

Advanced Material Processing

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ABSTRACT: *The thermal treatment of metal must certainly be regarded as one of the most important development of industrial age. After more than a century, research continues into making metallic Components stronger and more wear resistance. One of the modern processes being used to treat the metal (as well as other materials) is Cryogenic tempering. While the science of heat treatment is well known and widely understood, the principles of cryogenics remain a mystery to most people in industry. Information regarding this process is full of contradiction and unanswered questions. Until recently cryogenic tempering was viewed as having little value towards this process because of its brittle nature of finished product. It is only since the development of computer modeled cooling and reheat curve that the true benefit of cryogenically treated materials have become available to industry and the general public.*

The purpose of this work is not to break new ground in cryogenic science, nor will it answer all of the questions surrounding this process. Rather this is a Condensation of much of the information available concerning the effect of Cryogenic Tempering has on metal structure, as well as overview of the actual process involved in process parts. Also include theories and Conclusion regarding the optimum use of cryogenic tempering on steel, cost and feasibility. All information is as up to date as possible, having been gathered from various scientific and industrial databases.

1.INTRODUCTION

The word Cryogenics is Derived from two Greek word: "Kryos", which means cold or freezing, and "genes", which means beings born of or generated. Deep Cryogenics (below -240F) has created many new applications for the racing industry, manufacturing, too & die shooting, and as well as Many others. Deep cryogenic tempering can significantly extend the performance and Productive life Of metal tools, machine part, gears, engines and transmissions, with more and more application Being discovered every day. Cryogenic tempering has its roots dating back over 100 years.

Cryogenics started in the late 1800's when Sir James Dewar perfected a technique for Compressing and storage of gas from the atmosphere into liquids. These Compressed gases were super cold and any metal that come in contact with ultra low Temperature showed some interesting changes in their characteristics.

Now that these super cold liquid could be stored and transported experimentation with the liquids Could expands. Experimentation with cryogenic temperatures continued and at the beginning of WW II. Scientist Discovered that material is subjected to super low temperature showed signs of increased resistance to wear. In the early 1960's , aerospace engineers applied the benefits of the cryogenics temperature to Stress relieve part for use in space. soon after. Military used the super cold Treatment on aircraft. In the early 1970's, scientist from universities and research centers began documenting Test result on industrial tooling as well as other applications. In the 1980's, cost associated with the process drooped and commercialization of the process began.

Today, one cryo has achieved an advanced level in quality Controll, precise temperature Regulation and affordability.

1.1 CRYOGENICS

Cryogenic is the study of how to low temperature and how material behaves when they get There. Beside the familiar temperature scales of Fahrenheit and Celsius. The cryogen cist use other temp. Scale One of modern process being used to treat the metal is cryogenic tempering. While the science of heat treatment is well known and widely understood, the principles of cryogenic tempering remains mystery to most of people in industry. Information

regarding this process is full of Contradiction and unanswered questions. Until recently, Cryogenic tempering was view as having little value due to often brittle nature of finished product. It is only since the development of computer modeled cooling and reheat curves that the true benefits of cryogenically treated materials become available to industry and the general public.

1.2 Research and Development:

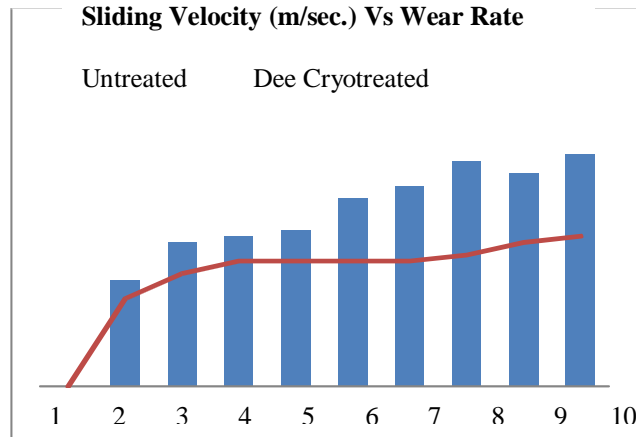
Research at national bureau of standards, speaking about cryogenic tempering ,stated, “When carbon precipitates form, internal stress in the martensite is reduced ,which minimizes the susceptibility to micro cracking. The wide distribution very hard, fine carbides, from deep cryogenic tempering, also increases wear resistances.”The study Concludes, ”...fine carbides and resulting tight lattice structure are precipitated from cryogenic treatment.

The particles responsible for the exceptional wear characteristics imparted to materials by the process, due to denser structure and resulting larger surface area of contact, reducing friction, heat and wear.” Deep cryogenic tempering is not coating or a surface treatment, but a onetime permanent, Irreversible process the retained austenite into martensite (a more refined grain structure, which is more uniform than austenite). Cryogenic tempering transforms the microstructure into a more uniform structure that is more Durable, stronger, longer lasting, and more dimensionally stable. Cryogenics: Deep cryogenic tempering can significantly reduced retained internal stresses on Most alloys Stress imparted uniquely can in most alloys cause a decrease in strength and durability.

Stress boundary areas are more susceptible to micro cracking, which can lead to premature fatigue and even failure of stressed part.

TABLE 1. Test Result (% Wear increased after Cryogenic Tempering)

Type of Steel		% Improvement	
AISI	Description	(- 110°F)	(-310°F)
D-2	High Carbon/chromium die	316	817
A-2	Chromium cold work die	204	560
S-7	Silicon tool steel	241	503
52100	Bearing steel	195	420
O-1	Oil hardening cold worked die.	221	418
A-10	Graphite tool steel	230	264
M-1	Molybdenum high speed	145	225
H-13	Chromium/moly hot die	164	209
M-2	Tungsten/moly high speed	117	203
T-1	Tungsten high speed	141	176
CPM- 10 V	Alloy steel	94	131
P-20	Mold steel	123	130
440	Martensitic stainless	128	121
303	Austenitic stainless	105	110
C1020	Carbon steel	97	98
T-2	Tungsten high speed steel	72	92
AQS	Graphite cast iron	96	97
8620	Nickel-chromium-moly steel	112	104



II. CRYOGENIC LIQUID

Cryogenic liquids are used for accessing low temperatures. they are extremely cold, with boiling point below 22K [or - 60°F(-51°C)].Carbon dioxide and nitrous oxide, which have slightly higher boiling points, are sometimes included in this category.

Cryogenic have high expansion ratios, which average ~ 700:1When they are heated (i.e. exposed to room temperature),they vaporize(turn into gas) very rapidly. If the volume cannot be expanded (no outlet), the pressure will increase approximately 700-fold or until it blows something out.

TABLE 1:Physical Properties of Common Cryogenic Liquids

Cryogen	Boiling point (1atm) °C(° F)	Critical pressure PSI	Liquid Density g/L	Gas Density (27°C),g/L	Liquid -Gas Expansion ratio	Type of gas
Ar	-186(- 303)	710	1402	1.63	860	Inert
He	- 269(-452)	34	125	.16	780	Inert
H2	-253(-423)	188	71	.082	865	Flammable
N2	-196(-321)	492	808	2.25	710	Inert
O2	-183(-297)	736	1410	1.4	875	Oxygen
CH4	-161(-256)	673	425	.72	650	Flammable

pound per square inch gauge's)although oxygen does not burn ,it will support combustion. Oxygen-enriched atmospheres may lead to violent reactions, such as rapid combustion Or explosions, with incompatible materials.

The typical container used to store and handle cryogenic fluids is the dewar. The dewar is multiwall designed with vacuum jacket for insulation and pressure relief valve to protect against over-pressurization. Cryogen normally are stored at low pressures.

Liquid nitrogen dewars have one pressure relief valve set at 22psi.Liquid helium dewars need two pressure relief valve. They are initiated at .5psi and 10psi at room temperature, respectively. The 0.5psi relief value can be used to perform liquid transfers.

All cryogen dewars should be clearly labeled and operated in accordance with the manufacturers instructions. The pressure relief valve should be periodically inspected for ice formation. Proper personal protective equipment must be worn whenever handling cryogenic liquids.

2.1 SAFE HANDLING AND USAGE

If liquid not handled properly, cryogenic liquids can be hazardous to personnel. By reviewing this fact sheet you will become aware of the conditions that increase the risk of accident and injuries that can occur when working with cryogenic liquids. You will learn what can make your work place safe.

A] Hazard associated with Cryogenic Liquids i) Skin and Eye hazards Cryogenics are extremely cold and cause instant, severe frostbite. A jet of cryogen vapor can freeze the skin or eyes faster than liquid contact, and even faster than metal contact. Also, direct contact with cryogenic liquids, uninsulated cryogenic pipes or equipment can cause freeze burns and tissue damage. The eye's fluids will freeze in contact with a cryogen, causing permanent eye damage. If the funnel used to transfer cryogen (which you should not be using) freezes, it will discharge the cryogen upward into your face.

III. BENEFITS OF CRYOGENIC TEMPERING

Deep Cryogenic Treatment at -300°F can make major contribution to solving these problems:

1. HIGH ABRASIVE WEAR in cutting tools, molds, dies, bearings, etc.
2. HIGH CORROSIVE WEAR in chemical, food and oil equipment application.
3. HIGH EROSIVE WEAR from wind, water and other abrasive grit carriers.
4. DISTORTIONS induced by design, forming, machining or environment.
5. STRESS RELIEF in complex tools, component and welds.
6. STRESS RELIEF CRACKING in weld zones in corrosive atmosphere.
7. SURFACE FINISH in any applications where long life is needed.
8. STABILISATION in parts and component as a result of stresses.
9. MACHINABILITY in aluminum and copper parts.
10. ELECTRODE LIFE in copper resistance welding.

What happens during Deep Cryogenic Tempering? (Ferrous Components)

1. Most of retained austenite is transformed into martensite. The Martensite is tempered to change it into tempered martensite.
2. Small complex carbides called eta carbides are precipitated out.
3. Residual stresses are greatly reduced.

Alloys with greater than 0.40% carbon required cryogenic tempering to finish martensite transformation.

Materials are favorably affected by deep cryogenic tempering.

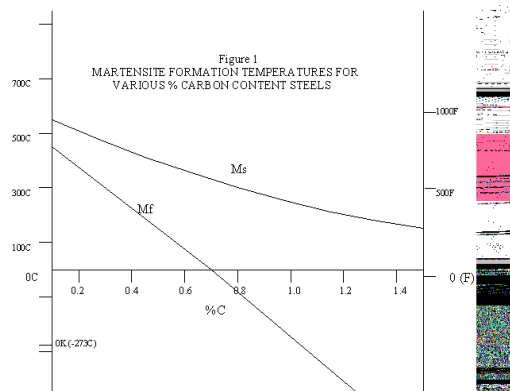
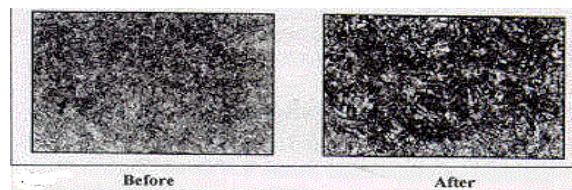
Ferrous materials:-

1. Tool Steel
2. High carbon high alloy materials.
3. Martensite stainless steel
4. Gray Cast iron

IV. ALTERATIONS IN METAL STRUCTURES

An explanation of the effect of deep cooling on metallic structure requires a connection be drawn to the more standard elevated temperature treatment processes. When a metal (high carbon steel, for example) is heated, the increase in energy expands the molecules. A ferrite (iron) molecule, like everything else, is mostly empty space between tiny atoms. As the iron atoms separate, atoms of carbon present in the steel "fall" into the larger empty spaces, creating a condition known as interstitial solid solution. This hot, carbon enriched iron is known as austenite. Hardened steel is simply austenite which has been rapid quenched to trap the carbon atoms in solution. This hardening process is the first step in any thermal treatment of steel. Because the grain structure of austenite is normally unstable at ambient temperatures, simply quenching results in steel which is brittle and of little value to industry. If the steel is partially quenched and held at a certain elevated temperature (dependent on actual carbon content) austenite will re-form into a much more stable structure known as martensite. After the steel has reached thermal equilibrium at the martensite start temperature (Ms), it is allowed to cool slowly to promote Martensitic transformation.

It is at this point that cryogenic tempering becomes important, especially in the hypereutectoid steels (above 0.83% carbon content). Martensite structures do not form at a constant temperature, rather the austenite is converted to martensite as the steel cools to ambient temperature. The temperature range for martensite formation is determined by the particular carbon content of the material. Figure 1 is a graph of martensite formation temperatures as they relate to carbon content. The ranges are not exact; they are merely intended to show the concept of martensite growth with cooling. As the graph shows, the marten site growth completion line (Mf) drops below 0C at approximately 0.7% carbon content. As most steel producing plants are considerably warmer than this, it is easy to see that the higher carbon steels cannot undergo a complete austenite conversion without artificial refrigeration.



The Mf line is extrapolated below 0C, but it serves to point out the major reduction in temperature necessary to completely transform austenite in the higher carbon steels. Obviously, the cryogenic process is key to continuing the transformation of retained austenite into martensite in hypereutectoid steels. While roughly the same amount of free carbon is present, the cryogenic process seems to slow the development of these "lumps of coal", distributing the carbon atoms more evenly and allowing a tighter overall grain structure with less voids (Fuerst). One hypothesis is that the very low temperatures inhibit the formation of covalent atomic bonds in the free carbon, preventing the larger carbide structures from forming. Figure 2 shows microscopic views of Martensitic steel before and after cryogenic tempering. Note the more even carbon distribution and larger grain structure visible even at relatively low magnification (100X).

4.1 Importance of Cryogenic tempering

Why Cryogenic Tempering is Important Possibly the most important restriction to industrial productivity is metallic part wear. Tool bits punch dies, and bearing surfaces all are all subjected to wear under normal use conditions. The cost and downtime associated with parts replacement has limited the speed of production equipment since the beginning of industrial age. Proper cryogenic tempering offers impressive gains in terms of tools and component life. Increase of 400% in number of operation before resharpening are not uncommon and claims to beyond 25 times the normal tool life in some applications (frozen gears). Cryogenic treatment has also found favorable result in auto racing, sporting goods. In short there is a little doubt about the effectiveness of the process in enhancing wear and fatigue resistance. Questions remains however, as to what actual structure changes takes place during the cryogenic process.

Cryo-Processing Advantages

- a) Increase abrasive wear resistance.
- b) Require only one permanent Treatment.
- c) Create a denser molecular structure,
- d) Which results in a larger contact surface area that reduces friction, heat and wear.
- e) Changes the component entire structure, not just the surface. Subsequent finishing operation or regrind do not affect permanent improvements.
- f) Eliminate thermal shock through dry, computer controlled process.
- g) Transforms almost all retained austenite into hard marten site.
- h) Form micro fine carbide fillers to enhance large carbide structure.
- i) Increase durability or wear life.
- j) Decrease residual stress in steel tools.
- k) Decrease brittleness.
- l) Increase tensile strength, toughness and ability coupled with the release of internal stresses.

V. THE IDEAL ROLE OF CRYOGENIC TEMPERING

As previously discussed, the transformation of austenite into useful martensite is dependent on two factors, carbon content and temperature. The steel must first be heated to a temperature sufficient to allow carbon atoms to enter into solution. This temperature must then be maintained until enough time has passed for a complete austenitic reaction to take place. This is known as soak time, and is dependent on the mass of the part being treated. Next, the part must be partially quenched down to the martensite start temperature for the particular carbon content of the steel. The part is then held at this temperature until thermal equilibrium is reached (the entire thickness of the part is the same temperature). Under ideal circumstances, the part would immediately be placed into the cryogenic chamber and cooled to the relevant Mf temperature for carbon content and maintained at that temperature until thermal equilibrium was once again reached at Mf. It is at this point that complete martensite transformation will have occurred and the part may be allowed to return to ambient temperature at a rate which will minimize internal stresses. Cryogenic tempering of room temperature steels is effective at transforming retained austenite, however, the resulting crystalline structure is not as uniform as martensite which has all formed at the same time, as in the above

Advanced Material Processing

example. Integral cryogenic tempering is not cost effective for volume production parts, as the logistics of having a large cryo chamber in close proximity to a steel furnace would be interesting, to say the least. Interrupted tempering or tempering of room temperature steels are much more practical ways of obtaining a majority of the benefits of cryogenic treatment.

An Overview of How Cryogenics Works

Cryogenic tempering may be oversimplified into a process of chilling a part down to relatively near absolute zero and maintaining that condition until the material has cold- soaked. The temperature is then allowed to rise until ambient equilibrium is reached. The part may then be subjected to a normal tempering reheat, although this step is not always included in the process. The complexity of the process involves determining and achieving the proper duration for the cooling, soaking, and warming cycles. It is here that developments in computer modeling and controls have placed cryogenic tempering on the cutting edge of metal treatment. Scientists in provinces of the former Soviet Union typically disagree with western methods of cryogenic treatment, as tests there have revolved around unceremoniously dumping parts into a flask of liquid nitrogen, removing them, and allowing the material to cool uncontrolled in ambient air. Predictably, reports of extended tool life have not been as favorable as those achieved using more tightly controlled processes (History).

Cryoprocessors

Custom Oversized Processor \$ 60,000.00

CP-500 vi \$45,000.00

CP-200 vi \$35,000.00

About the Cryoprocessor

A computer controlled, Vacuum insulated environmental chamber capable of executing complex time-temperature prescriptions in the temperature range of -300 F to $+300$ F, provide the capability to:

- Perform Cryogenic processing to enhance the wear resistance of steel and cemented carbide, chromium or TiN coated tools and wear parts, and copper resistance welding electrodes.
- Dimensionally stabilize metal optics and precision ground parts prior to final polishing / Grinding to produce a superior surface finish;
- Stress relieves metals for tear free drawing and enhanced acoustic characteristics.

Principles of Operation

The CP-500 vi cryoprocessor is capable of automatically cycling payloads between the temperature limits of -300 F and $+300$ F. Payload temperature is reduced by cooling an internal heat exchanger with a controlled flow of liquid nitrogen, while a blower circulates dry gaseous nitrogen between the payload and the heat exchanger to minimize temperature gradients. A digital computer is provided for the programming and storage of complex time-temperature prescriptions. An integral temperature sensor and controller form a servo system to meter liquid nitrogen or electric heat to ensure compliance with the program. The system is capable of unattended operation for periods of days. A chart recorder provides a permanent record of the thermal history of the payload.

Specifications

- Internal dimensions: 31" (Dia) x 46" (H)
- Overall external dimensions: 70" (H) x 46" (W) x 49" (D)
- Overall height (lid open): 92" Controls: Digital programmable with 6 ramp / soak segments per program, up to 8 Programs; expandable.

- Power requirements: 120 VAC, 30 AMP, 60 Hz, or 240 VAC, 20 AMP, 50 Hz, Low pressure liquid nitrogen required.

VI.CONCLUSIONS

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 this paper discussed only the effect on high carbon steel, the concept of continuing alloy grain structure formation through temperature reduction applies to these other materials in the same fashion. 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.

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