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NUTS & BOLTS

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Embrittlement of Steels

This issue of Nuts and Bolts is a wakeup call for our clients that make parts out of hardened steels. Throughout this issue I am referring to only hardened steels. Don't read into this discussion anything about the behavior of any ductile metals.

New steels are becoming available that can enhance the performance of critical parts such as bearings, gear teeth, parts subjected to high and low cycle fatigue, and large parts including turbines and paper mill rolls.

The changeover to the new steels has taken place in steam turbine forgings. My crystal ball says that rolling contact bearings are the next candidates and there are murmurings that some bearings are now being produced from the new steels.

These new steels take advantage of finer grain sizes than ever achieved before in mill quantities and/or lower impurity levels than we could have ever imagined. It has been found that the impurity atoms tend to migrate to the grain boundaries. The finer the grain size the greater the total grain boundary surface and the more "dilute" are the impurity atoms. It is also well established that the higher the strength and hardness, the greater the detrimental effects of the impurity atoms.

Why is embrittlement important?

Perhaps most crucial are its effects on damage tolerance and working stress through decreased impact strength, decreased low cycle fatigue strength, and the rather different phenomena of high cycle fatigue fracture initiation and fatigue fracture propagation. With the new steels we can operate at significantly higher levels of service stress, stress intensity and impact strength.

The performance level of any hardened steel is determined by the stress levels at which cracking commences in the grain boundaries. The cracking starts as either decohesion of the grain boundaries or cracking across or around hard particles in the grain boundaries. More often than not the hard particles are carbides.

How do we describe embrittlement?

One way is via the Izod and Charpy tests that measure the energy to break a notched bar 1 cm square by 10 cm long at a strain rate in the ballpark of 1000 strain units per sec. Higher strain rates interest the military. Higher strain rates also occur during impacts such as railroad wheels impacting across a gap in the track at a switch or crossing. High strain rates include a cam being slammed by a cam follower. Low strain rates include the tensile tests, tests of stress rupture and hardness tests.

It is very important to note that the low strain rates of a hardness test will not detect embrittlement.

What are Temper Embrittlement and Tempered Martensite Embrittlement? They are the embrittlements that are seen after tempering or slowly cooling hardened steels or using them too long within a critical temperature range. The low temperature phenomenon is called "tempered martensite embrittlement" and it is irreversible except by reaustenitizing and repeating the entire heat treating cycle. In a higher temperature band it is called "temper embrittlement". Depending on the steel chemistry there can be one embrittling band or two.

Examples

Consider the "tempered martensite embrittlement" of 4140, figure 2. Because of this embrittlement 4140 cannot be tempered or used in the range 180-500ºC (350-930ºF).

Now consider the same pair of curves for 4340, figures 3 and 4 (pg 3). As before, "tempered martensite embrittlement" occurs in a low temperature range while this time we add "temper embrittlement" in a high temperature range. The high temperature "temper embrittlement" is reversible through appropriate retempering that either redissolves the harmful grain boundary precipitates or disperses the solute atoms that have migrated to the grain boundaries. "Tempered martensite embrittlement" is not reversible.

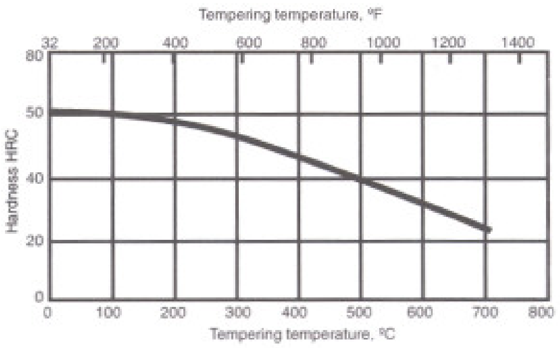

Figure 1. The hardness of 4140 steel following tempering. With the low strain rates of a hardness test the curve drops smoothly with increasing tempering temperature. Ref Metals Handbook, ASM, 9th ed, vol. 1, p469

As shown in figures 1 and 3, hardness varies smoothly through the tempering range however at the higher strain rates of the impact tests there is the unacceptable embrittlement, figures 2 and 4. That's why we have to stay away from tempering in those ranges, and that's why the bands of hardness values and strengths we would expect following tempering in those ranges are, practically speaking, unavailable to the engineer.

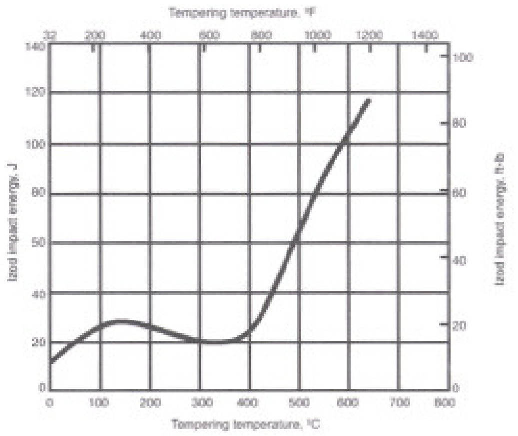

Figure 2. The notch toughness of 4140 steel following tempering. We see the dramatic loss in toughness accompanying tempering in the range spanning 180- 500ºC. Ref Metals Handbook, ASM, 9th ed, vol. 1, p469

Or suppose your bearing or hardened part is subject to soak-back heating to near 375ºC after normal shut down of a gas turbine or emergency shutdown of high temperature processing equipment. Well, these hardened steels can't be used. Too bad because the alternative steels tend to be expensive.

The Trace Elements

The irreversible, low temperature embrittlement is attributable to fracture in the prior austenite grain boundaries. These fractures initiate at grain boundary carbide particles. With these particles present phosphorous, manganese and silicon correlate with increased embrittlement.

Sulfur and phosphorous are the principal contributors to reversible temper embrittlement. Neither can be adequately refined out of the steel so control is through pure melting stock, often made via chemical processes rather than traditional steel making. Sulfur levels of 0.002% are available.

Tin and antimony contribute to embrittlement. They operate through cosegregation with nickel so that low nickel steels are sometimes preferred.

Besides being one of the least expensive contributors to hardenability, manganese contributes to embrittlement. When the sulfur is extremely low there is no longer a necessity for the manganese. However we must look to other alloying elements to enhance hardenability.

Carbon that preferentially diffuses to grain boundaries makes important contributions to grain boundary strength. We must be watchful lest elements such as chromium precipitate carbides in the prior austenite grain boundaries, thereby reducing the amount of available carbon and thereby denying us the beneficial effects of carbon on grain boundary strength.

Molybdenum and vanadium tend to be beneficial to grain boundary strength, apparently by not localizing the carbon atoms the way that chromium does. Additionally, molybdenum is principally responsible for the secondary hardening that we exploit in the tool steels and numerous other high temperature applications for hardened steels.

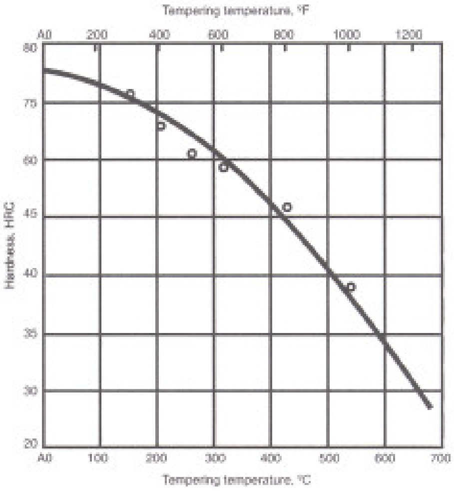

Figure 3. The hardness of 4340 varies smoothly with tempering temperature. Ref Metals Handbook, ASM, 9th ed, vol. 1, p425.

Dissolved hydrogen in hardened steel migrates in response to stress, either applied or residual. Hydrogen works together with the other embrittling elements to cause grain boundary fracture. Low temperature sensitivity to hydrogen is therefore reduced when the other elements are kept at low levels.

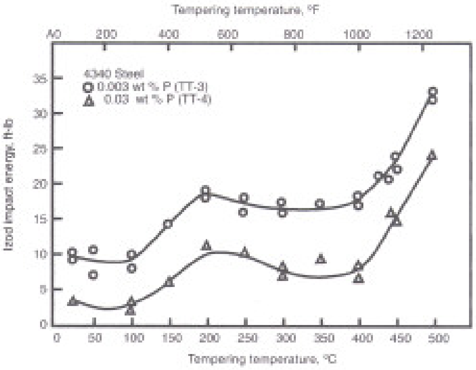

Figure 4. Toughness v Tempering Temperature for 4340 showing the pair of embrittlement ranges as well as the dramatic improvement that comes with 30 ppm phosphorous. Ref. J. P. Materkowski and G. Krauss, Metallurgical Tr. v10A, 1979, p1643

Looking Forward

Keep your eyes and ears open! Just as low phosphorous enhanced the 4340 in figure 4 (pg 3) expect that many more enhancements in the hardened steels will be coming along.

Areas of embrittlement of hardened steels that I will save for another day's discussion include quench embrittlement, liquid metal embrittlement, low temperature embrittlement, weld cracking, and more about hydrogen. Also available if there is a ground swell of requests would be a Nuts and Bolts discussing damage tolerance.

For an excellent overview see C. J. McMahon, Jr., Brittle Fracture of Grain Boundaries, Interface Science 12, 141-146, 2004.

For a review of the metallurgy of steels see G. Kraus, Steels, ASM International, 2005.

Fred Hochgraf
Senior Scientist

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