NUTS & BOLTS

VOLUME 18
FALL 2002

NH Materials Laboratory • Somersworth, NH • 800-334-5432 • 603-692-4110 • Fax 603-692-4008

Hydrogen in Metals

Background

If you are a user of metals that are strong but not very tough, or maybe you have had some parts break and are contemplating changing to a stronger alloy, then you need to know that hydrogen in the metal can bite you. If you take to heart the information in this Nuts and Bolts series then just maybe you won't be bitten.

Where does the Hydrogen Problem Start?

Like any metal, hydrogen atoms dissolved in liquid or solid metal give up their valence electrons most of the time.

That leaves only the nucleus of the hydrogen atom, and that's very, very, small! However, like any metal, for a fraction of the time they reacquire their valence electrons, making them more or less the same size as ordinary metal atoms. It is while they are very small that they are able to zip around inside the metal.

While inside the metal the traveling hydrogen atoms find lots of different ways to spend their time. If there is a crystal defect that offers a little more space, then the hydrogen atoms will spend more time there than in the ordinary spaces. If there is an area with tensile residual stress they will spend more time there than in metal that is unstressed. They are probably rather reluctant to hang around anyplace that is under serious residual compressive stress, as in a carburized or nitrided layer.

Once hydrogen (H^1) atoms start to hang out in a particular area they become more likely meet like minded atoms and to join up to become hydrogen molecules (H_2). That's trouble because the H_2 molecules are more or less the same size as a regular metal atom. When they form they expand the crystal lattice, creating a tiny tensile stress field. This tensile stress is like sugar for flies, drawing more H^1 atoms together where they form more H_2. The tensile stress field grows, causes micro cracking, the mechanical properties start to suffer, in particular fracture toughness and high cycle fatigue strength.

Biaxial tension is worse than uniaxial, and triaxial tension is worst of all...

Herein lies the problem for strong metals vs ordinary metals. In the more ductile metals the crystals can deform to accommodate the insertion of a cluster of H_2 molecules.

The microscopic tensile stress field is relieved so more hydrogen atoms aren't drawn in and microcracking is avoided. In the stronger and less ductile metals the opposites are true: more hydrogen atoms are drawn in and microcracking gets started.

Metallurgical research is showing us that the wandering H^1 atoms may also enter into reactions, to form, for example, metal hydrides. When the metal that is joining the hydrogen is an impurity, then wherever the impurity atoms tend to hang out is where we expect to find the metal hydride molecules.

Now the metal hydride may or may not be a larger molecule than the constituents from which it formed. If it's larger, then it can rupture the crystal lattice the same way as the coupling up of the H^1 atoms that was described above. Apparently some of the well known bad actors among impurity atoms do their dirt by entering into this type of hydride reaction.

When an impurity atom tends to hang out in the grain boundaries it may be reasonably benign until along come some hydrogen atoms when it forms hydrides. Grain boundary embrittlement may be the result, giving us deadly intergranular cleavage fractures.

Room Temperature Sources of Hydrogen

Chemical reactions that release hydrogen at the surface are the problem.

Chemical reactions release their hydrogens as atoms: H^1. If the atom joins a friend and wanders off into the air as an H_2 molecule, that's no problem. Or it may grab an oxygen and then another hydrogen to make a water molecule, and also wander off into space.

The problem, as before, is the extremely small size of the newly released H^1. To this tiny creature, a piece of metal looks just like empty space! So the probability of the H^1 entering the metal is nearly as high as the probability of its wandering off into space! That's the source of low temperature hydrogen.

All steels can pick up hydrogen through these processes:

Rusting The rusting reaction releases H^1 and all steels will pick up their share of the hydrogen.

Electroplating Many kinds of electroplating release H^1 at the surface along with metal being deposited.

Acid Pickling introduces H^1.

Tumbling in wet media may introduce H^1.

Electrochemical Corrosion can inject H^1 at the anodic area.

Soldering and brazing fluxes may introduce H^1.

Which ones tend to get into trouble?

Any steel having tensile strength over about 130,000 psi or hardness in excess of about HRC 35 is at risk for hydrogen cracking.

If there is continuing tensile stress from any source then brittle fracture is likely in the tensile zones. The residual stress problems include tensile stress area around welds, heat treating stress, solidification stress in castings, and residual stress following straightening.

Hydrogen in an application that continuously applies tensile elastic stress can also lead to brittle fracture. These include centrifugal stress at the center of a steam turbine rotor, and a high strength bolt that has been torqued well up in its range, and a bolt that was supposed to be squarely seated when it was actually seated on a tapered surface.

The logic that has grown up around high strength bolts is worth considering. Inside the transmission of your car there are some high strength bolts and other parts that are very highly stressed. These parts are meticulously fabricated to avoid picking up hydrogen and throughout their lives they operate in a corrosion-free environment.

Look out if you neglect your transmission seals! The first water to get in is sequestered by the oil additives. The next water to get in starts rusting... Hydrogen embrittlement will soon reward you with a trashed transmission!

Long experience has shown the world that in ordinary environments bolts over about HRC 35 are unreliable. Why? Hydrogen introduced by rusting.

Why are pipelines so successful when the steels have moderately high strength and there is lots of residual stress from settling, frost heaves, thermal stress and pressure stress? ***Two answers:***

- absolutely continuous barrier coatings that are regularly checked for conductivity to ground and
- continuous galvanic protection with the voltage and current regularly monitored.

The back hoe operator that accidently tears up a patch of a pipeline's coating doesn't get to see the excitement. The failure is delayed until rusting starts and hydrogen gets into the steel. Maybe a few weeks later; maybe a few months later, there is a hydrogen embrittlement failure...

Hydrogen from Liquid Metals

A metal's solubility for hydrogen increases strongly with temperature, as shown in figure 1.

While the metal is liquid, as in either molten metal for a casting or a weld fillet or a braze filler metal, the metal can hold a lot of hydrogen in solution.

But look at room temperature on the graph. We've gone from a lot of dissolved hydrogen at high temperatures to mighty little at room temperature.

As the metal cools, all that hydrogen has to go somewhere. Most of it escapes to the outside world where it joins oxygen and falls back to earth in the next rain storm. What's stays behind inside the metal is more than the metal can hold so it starts doing all of the bad things mentioned above.

Rusty metal is the biggest source of hydrogen in ferrous castings and welds. Red rust is not iron oxide. (Now that's a surprise, isn't it.) It is hydrated basic iron oxide. For every molecule of iron oxide there may be a hydroxyl and several molecules of water—and that water's bound! It's not like a wet rag that dries out at room temperature. This bound water doesn't escape until the temperature is raised very, very high. At the elevated temperature, when the rust molecule starts to break down into iron oxide and water etc, some fraction of the newly released hydrogen goes into the metal where it is happy to stay thanks to the hydrogen's higher solubility limit at the higher temperature.

Managing Hydrogen in Castings

1. **Master Alloy Ingots** The foundry purchases certified master alloy ingots that are then melted to obtain metal for the castings. Rust and dirt on the master alloy ingots introduce moisture into the metal.

✓ Are the master alloy ingots always kept indoors, under protective cover?
✓ Are they kept from rusting?
✓ Are they kept free from dirt?

If there is any hydrogen already dissolved in the master alloy ingots it will be carried into the final casting. This can be a problem with master alloy ingots that originate with eastern block and third world countries. Discuss with the foundry how to write into your purchase specification assurances that purchased master ingots are hydrogen free.

2. Remelts, Sprues, Risers and Rejected Castings are often remelted. Expect significantly higher expense if you elect not to allow remelts. If remelt is allowed:

✓ Does the foundry maintain strict segregation of the different alloy remelt stock?

✓ Is the remelt stock is kept free from rust and is thoroughly clean before going into the melt?

If the foundry practices remelt on some castings however not on yours, check on how effectively the melt floor workmen are informed that there is to be no remelt in your heats.

3. Finished Castings If the castings are allowed to rust or become dirty before going to heat treatment then they will absorb the hydrogen during heat treatment.

✓ Are castings kept indoors, under cover, and are they kept free from the opportunity to either rust or accumulate dirt?

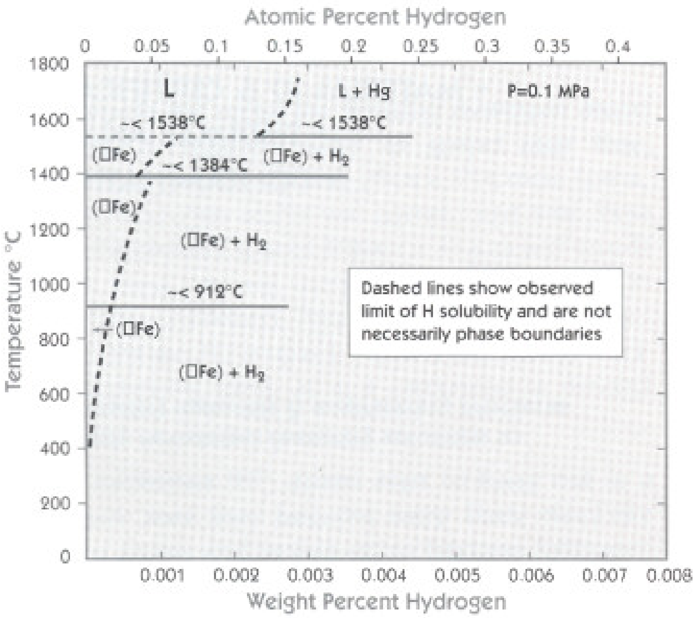

FIGURE 1: Solubility for hydrogen increases strongly with temperature

4. Grit Blast and Wheelabrator No matter how minor, moisture, rust or dirt in the blasting media will introduce hydrogen into the castings.

✓ What are the foundry's standards for maintaining cleanliness of their blasting media?

Moisture deliberately added to blasting media increases the throughput. If the foundry has both "wet" and "dry" machines check on how they insure that your castings do not get cleaned in a "wet" machine.

5. Moisture in Refractories Over a weekend and during any idle time the refractory linings of the melting and pouring crucibles will pick up moisture. That moisture is quickly transferred to the metal in the first few melts of the day. To drive out the moisture all of the crucibles are preheated for an extended time, using either a gas flame or a high temperature oven. For example, on Monday morning it is not uncommon for the drying to start around 6 AM if melting and pouring are to commence at 8:00.

✓ Are all refractories that contact the molten metal thoroughly heated prior to the first pour?

✓ Are crucibles covered so they remain hot during idle times during the day, such as lunch break?

6. Moisture on Tools Rust and oxidation on the various tools that come into contact with the liquid metal will pick up moisture and introduce hydrogen into the melt.

✓ Is there is a small, gas fired furnace on the foundry floor into which the working ends of all tools are placed at all times when not actually in use? Preheat of these tools usually starts at the same time as preheat of the crucibles.

✓ During the day are these tools are never laid down but actually put into the furnace.?

A Buyer of Castings Has Work to Do

From time to time you will need to review your foundry's practices. It is not uncommon to find that after your specifications and their foundry practice have achieved satisfactory levels a visit by the buyer about three times a year is enough to keep everything on track. This coordination between buyer and foundry is indispensable when purchasing high strength and high alloy castings.

The culture of heat treating shops is similar to that of foundries so that the same sort of high level coordination is essential.

You cannot "pass off" the continuing coordination with the foundry to a third party so I suggest you become involved right from the start!

The Hydrogen Bakeout

After any operation that has introduced hydrogen into a hard steel it is downright frightening to listen to an acoustic emission microphone on the surface. The microphone chatters away for several days!

Part of those noise emissions are from microcracking. Don't ever forget that! It is absolutely essential that the part be put into the hydrogen bakeout oven directly from the operation that introduced the hydrogen. Delays measured only in minutes can severely hurt a part's fatigue strength. Short of hipping, there's no way to turn back the clock and close the microcracks.

Why does the hydrogen bakeout work sometimes and not others? Probably through a combination of breaking down the metal hydrides so their hydrogen can escape, and by relieving the stress fields around various crystal defects. However, even at best, the hydrogen bakeout cannot get the hydrogen level low enough to restore the metal's full reliability. Best to not let the hydrogen get in.

Can We Help You?

Name __________
Title __________
Company __________
Address __________
City, State __________
Zip Code __________
Phone __________
E-mail __________

Please call me, I have questions ____
Send info on: Lab Services ____
Failure Analysis ____
Mechanical Testing ____
Please take me off your mailing list ____

Complete this information and FAX it to 603-692-4008

Everything you ever wanted to know about...

Hydrogen Embrittlement

CALL OUR HELP LINE
800-334-5432

- LABORATORY SERVICES
- FAILURE ANALYSIS
- MATERIALS APPLICATIONS
- MECHANICAL TESTING
- CORROSION ID
- METALLOGRAPHY
- MATERIAL ID & CERTIFICATION
- THERMAL ANALYSIS
- CONTAMINATION ID

Contact us at:
www.nhml.com
email: lab@nhml.com
FAX: 603-692-4008

A quarterly newsletter featuring solutions to
manufacturing materials & engineering problems

Nuts & Bolts Publication
NH Materials Laboratory
22 Interstate Drive
Somersworth, NH 03878-1209

Address correction requested