Hydrogen Embrittlement of Spring Steel

This article reviews the physical metallurgy of hydrogen embrittlement of spring steel and discusses mitigation methods.

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Hydrogen embrittlement has been the cause of many unexpected failures of springs. Springs are frequently fabricated from high strength steels in order to avoid permanent deformation in service. These steels are also frequently plated for corrosion protection. Unfortunately, these high-strength steels are particularly susceptible to hydrogen embrittlement and require special processing to avoid failure.

Hydrogen Embrittlement

A typical failure of an electroplated steel spring caused by hydrogen embrittlement is a delayed, brittle failure. The classic hydrogen embrittlement failure occurs at some time after the spring is loaded. A spring is installed during assembly and a broken spring is found the next day or several hours later. In hydrogen embrittlement failures, there is always a time delay between loading the spring and the failure, even if only a second. Visual inspection of the broken spring shows no plastic deformation. An examination of the fracture surface reveals a brittle fracture with no signs of ductility. The higher the loading on the spring, the shorter the time to failure.

Hydrogen embrittlement failures occur only in the presence of the following three criteria (**Figure 1**). First there must be a source of hydrogen (acids and plating solutions). Second, the steel must be susceptible to hydrogen embrittlement. Higher strength steels are more susceptible to hydrogen embrittlement. And third, the spring must be stressed. This stress may be due to applied stress as well as residual stress.

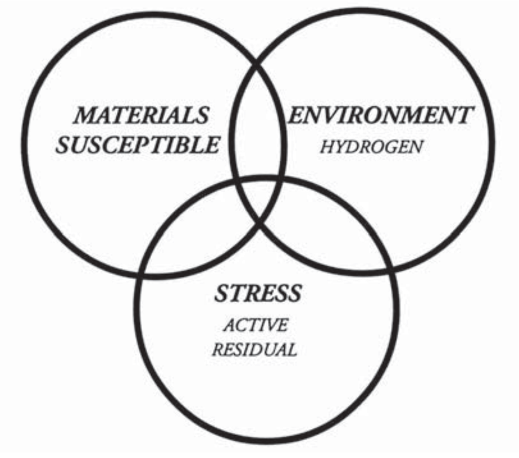

Fig. 1 — The requirements for hydrogen embrittlement of spring steel.

Hydrogen embrittlement occurs by a sequence of events that lead to the failure:

- Hydrogen absorption by the steel spring.
- Hydrogen diffusion to high stress regions in the steel spring.
- Hydrogen segregation to microstructural traps (grain boundaries).
- Hydrogen concentration at the traps reach a critical value.

Hydrogen Absorption

In hydrogen embrittlement failures, the source of the hydrogen is from the manufacturing process. For electroplated springs, hydrogen is available during acid cleaning and electroplating. During acid cleaning, iron is dissolved as iron ions in the acid as the anodic reaction. Hydrogen gas is evolved in a two step cathodic process:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \qquad \text{anodic reaction}$$

$$2H+ + 2e^{-} \rightarrow \boldsymbol{2H} \rightarrow H_2 \qquad \text{cathodic reaction}$$

During the cathodic reaction, nascent hydrogen (H) atoms are formed on the steel surface. Two of these atoms must then join to form an H_2 molecule. These H_2 molecules will then join together to nucleate hydrogen gas bubbles. It takes some time for the nascent hydrogen to form an H_2 molecule. During this time some of the nascent hydrogen will be absorbed by the steel. The total quantity of hydrogen absorbed by the steel depends on the time in acid cleaning and the chemistry of the acid. The hydrogen generated during acid cleaning has a very high effective gas pressure and can cause the absorption of significant quantities just below the steel surface.

After acid cleaning, the spring is electroplated to provide corrosion protection. During electroplating, the metal (Zn, Cr, and Cd) ions in the plating bath are deposited onto the steel surface by a cathodic reaction:

$$Zn+2 + 2e^{-} \rightarrow Zn \qquad \text{cathodic plating reaction}$$

However, because the plating process is not 100% efficient, some hydrogen is also plated out along with the metal:

$$2H+ + 2e^{-} \rightarrow \boldsymbol{2H} \rightarrow H_2 \qquad \text{cathodic reaction during plating}$$

This hydrogen can also be absorbed by the steel as well as trapped within the electroplated coating. Similar hydrogen generation and absorption occur during electroless plating as well as conversion coating processes.

Hydrogen Diffusion

After hydrogen has been absorbed into the steel to form the hydrogen— iron solid solution—the hydrogen atoms can diffuse within the solid steel. Hydrogen dissolves in the steel as H atoms not H_2 molecules. Since the hydrogen atom is slightly larger than the interstitial site that it occupies (i.e., a positive partial molar volume), the hydrogen atom will tend to segregate to regions of high tensile stresses. In fact, the mobile hydrogen will diffuse from great distances within the steel to these highly stressed regions. These highly stressed concentrated regions are created at flaws and inclusions in the steel under the applied load. With time, the concentration of hydrogen increases in these highly stressed regions.

Hydrogen Segregation

Hydrogen also tends to segregate to certain microstructural features in the steel. As discussed above, hydrogen has a positive partial molar volume and wants to find locations that will more easily accommodate its size. These microstructural features are typically prior austenite grain boundaries, martensite/carbide boundaries or other interfaces. The segregation to these traps increases with time as the hydrogen atoms diffuse through the steel lattice to the traps.

Critical Hydrogen Concentration

As discussed above, after a load is applied, hydrogen will diffuse to the highly stressed regions of the spring (i.e., defects, surface flaws and inclusions – any regions that can concentrate the stress). Once the hydrogen is concentrated in these regions, it will segregate to the microstructural features (i.e., traps). The result is an increase in concentration at the traps in the highly stressed regions with time. In fact, the increase in concentration may be many orders of magnitude over the concentration of mobile hydrogen.

Based on the experimental observation of time delayed brittle fracture at prior austenite grain boundaries, it can be assumed that hydrogen has caused the brittle intergranular fracture as seen in **Figure 2**. In fact, hydrogen has segregated to the prior austenite grain boundaries and weakened the boundaries to the extent that the applied stress exceeded the strength of those grain boundaries. **Figure 3** presents a schematic plot of the strength of the boundaries as a function of hydrogen concentration. As presented in **Figure 3**, as the hydrogen content of the grain boundary increases, the strength of the boundary decreases. After a load is applied, the hydrogen concentration in these boundaries increases with time as the hydrogen diffuses to the high stress regions and then segregates to the grain boundaries until the boundary is weaken enough to cause a fracture.

Hydrogen embrittlement failures can also occur in steels that are strengthened by cold work. In these cases, the fracture paths will be quasi-cleavage or other brittle mechanisms.

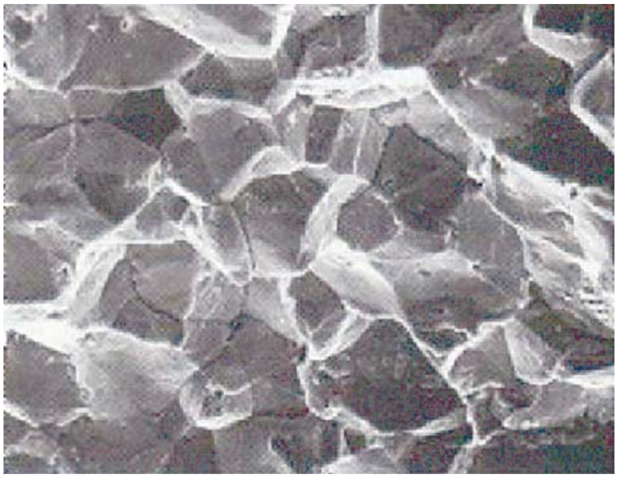

Fig. 2 — Brittle intergranular fracture of hydrogen-embrittled, quenched and tempered steel.

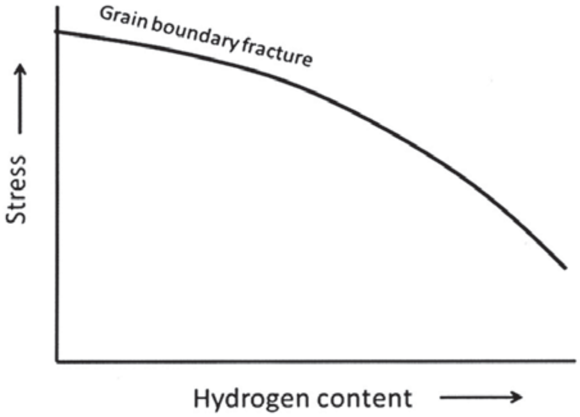

Fig. 3 — The effect of hydrogen content on grain boundary fracture strength.

Mitigation Methods

Hydrogen absorbed during the manufacturing process is the cause of hydrogen embrittlement failures. Therefore, processes that minimize or eliminate hydrogen absorption should be employed whenever possible. A simple process modification is the elimination of acid cleaning or a reduction in the time of immersion during acid cleaning. There are also modifications to the acid solution that may inhibit hydrogen absorption.

The most widely used method to mitigate hydrogen embrittlement in electroplated high-strength steels is a post-plating hydrogen embrittlement relief heat treatment—better known as "baking". This heat treatment is typically specified as 190°C (375°F) for two to 24 hours depending on the size of the part and its hardness. The parts must be given this heat treatment within one hour of plating. The goal of this baking heat treatment is to redistribute the hydrogen uniformly throughout the spring. While some hydrogen may be removed from the steel, much is retained because the plating acts as a barrier to removal.

Immediately after acid cleaning and plating, the hydrogen concentration in the steel is very high just below the steel surface. This 190°C (375°F) heat treatment causes the hydrogen to diffuse throughout the spring, which will bring the concentration near the surface to the much lower average concentration. In addition, this heat treatment will also trap most of the hydrogen at deep traps throughout the spring. This will greatly reduce the quantity of mobile hydrogen, which causes the embrittlement. It is critical that this heat treatment be performed as soon as possible after plating because any residual stresses in the spring will cause the hydrogen near the surface to segregate to the stressed regions associated with any surface defects and cause embrittlement. Due to the local nature of the residual stress, cracks will form, but probably not propagate. Since these new cracks will not be visible beneath the coating, they may lead to failure immediately upon loading or to premature failure in fatigue.

Conclusion

Hydrogen embrittlement is an ever-present concern with plated high-strength steel springs.

However, with the proper fabrication processes and mitigation methods, failures can be eliminated or greatly reduced. **WFTI**

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