techcommentary

EPRI

Cryogenic Processing of Metals

Introduction

Cryogenic processing, originally developed for aerospace applications, has been used for over 30 years to improve the properties of metals. Many fantastic claims have been made as to the degree of improved performance achieved by cryogenic processing. Practitioners claim that properties such as wear resistance can be improved by factors of two, three, or 10 compared to traditional heat treatment. Others claim improved dimensional stability, increased hardness or shifts in resonant vibrational frequency of cryogenically treated materials. Some claims have been validated by research, many have not. However, the use of cryogenic processing is growing. The recent creation of a Cryogenics Technology Group within ASM International's Heat Treating Society, and an increasing number of technical articles being published in trade publications has bolstered the acceptance of this process technology.

Cryogenic processing of metals involves the "freezing" of parts by lowering their temperature to that of liquid nitrogen (-320°F, -196°C) for some period of time. Either liquid nitrogen or dry nitrogen gas is used from bottles or Dewar flasks.

While only a moderate amount of electricity is consumed in the cryogenic process itself, a considerable amount of electricity is used in producing liquid nitrogen. The limited acceptance and use of cryogenic processing is generally attributed to a lack of understanding of the technology, as well as the absence of generally accepted procedures for applying it.

Process Fundamentals

Refrigeration of metals to improve performance is divided into two categories: cold treatment and cryogenic treatment. Common practice identifies -120°F (-84°C) as the optimum temperature for cold treatment at which parts are held (soaked) for 1 hour per inch of thickness, then subsequently warmed in ambient air. Typical cryogenic treatment consists of a slow cool-down of -5°F per minute (-3°C per minute) from ambient to -320°F (-196°C), a soak for 24 to 72 hours, and warm up to ambient temperature. The cryogenically treated parts are then subjected to a temper treatment (300° to 1000°F or 149°C to 538°C) for a minimum of one hour.

Figure 1. Heat Exchanger Cryogenic System

Cryogenic processing is applicable to both newly fabricated parts and to parts already in service. Some practitioners cryogenically treat parts after traditional heat treatment and tempering as an add-on process. Some heat treaters integrate cryogenic processing into the heat treat process, after austenitizing but before the first temper. In this case, part temperature is first reduced from austenitizing temperature to room temperature by traditional quenching techniques. The parts are then further cooled by cryogenic treatment, slowly warmed to room temperature, and then subjected to a temper treatment.

Deep Freeze: The Inside Story

Steels are mixtures (alloys) of iron and carbon and are generally divided into five groups: carbon steels, alloy steels, stainless steels, tool steels, and special-purpose steels. Of great significance to the heat treater is the fact that iron is an *allotropic* element, which means that it can exist in more than one atomic arrangement (dependent upon temperature).

The process by which iron changes from one atomic arrangement (crystalline form) to another is called a *transformation*. Heating or cooling the material induces the transformation. When steel is heated to a high enough temperature, the resulting iron crystal structure is called austenite. When steel is rapidly cooled from above the austenitizing temperature, the austenite transforms to an extremely hard, almost brittle crystal structure called martensite. With some richly alloyed steels (such as tool steels), the transformation is not complete even at room temperature. Some austenite will be retained in the martensite structure unless the steel is refrigerated. This transformation from austenite to martensite is not time dependent, but related to the degree of cooling. Further cooling to cryogenic temperatures continues the transformation in all metals.

Applications

There are several categories of industrial applications and representative parts:

Paper and Corrugated Board Industry

- Chipper knives
- Envelope dies
- Refiner disks
- Jordan bars
- Tissue perforators
- Slitter knives
- Tape cutters
- Paper drills
- Trimmers
- Sheeters

Metalworking Industry

- Mill cutters
- Ball screws
- Forming tools
- Punches
- Broaches
- Drills

Plastics Industry

- Trimmers
- Mill knives
- Granulating blades
- Dies
- Feed screws

Performance Vehicles

- Crankshafts
- Brake rotors
- Push rods
- Heads
- Pistons
- Blocks
- Cams

Other Applications

- Copper electrode
- Sporting goods
- Musical instruments
- Gun barrels
- Razor blades
- Plastics

The cost effectiveness of cryogenic processing for these applications must be individually assessed to determine if adequate value added is achieved to offset the cost. Some industries such as aerospace, defense, and performance racing are willing to pay a premium even for marginal increases in performance.

Advantages

A wide range of material property improvements has been claimed for steels treated at low-temperatures:

- **Wear Resistance**
  One of the most prevalent claims for cold or cryogenic treatment of metals is an increase in wear resistance (with or without a hardness increase).
- **Dimensional Stability**
  The original purpose of cryogenic treatment was to stabilize part dimensions by eliminating the possibility of spontaneous transformation of retained austenite to martensite during fabrication or in service.
- **Hardness**
  In many cases, hardness increases of 1 to 3 points Rockwell C-scale hardness (HRC) have been claimed, although some report little increase in hardness.
- **Resonant Frequency**
  Shifts in resonant frequency have been documented and are being applied to musical instruments such as trumpets and trombones.

The practical cost savings from increased wear resistance of low-temperature treating of tooling include:

- Delayed purchase of new tooling
- Decreased resharpen, regrind, and rework
- Less scheduled downtime to change tooling
- Lower labor costs
- Decreased loss of production parts when tooling is out of spec

Process Equipment

Cold Treating

Dry ice placed on top of parts in a closed, insulated container is commonly used for cold treating. The dry ice temperature is -110°F (-78°C) but the chamber temperature is normally about -75°F (-60°C). Mechanical refrigeration units with circulating air at approximately -125°F (-87°C) are commercially available.

Cryogenic Treating

Liquid nitrogen systems have been the customary method for achieving cryogenic temperatures. Three types of systems have been developed: heat exchanger systems, direct spray systems, and step-immersion systems.

A **heat exchanger** system (Figure 1) passes liquid nitrogen through a heat exchanger and the exhaust gas is recovered for use as a furnace atmosphere. The chamber atmosphere is drawn over the heat exchanger coils by a fan and circulated around the parts. Neither liquid nitrogen nor dry nitrogen gas ever comes in contact with the parts.

A **direct spray** system (Figure 2) sprays liquid nitrogen directly into the chamber, while a fan circulates the gas over the work. In this case, the spent gas cannot be recovered. Liquid nitrogen does not come into contact with the parts.

A **step-immersion** system for treating a part involves immersing the part at ambient temperature into liquid cryogenic material for a time period of about ten minutes. The part is then withdrawn from contact with the liquid cryogenic material and immediately subjected to a flow of air sufficient to raise the temperature of the article to ambient temperature. The time period necessary to complete a cycle of the step-immersion process generally is a maximum of about one quarter hour per cross section inch of the article being treated. Cycle times of 1 to 2 hours are common.

Figure 2. Combined Cryotreating and Tempering Unit

Technical Considerations

Process Kinetics

Most sources agree that three mechanisms are responsible for improved performance by parts that undergo low-temperature treatment:

1) In both cold treatment and cryogenic treatment, retained austenite transforms to freshly formed martensite at low temperature.

2) In cryogenic treatment, and possibly cold treatment, the atomic spacing within freshly formed martensite decreases upon cooling and remains less than original martensite atomic spacing even upon heating.

3) During tempering after cryogenic treatment, rod-like carbides of nanometer size precipitate into the martensite matrix up to roughly 3% to 6% by volume.

Studies by Penn State University researchers in 1996 showed that retained austenite was reduced from near 18% to roughly 8% in T15 tool steel upon cryogenic treatment. Hardness increased 2 points (HRC) with cryogenic treatment and subsequently decreased (in some cases more than 2 points) after a temper cycle. Increasingly longer soak times at cryogenic temperature for D2 tool steel increased the density of carbides during tempering, according to a study conducted by the National Heat Treat Centre at University College in Ireland. The same study also showed that increasingly higher temper temperatures following cryogenic processing, also increased the density of carbide which resulted in lower wear rates.

Still, there has not yet been enough investigation to precisely determine optimum processing parameters, even for tool steels. Some claim that tools should be sharpened after cryogenic treatment rather than before. Variables such as original austenitizing temperature, soak time at cryogenic temperature, and both temper temperature and temper time still vary widely between processors for the same material. Almost everyone agrees though, that for heat treated tool and die materials, cryogenic treatment should occur prior to the traditional heat treat temper that normally follows after austenitizing and quenching.

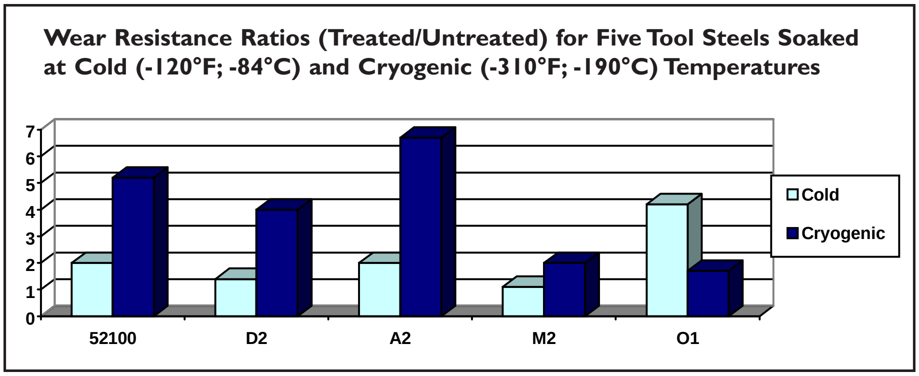

Figure 3. Wear Resistance Ratios

Wear Test Results

R. F. Barron, considered the father of cryogenic processing, published test results for five tools steels in research conducted at Louisiana Tech University in 1973. These are reproduced in Figure 3.

The lower cryogenic processing temperature resulted in significantly better wear resistance compared to both untreated and cold treated tool steels in almost every case.

The Penn State study produced the following results (Table 1) in tests of wear resistance for cryogenically treated T15 tool steel.

Mean tool life increased significantly compared to non-cryogenically treated T15 tool steel with few exceptions. Increasingly higher temper temperatures and longer tempering times generally increased mean tool life. In one case, however, the longer 4 hour temper for Group 5 decreased hardness to 60.2 HRC, compared to Group 1 untreated hardness of 62.6 HRC resulting in poorer wear performance.

Economic Considerations

Cryogenic processing chambers up to 4′ × 5′ × 8′ (0.3 m × 1.5 m × 2.4 m) in dimension can be purchased for between $20,000 and $40,000. Combination chambers that can both cryogenically treat and subsequently temper parts up to 1200°F (649°C) are available for under $75,000. This cost does not include the supply, storage and handling of liquid nitrogen. Cryogenic processing shops charge anywhere from $2/lb up to $10/lb for cryogenic treatments.

Table 1. Mean Tool Life for Various Tempers After Cryogenic Treatment

Group	Cryogenic Treatment	Temper		Mean Tool Life (seconds)	
		Temperature °F (°C)	Time (Hours)	200 fpm	300 fpm
1	No	None	None	960	81
2	Yes	None	None	737	93
3	Yes	400 (204)	1	1122	77
4	Yes	400 (204)	2	1231	91
5	Yes	400 (204)	4	900	67
6	Yes	1000 (538)	0.5	1080	122
7	Yes	1000 (538)	1	1265	150
8	Yes	1000 (538)	2	2180	155

Other Applications

Many cryogenic treatment job shops will state that the process will benefit almost any material. Interesting, but as yet inexplicable, results have been obtained with nonferrous metals such as aluminum and copper, as well as plastics. Vendor literature claims that the process will change the vibrational characteristics and reduce the electrical resistance of metals, increase the life of electrical circuits, increase the flight of golf balls, and make metals and plastics easier to polish. However, most published experimental evidence has been related to improving the performance of tool steels.

Summary

Throughout history, practice has normally led to understanding, but to effectively control and develop technology, a basic understanding is needed. This is the case with cryogenic treatment: practice has been leading the way with understanding trailing behind. However, in the case of improving wear resistance of tool steels, enough study has been undertaken to justify practical application of this useful process technology.

Sources used in this issue of *TechCommentary* include:

ASM Handbook, *Heat Treating*, Volume 4, 1991.

Pen-Li Yen and Dennis J. Kamody "Formation of Fine Eta Carbides in Special Cryogenic and Tempering Process Key to Improved Properties of Alloy Steels." *Industrial Heating*, January 1997

S. Wiberg and J.M.C. Roberts "Cryogenics - Fact or Fiction: A Metallurgist's Viewpoint." *Metal Heat Treating Digest*, July 1997

David N. Collins "Cryogenic Treatment of Tool Steels." *Advanced Materials & Processes*, December 1999.

Figure 2 courtesy of Durable Metal Products

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