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Cryotempering: A Novel Method of Improving Properties of Steel

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Cryotempering: A Novel Method of Improving Properties of Steel

Sonal Desai, Ph.D.

COURSE CONTENT

Considering the age and wide uses of steel, it is surprising to many people that there is still much we do not know about it. One of the areas related to steel that we are still acquiring knowledge about is cryogenic tempering. Present content will review what is known about cryogenic tempering and future scope of work. Cryo tempering is a permanent, non-destructive, non-damaging process (not a coating) which reduces abrasive wear (edge dulling), relieves internal stress, minimizes the susceptibility to microcracking due to shock forces, lengthens part life, and increases performance. Cryo treated pieces are also less susceptible to corrosion.

INTRODUCTION

Cryogenics, the science of producing and maintaining low temperatures, had its beginning in the latter half of last century. It is concerned with design and development of cryocoolers that are capable of producing and maintaining low temperature. Some major applications for cryocoolers are

1. Cooling infrared sensors useful in missile guidance, night vision and rescue, atmospheric studies involving ozone hole and green house effect.
2. Commercial purposes such as cryopumps for semiconductor fabrication, superconductors for cellular-phone stations, voltage standards, high-speed computers and process monitoring.
3. Medical purposes like cooling super conducting magnets for MRI systems, SQUID magnetometer for heart and brain studies, Cryogenic catheters and cryosurgery.

Cryogenic tempering takes place in a chamber, where the materials are gradually lowered in temperature. Shallow cryogenic tempering is performed at about -85ºC for 10 hours or so, whereas deep cryogenic tempering takes the material below -185ºC for more than 24 hours. The materials are then slowly raised to room temperature and usually annealed at about 149ºC for several hours. Cryogenic tempering has shown to give the greatest improvement in wear resistance.

Controlled experiments and industry experience have demonstrated that many materials benefit from this treatment. Increased wear life and better corrosion resistance, while at the same time maintaining or even improving toughness have been observed. However, few materials benefit more than tool steels. Tool steels that are deep cryogenically treated will typically last more than 50 % longer than as quenched specimens. In addition, tool steels have been studied extensively to understand the cryogenic phenomena.

1 MARTENSITE FORMATION IN STEEL

The rapid quenching produces a metastable phase in steel called martensite. This transformation process is rapid and diffusionless (i.e. no long distance motion of molecules is required.) To form martensite the steel must initially be in the face center cubic (FCC) form of iron called austenite. To establish austenite in the steel, one typically has to "soak" the steel at temperatures above 750ºC. There is another form of iron called ferrite. If the steel is ferritic, it cannot form martensite.

From the figure 1- phase diagram, plain carbon steel with 0.6% carbon must be heated and "soaked" at about 760ºC to produce austenite. Rapid cooling from this temperature will produce martensite. If the steel was only heated to 700ºC ferrite and iron carbide would be the starting structure. Marteniste cannot be produced from these phases.

The martensite reaction occurs as the FCC austenite transforms to a BCT (body centered tetragonal) martensite. Carbon atoms are trapped in interstitial sites during the rapid transformation. See Figure 2. As the carbon content increases a greater number of carbon atoms are trapped. If the temperature quench is not rapid, stable pearlite, bainite and other constituents can form.

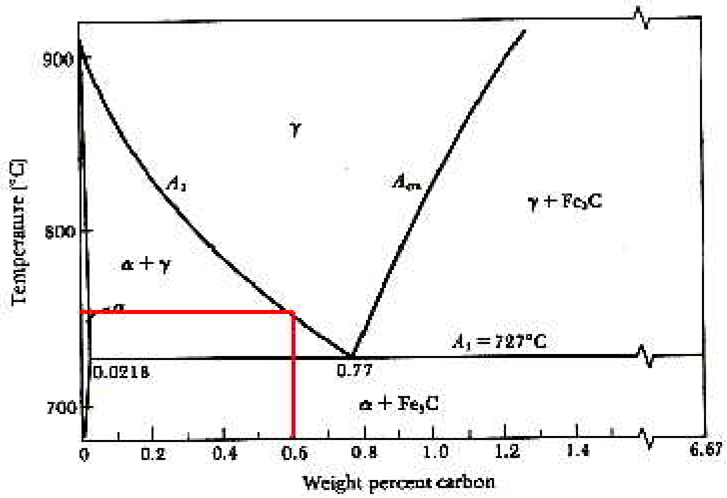

Figure 1. The steel phase diagram.

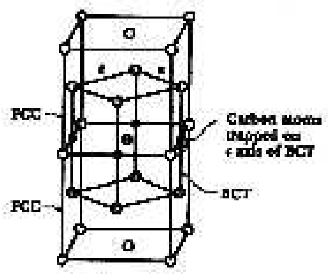

Figure 2. Martensite crystal structure.

As the steel is quenched, the martensite starts to form at a given temperature for the material. This temperature is called the martensite start temperature (Ms). To completely form martensite, the martensite finish temperature must be reached before pearlite and cementite can start to form. This mechanism can be seen on a time-temperature-transformation chart (TTT chart) shown below.

The addition of carbon reduces the temperature at which martensite stops forming as we can see in the above TTT charts. The Mf temperature is the temperature at which 100 percent of the martensite has formed. Mf for 1050 steel (0.5% carbon) is 245ºC, whereas it is 85ºC for 10110 steel (1.1% carbon). The presence of other alloying materials such as manganese, chromium and vanadium tends to reduce the Mf temperature and provides the added benefit of suppressing the formation of pearlite and bainite. The combination of the carbon and the alloying metals can reduce Mf to below room temperature, with no possibility of other constituents forming. The TTT below, for A2, shows this effect.

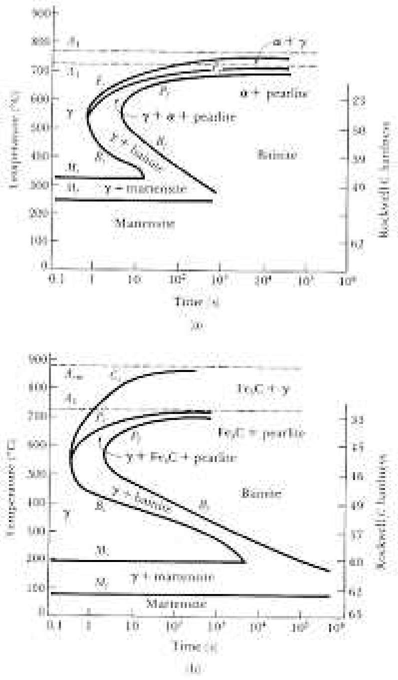

Figure 3. TTT Diagrams for (a) 1050 and (b) 10110 steels

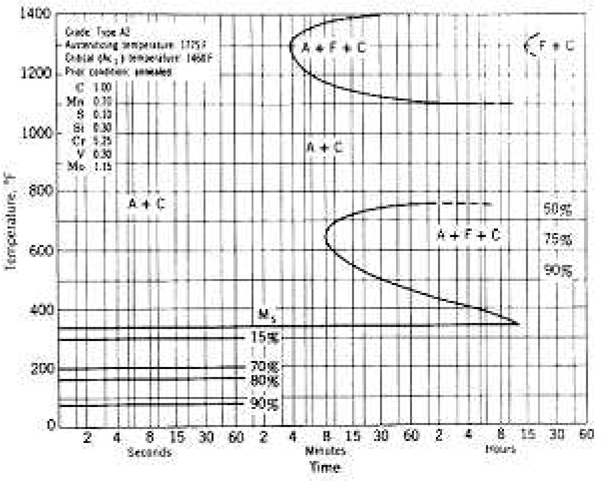

Figure 4. IT diagram for A2 tool steel

The first mechanism of cryogenic tempering: finishing the martensite formation process if Mf is below the final quenching temperature. This mechanism would most likely be found in tool steels as their high carbon and alloy content makes the reduction of the Mf temperature below typical quench temperatures common. However, it would be surprising if this mechanism required temperatures below -101ºC. The change in metal structure after cryogenic tempering of an S7 tool steel is shown in Figure 5.

1.1 The Role of Eta (h) Carbides

It is proposed that the dominant mechanism for enhancing wear in tool steels is eta carbide formation. Their work is experimentally well supported and the analysis of eta carbides was performed with transmission electron microscopy.

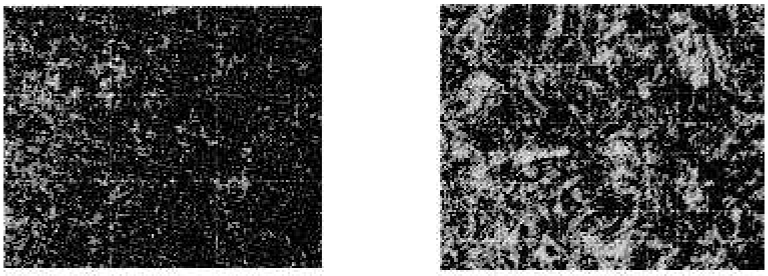

Figure 5. Before and after micrographs of an S7 tool steel. The increased martensitic structure is evident in the after micrograph on the right. Original magnification was 1000x.

Their conclusions, from experiments, were:

1. Finishing the martensite formation process results in a barely measurable improvement in wear resistance.
2. The martensite formation process can be finished with shallow cryogenic treatment (i.e. about -73ºC.)
3. The dominant method of wear reduction is the formation of eta carbides

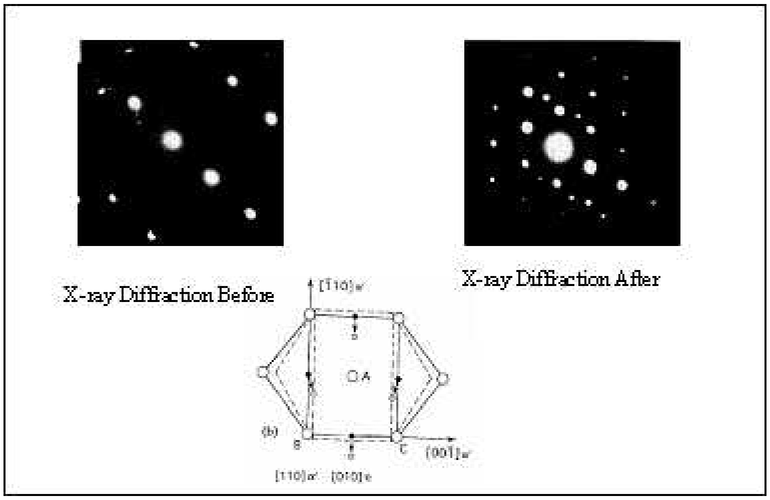

Figure 6. Cryogenic tempering appears to cause a movement of carbon atoms in the steel molecular structure as shown in the diagram. The results are evident in the before and after x-ray diffraction pattern.

Eta carbides actually form a crystal structure intermeshed with the martensite. They can only be seen at the types of magnifications produced in electron microscopy (e.g. > 20,000X) or by using x-ray diffraction. Their formation involves a sub-atomic movement, which is a non-diffusional process understandable at low temperatures. Eta carbides are molecular in size. Figure 6, shows both the eta carbide structure and how it forms and x-ray diffraction patterns before and after eta carbide formation.

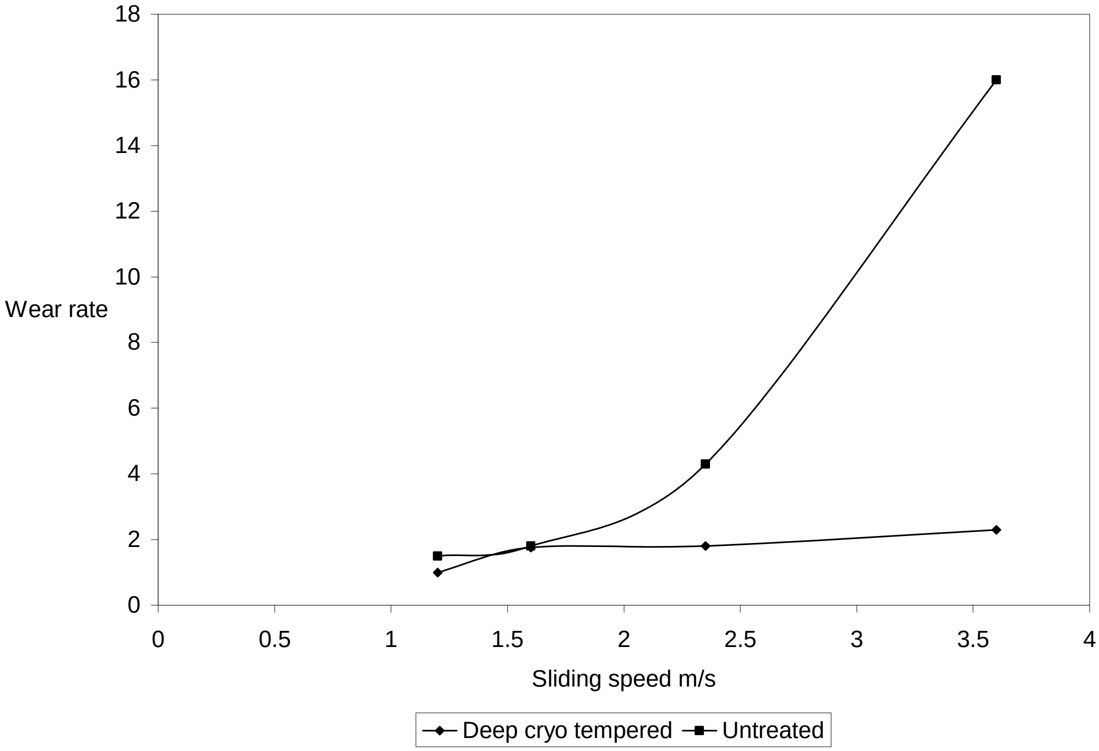

Figure 7. Wear Rate (10^{-5} mm^3 / N m) Sliding Speed. Note that the deep cryo tempered steel has < 1/7th the wear rate of the untreated steel.

1.2 Carbide Particle Formation (Fe3C)

Part of the cryogenic process typically involves tempering after the cold processing. It was proposed that: For higher carbon steels the cryogenic effect is more understandable given the dependence of Ms and Mf temperatures on carbon concentration and potential effects of nucleation of Fe3C on final tempered particle size.

When marteniste is tempered a mixture of ferrite and cementite (Fe3C) is formed. Kramer is suggesting that the cryogenic and tempering processes produce a grain structure of these two phases that has greater wear resistance. It is almost like the hard cementite is held like sand in sand paper in a matrix of ferrite. This would create a tough yet wear resistance material. The cementite particles would be on the order of 0.1-1 micron in size.

1.3 Stress Relief

It is believed that the process of deep cryogenic treatment and tempering provides relief of internal stresses in the metal. This phenomenon should result in better corrosion resistance.

TYPES OF CRYO TEMPERING

There are two basic forms of Cryotempering:

Standard cryogenic tempering: which takes about ten hours brings the metal down to a temperature of -120°C. This is the process which has been around for some thirty years.

Deep cryogenic tempering: which reduces the temperature of the metal to -195°C. There are two sub-categories of this process, wet and dry. The wet process, although good, has the potential of creating thermal shock to the metal, resulting from the submersion in liquid nitrogen. Presently the second method is widely used. During this process it takes 9 hours to cool the material to the temperature of -195°C. It remain at that temperature for thirty hours, at which time an additional 9 hours is utilized to bring the material back up to room temperature. This process takes a total of 48 hours to perform. The process of cryogenic tempering is shown in figure 8.

The application of Cryotempering is very wide. It includes industry like Aerospace, Automotive, Defense, Mining, Medical, Motor sports, Food Processing, Job Shops, Machine Shops, Oil, Paper, Printing, Tool & Die, Welding etc.

Cryotempering of tools can be performed on tools like Broaches, Crushers, Dies, Drill Bits, End Mills, Extruders, Face Mills, Grinders, Hammer Mills, Hog Mills, Key Cutters, Knives, Hobs, Punches, Shear Blades, Shredders, Scissors, Twist Drills and more

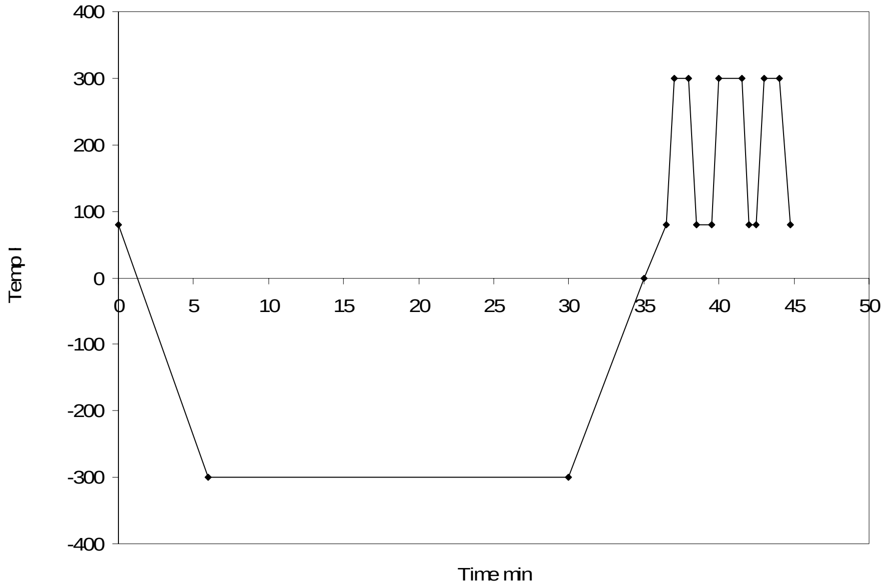

Figure 8 Process of Cryotemerping

Materials commonly treated are all metals such as aluminum, steel, stainless steel, copper, titanium, brass, tin, etc., some plastics, carbide, and others.

As a result of Cryotempering properties of material increases like durability, Stress Relief, Wear Resistance, Dimensional Stability, Production, Machineability and Surface Finish. While certain properties of material reduces like Wear, Down Time, Breakage, Heat, Friction, Cracking, Warpage, Hot Spots, Residual Stress, Tooling and Repair Costs

Following table shows percent of Increase In Wear Resistance After Cryogenic Tempering for different types of steel

Table 1 Percentage increase in wear resistance of different material.

Name of Steel	Description	-110°C	-184°C
D-2	High Carbon/chromium die steel	316%	817%
A-2	Chromium cold work die steel	204%	560%
S-7	Silicon tool steel	241%	503%
52100	Standard steel	195%	420%
O-1	Oil hardening cold work die steel	221%	418%
A-10	Graphite tool steel	230%	264%
M-1	Molybdenum high steel steel	145%	225%
H-13	Chromium/moly hot die steel	164%	209%
M-2	Tungsten/moly high speed steel	117%	203%
T-1	Tungsten high speed steel	141%	176%
CPM-10V	Alloy steel	94%	131%
P-20	Mold steel	123%	130%
440	Martensitic stainless	128%	121%
430	Ferritic stainless	116%	119%
303	Austenitic stainless	105%	110%
8620	Nickel-chromium-moly steel	112%	104%

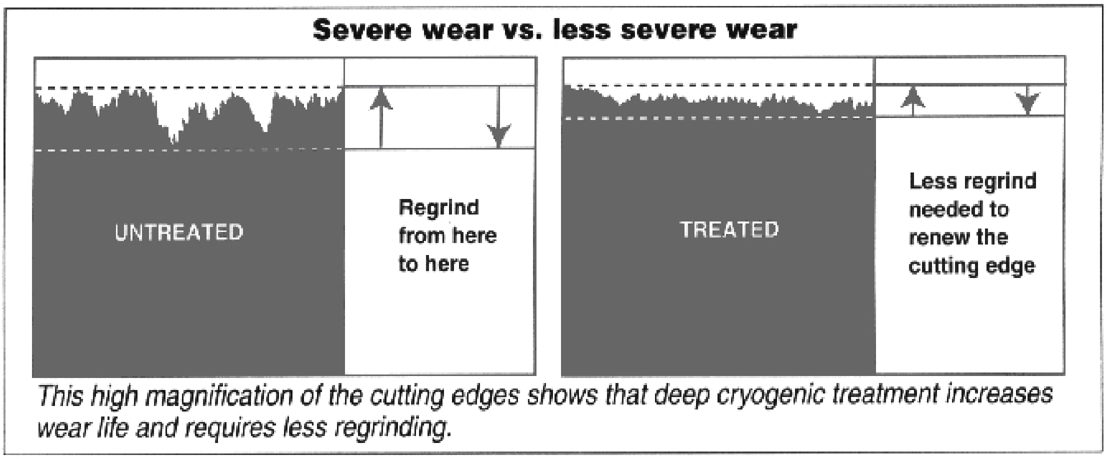

Figure 9 Effect of cryotermpering on tool life.

CONCLUSIONS

The dramatic improvement in wear resistance in deep cryogenicly treated tools steels, with no loss in toughness is most likely explained by the formation of molecular eta carbides and the formation of fine cementite particles in the final tempered structure. It would appear that the conversion of additional martensite, although often present, is probably a secondary mechanism. This understanding also supports the increase wear resistance in materials that don't readily form martensite.

It is apparent that cryogenic tempering offers many benefits where ductility and wear resistance are desirable in hardened steels. These benefits extend to cast iron, aluminum, stainless steels, and other materials. While various experts dispute the benefits of time-at-temperature control; available research, along with a correlation with standard heat treating processes indicates that this control is the key to maximizing the potential of cryogenic tempering. As is the case with many scientific discoveries, the cost factor limits the usefulness of this process in the production phase of the materials industry.