Hydrogen Embrittlement After Surface Treatments

Hana Hrdinová[1(✉)], Viktor Kreibich[1], Jan Kudláček[1], and Jakub Horník[2]

[1] Faculty of Mechanical Engineering, Department of Manufacturing Technology, CTU in Prague, Prague, Czech Republic
Hana.Hrdinova@fs.cvut.cz
[2] Faculty of Mechanical Engineering, Department of Materials Engineering, CTU in Prague, Prague, Czech Republic

Abstract. Metal materials pass through many different manufacturing technologies than are delivered to customers in the form of a finished product. These technologies can improve the properties of the material, but in the wrong choice and the process of execution, the material may be disturbed enough to cause it to be subsequently damaged. In this article we provide results of measurements of increased brittleness of steel materials due to diffused hydrogen formed on the surface of samples in surface treatment technologies by degreasing, pickling and tumbling. To detect hydrogen embrittlement was developed a simple device for cyclic loading of samples, since industrial products are often exposed to stress just this and it is important to be able to embrittlement this quickly and inexpensively detect. The hydrogen embrittlement is very susceptible mainly of high strength steel. These steels are used in the automotive and aerospace industries, so it is necessary to have an idea of how and when the brittleness of these steels occurs in order to prevent to this damage.

Keywords: Hydrogen atom · Cyclic fatigue · Hydrogen embrittlement · Tumbling

1 Introduction

Higher hydrogen content in steels may be due to surface treatment (degreasing, pickling, tumbling), where the treated material comes into contact with the electrolytes. This hydrogen causes a reduction in mechanical properties (especially elongation and notch toughness) in the steel, and also the brittleness of the material. Fragility is a very dangerous kind of breach. This damage with low energy consumption and low plastic deformation expand in the material at a high speed in steel material.

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2 Hydrogen Embrittlement

Hydrogen may be in the steel in a molecular state (H2), atomic (H), as ionic and chemically bonded. Because of its small size, it diffuses very strongly into coatings, pore layers and cracks in the steel surface, especially at low temperatures (−50 °C to 100 °C). Influence of the hydrogen is already evident when the content is over 2 to 3 ml in 100 grams of steel. Hydrogen embrittlement may be reversible or irreversible condition.

In atomic form hydrogen in the metal lattice interstitially dissolved and stably stored in the free interlattice cavities. The solubility of hydrogen in the steel depends on its chemical composition, structure and temperature. There are always large amounts of pores in the surface of steel. In the steels there are a number of defects, inclusions that represent energy-efficient locations on which hydrogen is absorbed. Generated hydrogen in the processing technologies or steel surface treatments mostly changes quickly to molecular and only a small amount of atomic hydrogen penetrates into the steel. Later, this hydrogen is also converted to molecular and it is already immobile due to the dimensional change in the metallic lattice.

Figure 1 shows the dimensions of atomic elements of iron, carbon and hydrogen. Thus, hydrogen in the metal lattice has no problem diffusing between the atoms of iron. The hydrogen atom is only 25 pm in size, the hydrogen ion even only around 0.0009 pm, while the hydrogen molecule has a size of about 202 pm. Molecular hydrogen has a much larger size than atomic hydrogen, developing high pressure on the surrounding material, which causes it to become brittle. At high hydrogen content, if not timely removed, the brittleness occurs irreversible. This is dangerous because the steel is damaged even at a lower stress than its strength limit [1, 2].

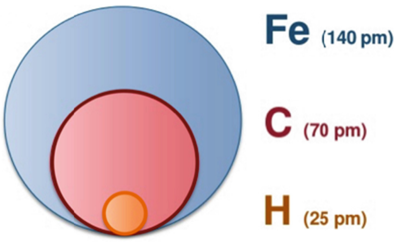

Fig. 1. Dimensions of atomic sizes of iron, carbon and hydrogen elements [11]

Hydrogen produced at normal temperatures in electrolysis at cathode reduction (degreasing, plating) or dissolving in the electrolyte (pickling). In both of these processes, hydrogen is present in the solutions as a hydrated ion. Hydrogen takes the electron out of the cathode and the hydroxide ion decomposes to water and hydrogen.

This reaction can be described as follows:

- in acidic environment : $2\,H_3O^+ + 2e^- \rightarrow H^2 + 2\,H_2O$
- in an alkaline environment : $2\,H_2O + 2e^- \rightarrow H^2 + 2\,OH^-$

Hydrogen may be present in the metals already in the manufacturing process, for example by casting, where the formed liquid contains H and, in the case of recrystallization from the melt into the solid structure, remains in this structure. Furthermore, hydrogen can be brought into the welding metal where the most frequent source of hydrogen is atmospheric humidity or moisture from the electrodes.

In order to avoid the brittleness of steel by the influence of hydrogen, heat treatment of steel (annealing) can be used at 180 °C to 200 °C. At these temperatures, the movement of atoms in the lattice increases towards less resistance, i.e. out of the material. The annealing must be conducted immediately after the operation, which occurred Hydrogen charging, to prevent the creation of hydrogen molecules, which can no longer be removed thermally. Thermal treatment is carried out in accordance with a valid and prescribed standard (ISO/DIN 9588 or ASTM F1940–017a(2014)) [3, 11, 12].

3 Hydrogen Corrosion

The difference between hydrogen corrosion and hydrogen brittleness is at the temperature at which this material damage occurs. As the temperature rises, the rate of hydrogen permeation is increased, there is no increase in the risk of damage from the accumulation of hydrogen in the defects and irregularities of the structure. Above 170 °C no hydrogen embrittlement was detected, the hydrogen molecules at this temperature were released from the defects and again dissolved in the metal in the hydrogen atoms.

Higher temperatures and elevated pressures give rise to other danger, resulting in a significant loss of ductility and metal strength.

$$8H + C + Fe_3C = 2CH_4 + 3Fe\ [6]$$

Methane molecules are too large, they are incapable of diffusing metal. A high increase of methane in the steel results in intergranular cracks and blisters. This form of damage often resembles the formation of blisters at low temperatures. Material decarburization (decarburized perlite) causes a reduction in ductility and tensile strength. The opposite carbonization process also occurs with a hydrocarbon mixture occurring in oil refining operations [6].

In hydrogen corrosion, metal is not attacked by hydrogen from the surface but inside of the material, the breakdown of the metal does not interfere with the same depths everywhere, but the depth depends on the thickness of the wall.

At atmospheric pressure, the steel begins to decarburize at temperatures of 540–600 °C. Carbon has a large effect on the mechanical properties of steel such as hardness and strength. The decarburization reduces these properties but, on the contrary, increases the toughness of the material [10].

4 Diffusion of Hydrogen into Steel

The diffusion of hydrogen into steels can be classified as diffusion from the gas phase into the solid phase. In surface treatment processes, the base material is metal. Metals consist of atoms that occupy the structure of the lattice in the solid state. The diffusion of a new element into this structure depends on the size of this element. If the element has a small dimension, it can take a position between the lattice or interstitial. If the radius of the new element is equal to or larger than the base material, it loses its ability to move within the lattice space. The smallest atomic radius has hydrogen (see Fig. 1). For this reason, it is very easy to enter the lattice of most elements. Mathematically, the first general law of Fick can determine this diffusion phenomenon (1).

$$\frac{dN}{dt} = -DS\frac{dc}{dx} \tag{1}$$

The formula describes the amount of substance passing through the surface S per unit of time $\frac{dN}{dt}$ is proportional to the diffusion coefficient D and the concentration gradient $\frac{dc}{dx}$. The diffusion coefficient can be expressed using the Arrhein equation.

$$D = D_0 \,.\, e^{-\frac{Q}{RT}} \tag{2}$$

D_0 – constant depending on the nature of the substance but independent of temperature ($cm^2\ s^{-1}$)
R – universal gas constant (8314,3 J $mol^{-1}\ K^{-1}$)
Q – the activation energy of the diffusion (J mol^{-1})
T – absolute temperature (K)

The diffusion of hydrogen into the metal material is a negative diffusion because it moves atoms from sites of lower chemical concentration that penetrate into places with higher chemical concentration.

Hydrogen diffuses into steels under two conditions: a large number of hydrogen atoms must be present on the surface of the metal, as well as the constant development of new hydrogen ions during electrolysis. A second condition is that the metal surface is devoid of the ability to connect hydrogen atoms to molecules and the ability to hydrogen diffusion metal.

The rate of diffusion of hydrogen into steels is mainly due to the concentration of atoms at the surface of the steel and the time in the steel material processing environment. Concentration on the metal surface is the result of the rate of release of hydrogen atoms, that is, the rate of their conversion to molecules and the rate of penetration into the metal surface. The more the electrolysis takes place, the more hydrogen atoms occur. The formation of hydrogen atoms affects the temperature of the electrolyte, the concentration of the solutions, the intensity of the current and the properties of the metal surface: composition, purity, surface roughness.

The diffused hydrogen velocity in steel depends on the steel condition, if steel annealing has not been carried out after cold forming or after welding, hydrogen penetrates into steel more easily. Hydrogen also penetrates into annealed steels, much more slowly, larger gaps that facilitate hydrogen movement occur only at the grain boundaries [1, 4] (Fig. 2).

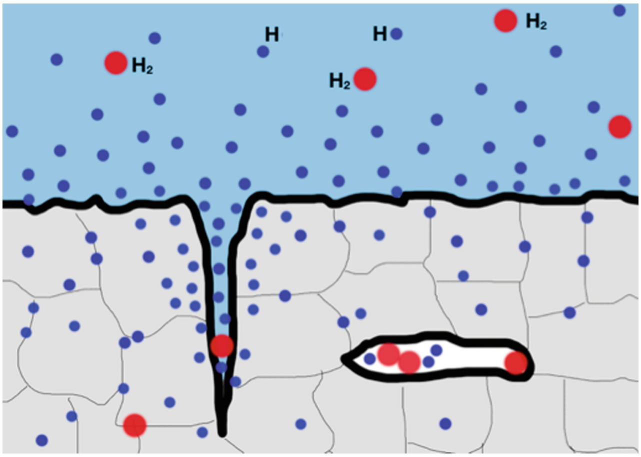

Fig. 2. Scheme diffusion of hydrogen into the metal material defects [4]

Hydrogen diffusing in the metal finds a grid error (interstellar, crack, cavity), gradually the atoms enter this disorder and begin to accumulate or form hydrogen molecules. These molecules act on the surrounding metal lattice with high pressures (10–100 thousand Pa) and can completely disrupt the coherence of the material [1, 2].

5 Choosing the Right Material

Choosing the right material can easily avoid problems caused by hydrogen and thus save the cost of future product replacement or repair. It is necessary to take into account the three main factors that need to be taken into account when selecting material:

- chemical composition of the material
- mechanical properties of the material
- microstructure of the material

Chemical Composition of the Material
When choosing a suitable material is necessary to know the composition of the material and requirement of preventing diffusion of hydrogen into the material should be selected material without contamination the grain boundaries sulfur, phosphorus, arsenic and tin. These elements increase the susceptibility to hydrogen attack [1, 7, 8].

Mechanical Properties of the Material

Mechanical properties, in particular the strength of the material, can significantly affect the potential for hydrogen attack. The resistance of steels to hydrogen brittleness decreases with the increasing strength of the material. High-strength steels are the least resistant, have a strength greater than 1400 MPa. More resistant steel to hydrogen brittleness are steel with a strength less than 700 MPa [1, 7].

Microstructure of the Material

The least resistant steel to the microstructure of hydrogen is the steel with a martensitic undisturbed structure. In the following order, they are Bainitic undisturbed, ferriotioperlitic, bainitic, and finally martensitic. The reason for this order may be untempered structures with local high hydrogen content. There is also a higher level of internal stress in these areas [1, 2].

6 Choosing the Right Material

Measures to Eliminate the Causes of Hydrogen Brittleness

- polarity change during electrolytic degreasing
- replacement of electrolytic degreasing by ultrasonic cleaning
- shortening the pickling time
- electrolyte change in galvanotechnics
- more suitable surface treatment technologies without the risk of hydrogen damage
- removing hydrogen from the surface during the surface treatment process
- moving the product in the electrolyte
- using lesser strength material
- by removing the stress concentration in the material
- the use of inhibitors [5]

7 Testing of Hydrogen Charging After Surface Treatments

Due to the severity of the possible hydrogen charging, it is necessary to have the equipment for a quick and easy test to check the condition of the material. For this reason was developer at the Faculty of Mechanical Engineering, CTU in Prague Equipment for cyclic loading (PCN, Fig. 3). It is possible to carry out a fatigue test of samples (e.g. retaining ring DIN 472), which are subjected to cyclic stress after the hydrogen charging. During the testing and verification of this methodology, a number of dependencies and findings on the brittleness of the material were confirmed, based on the number of cycles observed in the destruction of samples at cyclically defined stress.

In this presentation of the results and in particular the possibilities of this methodology are given examples, dependence on verification of the influence of tumbling and pickling on the steel hydrogen charging, respectively. to decrease the number of cycles of the test samples by cyclic loading.

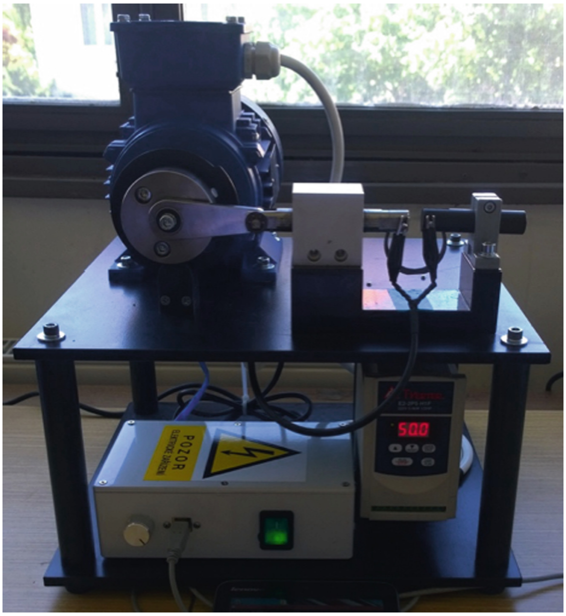

Fig. 3. Equipment for cyclic loading (PCN)

Samples into PCN are retaining rings DIN 472, Ø 40 × 2 in the raw state. These samples have been chosen because of the appropriate shape and possible dimensional variability. The PCN can be simply mounted and are also suited to the tumbling device. The strength of the samples is 990 MPa (Table 1 and Fig. 4).

Table 1. Chemical composition of test samples in %

Fe	Mn	Si	P	S	Al	Cr
92,49	0,59	4,47	0,141	0,012	2,1	0,19

Fig. 4. Samples – retaining rings DIN 472

8 Hydrogen Charging in the Tumbling Process

Tumbling in a circular vibratory tumbling machine manufactured by Rösler carried out verification Hydrogen charging material in the surface treatment. Tumbling is a chemical-mechanical process for surface treatment of the material where the grinding bodies (ceramic rollers) and the samples are placed in a relative movement in the working vessel. This surface treatment technology is used to remove burrs, grease and impurities from the surface of the metal. The surface of the product has a uniform roughness, or the use of suitable tumbling bodies and compounds create a mirror surface of the material.

During process of tumbling were used compounds from Pragochema, s.r.o., which are listed in Table 2.

Table 2. Composition of compounds

Compound	Composition
Pragopol 809	Diethanolamide cocoic acid, citric acid
Pragopol 812	Sulfuric acid, ethoxylated coconut amin
Pragopol 520	Sodium tetraborate, pentahydrate, trisodium decahydrate phosphate

Tumbling were always 30 samples, which were taken every 10 samples after tumbling times 60, 120 and 180 min. The samples were treated by demineralized water and protected against oxidation by the inhibitor. Subsequently, they were dried and tested using the PCN. The measurement results are shown in Table 3 as the average of 10 measurements.

Table 3. Measurement of the degree of influence compounds of Hydrogen charging (different tumbling time)

Tumbling time [min]	Raw state	Pragopol 809	Pragopol 812	Pragopol 520
60	11168	9433	8827	9879
120	11168	9178	7573	9789
180	11168	9127	7369	9573

From the results it can be seen that in the chemical-mechanical treatment by tumbling, the steel can be hydrogen charged using acidic compound. Compound Pragopol 812 contains a larger amount of sulfuric acid, this compound is not suitable for tumbling of higher strength steel. After this treatment it is necessary to use annealing to remove hydrogen from steel.

9 Hydrogen Charging During Pickling

Steel pickling is very often used as a surface pretreatment for removing oxide layers, corrosion and corrosion before galvanic deposition of metals, galvanizing and mechanical treatment. The pickling is normally carried out in sulfuric acid or hydrochloric acid. With this technology atomic hydrogen is formed on the surface of the metal. To prevent the diffusion of this hydrogen into the metal surface, pickling inhibitors are used. This prevents the action of acid on the stained material and the penetration of hydrogen into the metal.

The same samples as for tumbling were used to verify hydrogen formation in the HCl pickling process. Staining in 15% hydrochloric acid for 20 min did preparation of samples for measurement. In addition, the effect of the inhibitor on limiting the entry of hydrogen into the metal was verified. For better comparison of inhibitor activity, Pragolod AC 202 was added to 15% HCl in varying amounts of 1, 5 and 10%. Table 4 lists are the average of 10 measurements.

Table 4. Comparison of number of cycles to sample damage after pickling process

Raw state	15% HCl	15% HCL + 1% AC202	15% HCL + 5% AC202	15% HCL + 10% AC202
11101	3786	8873	9619	9480

According to the test results, the effect of the Inhibitor 202 on the hydrogen charge of the material is very pronounced. Samples in the raw state crack at an average of 11,000 cycles. After 20 min of pickling in 15% HCl, the material after cyclic stress cracked around 3780 cycles (35% of the raw state). Applying of inhibitor AC202 in 1% to HCl samples is cracked at 8800 cycles, and the inhibitor even increased the number of cycles in such a small amount. Using a 5% inhibitor, the number of cycles gradually increased.

10 Conclusions

Hydrogen embrittlement is very dangerous material damage that is not noticeable to the visual inspection and can occur after inclusion of finished products in common use. This paper presents the results of measuring the possibility of hydrogen charging in two different surface treatments. The first surface treatment was the chemical-mechanical cleaning of the surface in various compounds in the tumbling machine. The second treatment was chemical cleaning of surfaces by pickling in hydrochloric acid. Tumbling technology has been used to determine whether hydrogen can be produced and subsequently diffuse into the surface of samples when moving specimens with tumbling bodies and compounds. The formation of hydrogen was confirmed on the technology of surface treatment, which is often used for small products (screws, nuts).

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