], published in 2019. The technical report makes a fundamental change in proposing that the material used to manufacture the bolts is the ‘root cause’ in a bolt’s susceptibility to hydrogen embrittlement.

The technical report further proposes that a property class 10.9 'well-made bolt' in accordance with BS EN ISO 898-1 can be electroplated without the need for hydrogen de-embrittlement. This in a modified form has been adopted in BS EN ISO 4042:2018. BS EN ISO898-1 is a standard that defines the mechanical properties of the various property classes of metric bolts and only gives general information on the types of steel that can be used to manufacture the different property classes. The standard does not provide the information required to manufacture what the technical report refers to as a 'well-made bolt', which avoids the need for hydrogen de-embrittlement of property class 10.9 bolts; there is data available, but not in BS EN ISO 898-1, that indicates steels that are less susceptible to hydrogen embrittlement.

The general result of these changes would be that uncoated 10.9 bolts could not be purchased 'off the shelf' from a stockist for surface coating; only by special order or from a supplier with approved stock.

Research [(6)] carried out in Germany during the 1990's established that different steel compositions, in the carbon and low alloy categories, exhibit failure due to hydrogen embrittlement at different levels of tensile strength. The work showed that by providing 'irreversible traps' in the steel lattice the free movement of the absorbed atomic hydrogen could be reduced and with it the effects of hydrogen embrittlement.

The material used for manufacture of the bolts must be agreed (with the purchaser); the steel would need to meet the following requirements to reduce the effect of Hydrogen Embrittlement:

a) Have high ductility at high levels of tensile strength.

b) Have high hardenability to ensure 'through' hardening of the bolt cross section.

c) Have a high tempering temperature to achieve the required tensile strength.

d) Produce high levels of Cementite/Ferrite interfaces; these produce irreversible ‘traps’ which prevent movement of the atomic hydrogen.

The result of these requirements is that 10.9 bolts will need to be manufactured from more highly alloyed steels, than are currently used, which are more expensive.

When BS EN ISO4042:2018 was published by BSI, the fastener technical committee FME9 (which had voted against the adoption of the original ISO4042:2018) agreed to include in the standard a National Foreword that set out the United Kingdom’s objections to the revision. The technical committee FME9 recommended that regardless of the changes in BS EN ISO4042:2018 that all electroplated 10.9 bolts should be hydrogen de-embrittled.

The BCSA model specification makes the avoidance of hydrogen embrittlement a requirement of all surface coated property class 10.9 bolts.

Conclusion

The following recommendations are given to reduce the risk of hydrogen embrittlement in structural applications:

1. Avoid the use of any bolting assemblies that use bolts of property class 12.9 or above; have been surface hardened or work hardened and not stress relieved.
2. Choose processes to produce and surface coat fasteners that do not involve the generation of atomic hydrogen.
3. Ensure that the design of the connections of a structure does not put high tensile strength bolting assemblies into areas where water or other electrolytes are allowed to collect and remain.
4. Remember that self-coloured fasteners are susceptible to hydrogen embrittlement as well as those that have been surface coated.

5. Use structural bolting assemblies from approved suppliers and to specifications such as the BCSA model specification, which are designed to reduce the risk of hydrogen embrittlement. The National Structural Steelwork Specification for Building Construction 7th Edition makes the use of bolting assemblies to the BCSA model specification mandatory.

References

1. BS EN ISO 898-1 - **Mechanical properties of fasteners made of carbon steel and alloy steel** Part 1: Bolts, screws, and studs with specified property classes - Coarse thread and fine pitch thread (ISO898-1).

2. BS EN ISO 4042 - **Fasteners - Electroplated coating systems.**

3. BS 7371-1 - **Coatings on metal fasteners –** Part 1: Specification for general requirements and selection guidelines.

4. BCSA model specification - **BCSA MODEL SPECIFICATION for the PURCHASE of STRUCTURAL BOLTING ASSEMBLIES and HOLDING DOWN BOLTS**.

5. ISO / TR 20491 – **Fasteners** Fundamentals of hydrogen embrittlement in steel fasteners.

6. **Hydrogen – induced brittle fractures of screw joints** – Causes, influences, remedial measures. Prof. Dr. – Ing, K. H. Kloos VDI, Dipl. – Ing. St. Beyer and Dipl. – Ing. R. Landgrebe VDI, Darmstadt.

BSI translation – BSI Doc No 91/71636.