THE LINDE GROUP

White Paper.

# Sub-zero treatment. Technology, processes and equipment.

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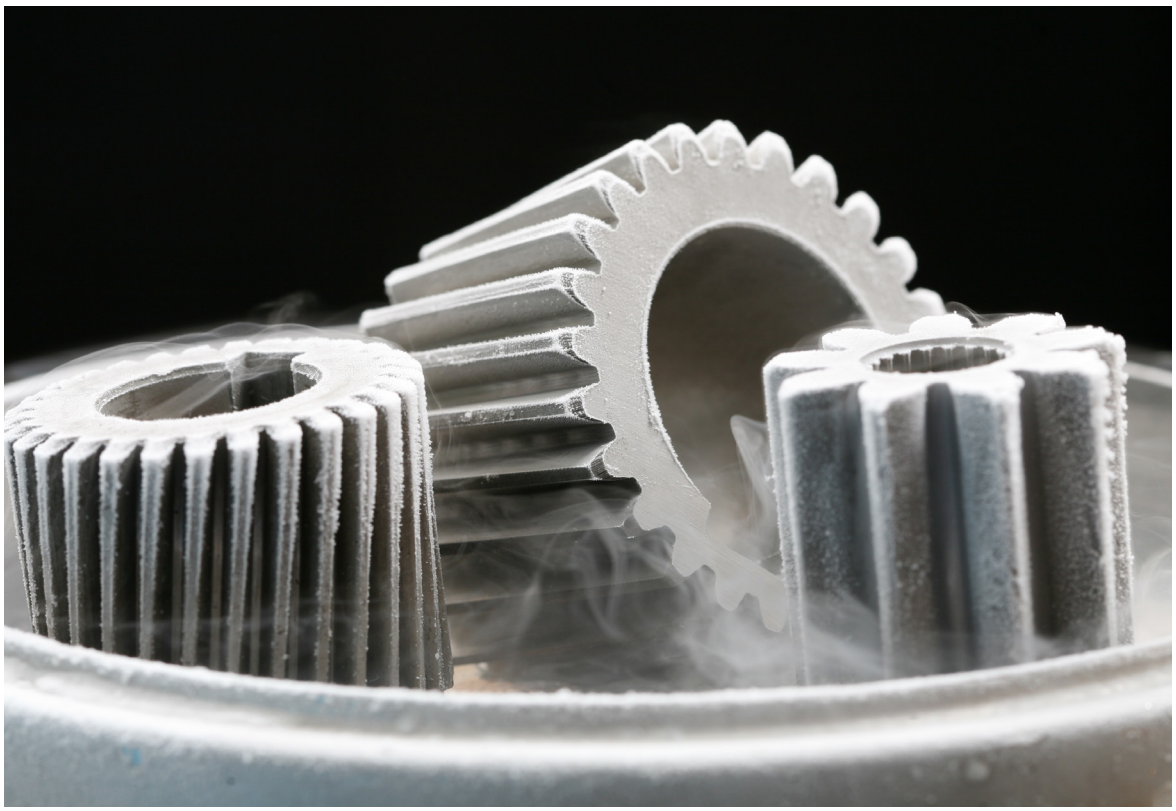
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# Abstract.

Sub-zero treatment is a process that is increasingly being applied in Europe, Latin America and Asia. Research into the metallurgy of the process casts light upon the underlying mechanisms of the processes, the reasons why the process only works well for certain alloys, and explains the variations in prior research results. The sub-zero treatment processes can be grouped in two broad categories which impact steel in the following ways:

- Cold treatment completes the metallurgical phase transformation of austenite to martensite during the hardening of steels via quench and temper heat treatment.
- Cryotreatment at temperatures below -190 °F (-120 °C) creates conditions for the subsequent nucleation of very fine carbides in higher-alloy steels.

This document discusses each of these treatment processes and delves into research on sub-zero treatment technology, safety, and cryogenic processing equipment. In addition, this document will discuss some less commonly known applications of sub-zero processing.



# 1. Introduction.

Over centuries, heat treatment of metals has transformed from black art to science. Through worldwide research, metallurgists have developed phase diagrams, continuous transformation diagrams, process/property correlations, and heat treatment cycles. Metallurgists understand how and why an alloy responds to a heat treatment cycle, but they also understand that changing any processing variable will influence the final properties.

Researchers have only recently begun to study sub-zero cooling cycles. For many years, sub-zero treatment of metals had the reputation of being a quick fix for poor heat treatment practice. Sub-zero processing technology has not been widely adopted by the metals industry due to a lack of understanding of the fundamental metallurgical mechanisms and due to the wide variation in reported research findings. Early un-substantiated claims that cryogenic treatments can solve every problem from bad golf balls to holes in woman's hosiery have further diminished the interest in exploring cryogenics as a credible process.

Recently however, researchers have conducted significant research into the fundamental understanding of the mechanisms governing sub-zero processing. Dr. Randall Barron at the University of Louisiana was one of the pioneers to conduct significant research [1, 2] into sub-zero processing. His research shows that sub-zero processing of steels can improve various mechanical properties, including:

- Hardness and strength
- Wear resistance
- Dimensional stability

**Table 1: Examples of tool life improvements using cryotreatment [2, 3, 5, 10]**

| Tooling | Average life before treatment | Average life after cryotreatment | Wear ratio |
|---|---|---|---|
| 5-cm end mills used to cut C1065 steel | 65 parts | 200 parts | 3.07 |
| Hacksaw blades used to cut bosses on M107 shells | 4 h | 6 h | 1.5 |
| Zone punches used on shell casings | 64 shells | 5,820 shells | 82.5 |
| Nosing thread dies used in metal working | 225 shells | 487 shells | 2.12 |
| Copper resistance welding tips | 2 weeks | 6 weeks | 3.0 |
| Progressive dies used in metal working | 40,000 hits | 250,000 hits | 6.25 |
| Blanking of heat-treated 4140 and 1095 steel | 1,000 pieces | 2,000 pieces | 2.0 |
| Broach used on a C1020 steel torque tube | 1,810 parts | 8,602 parts | 4.75 |
| Broaching operation on forged connecting rods | 1,500 parts | 8,600 parts | 5.73 |
| Gang milling T-nuts from C1018 steel with M2 cutters | 3 bars | 14 bars | 4.67 |
| AMT-38 cut-off blades | 60 h | 928 h | 15.4 |

As an early proponent of sub-zero processing, the paper and corrugated board industry has achieved significant improvements in wear resistance for different types of cutting tools. Cutting knives, chipper knives, trimmers, bracket trimmers, guillotine blades, slitters, score cutters, and envelope dies have increased their useful life by factors of 2 to 5 [3–8]. Table 1 shows the average useful life of particular tooling pieces with and without the benefit of sub-zero treatment.

A parameter called "wear ratio", defined as the ratio of life after sub-zero treatment/average tool life without sub-zero treatment, gives a measure of the amount of improvement this process can impart when applied correctly.

Differences in wear life, shown in table 2, between parts cold-treated at about -80 °C (-110 °F), and parts cryogenically treated at -190 °C (-310 °F) using liquid nitrogen, raised questions about the causes of the improved wear resistance. However, the overall results from these studies could not be disputed. Further research has been conducted to gain a better understanding of the underlying mechanism.

**Table 2: Percentage increase in wear resistance after cold treatment and cryotreatment [9]**

| US steel designation and corresponding German standards | | Description | At -79 °C (-110 °F) | At -190 °C (-310 °F) |
|---|---|---|---|---|
| **AISI** (USA) | **DIN** (BRD) | Materials that showed improvement | In percent | In percent |
| D2 | 1.2379 | High-carbon/chromium steel | 316 | 817 |
| S7 | | Silicon tool steel | 241 | 503 |
| 52100 | 1.3505 | Bearing steel | 195 | 420 |
| O1 | 1.2510 | Oil-hardening cold-work die steel | 221 | 418 |
| A10 | | Graphite tool steel | 230 | 264 |
| M1 | 1.3346 | Molybdenum high-speed steel | 145 | 225 |
| H13 | 1.2344 | Hot-work tool steel | 164 | 209 |
| M2 | 1.3341 | Tungsten/molybdenum high-speed steel | 117 | 203 |
| T1 | 1.3355 | Tungsten high-speed steel | 141 | 176 |
| CPM 10V | | Alloy steel | 94 | 131 |
| P20 | 1.2330 | Mold steel | 123 | 130 |
| 440 | | Martensitic stainless steel | 128 | 121 |
| | | Materials without significant improvement | | |
| 430 | | Ferritic stainless steel | 116 | 119 |
| 303 | 1.4305 | Austenitic stainless steel | 105 | 110 |
| 8620 | 1.6523 | Case-hardening steel | 112 | 104 |
| C1020 | 1.0402 | 0.20 % carbon steel | 97 | 98 |
| AQS | | Grey-cast iron | 96 | 97 |
| T2 | | Tungsten high-speed steel | 72 | 92 |

# 2. Theory and applications.

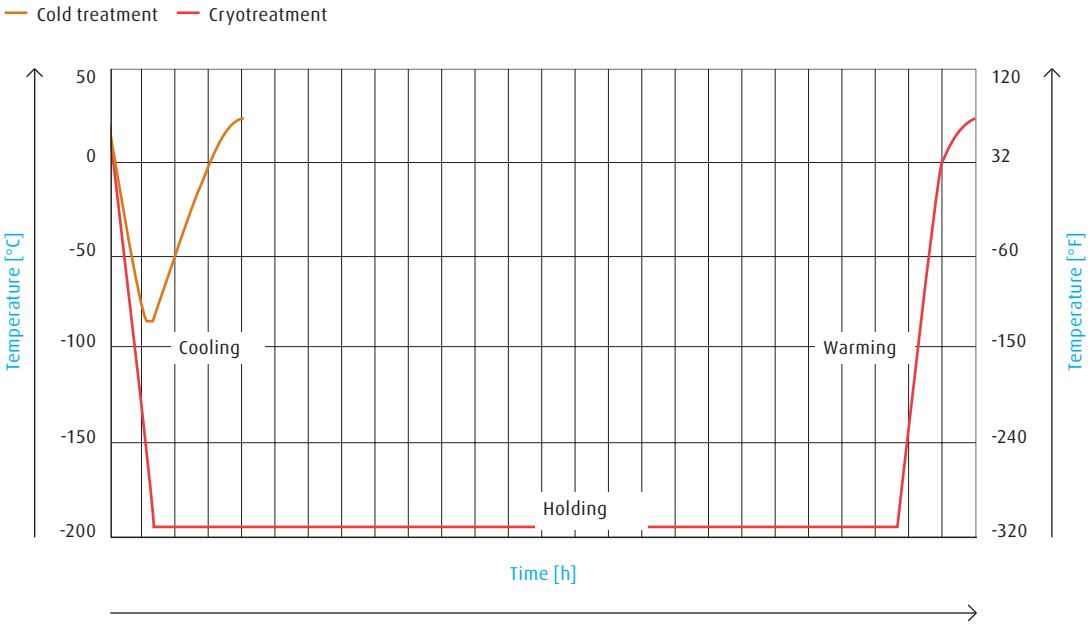
Numerous factors impact how sub-zero treatments affect an alloy. Processing factors such as time, temperature profile, number of repetitions and tempering practice, in conjunction with material parameters such as prior heat treatment and alloy composition will alter the final results.

The table below discusses two sub-zero treatment applications. Sub-zero treatment falls into the broad categories of cold treatment and cryotreatment. Figure 1 shows the differences in the basic processes regarding the time-temperature process cycle.

**Table 3: An overview of sub-zero treatment processes for metals**

| Process | Description | Parameters | Objective |
|---|---|---|---|
| Cold treatment of steels | Complete martensitic phase transformation | -70 to -120 °C (-90 to -190 °F) for 1 hour per 3 cm of cross section | → Transformation of retained austenite to martensite<br>→ Increased hardness<br>→ Dimensional stability |
| Cryotreatment of steels | Cryotreatment temperatures can create sites to nucleate fine carbides that improve wear resistance in tool steels | -135 °C (-210 °F) and below for 24 hours or longer | Improved wear resistance through carbide precipitation |

**Figure 1: Sub-zero process cycle profiles**




## 2.1. Cold treatment for retained austenite transformation of steels.

Cold treatment of higher-alloy and carburized steels is an additional step in the heat treatment hardening process. The cold treatment process occurs in the temperature range of -70 to -120 °C (-90 to -190 °F) and completes the transformation of the steel microstructure from austenite to the stronger and harder martensitic structure. The hardness of a steel increases with increased percentage of martensite in the structure. Thereby wear resistance increases as it correlates positively with hardness (wear resistance in addition depends on the presence of carbides, as further discussed in section 2.2). A specific percentage of retained austenite may be desired for applications such as bearings or gears where the metal may require some toughness to absorb impact or torsion loading.

### 2.1.1. Heat treatment process description

To harden steels, the heat treatment process includes heating to austenitizing temperatures. The microstructure is composed of the metallurgical-phase austenite plus the primary carbides. Austenitizing is followed by quenching, or rapid cooling, which transforms some or all of the austenite into the higher-strength martensitic structure, supersaturated with carbon. Tempering allows the supersaturated carbon to form carbides, called transition carbides, that relieve micro-stresses in the martensitic matrix and prevent the cracking of the part.

### 2.1.2. Increasing hardness by transforming austenite to martensite

The transformation from austenite to martensite begins at a well-defined temperature called the martensite start temperature or $M_S$. For most practical steels, the transformation is isothermal and progresses smoothly as the temperature falls to the martensite finish temperature, or $M_F$.

$M_S$ and $M_F$ are characteristic for particular alloys and can be found on steel specification sheets, heat treatment guides and standards, or metallurgical reference texts. Some austenite, called retained austenite, is always present after hardening. Higher martensite contents and carbon percentages increase the hardness of steel as shown in table 4. The amount of carbon also affects the temperatures where the martensite transformation begins ($M_S$) and is completed ($M_F$) as shown in figure 2.

**Figure 2: Effect of carbon content on $M_S$ and $M_F$ temperatures**

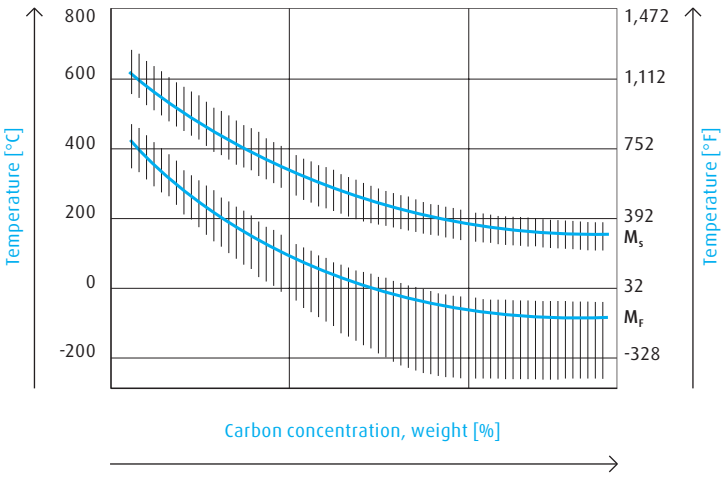



**Table 4: Steel hardness at various martensite percentages for some low-alloy steels (reprinted courtesy of ASM International [12])**

| Rockwell C hardness (HRC) with martensite contents of: | | | | | |
|---|---|---|---|---|---|
| Carbon, % | 50 % | 80 % | 90 % | 95 % | 99.9 % |
| 0.18 | 31 | 35 | 37.5 | 39 | 43 |
| 0.23 | 34 | 37.5 | 40.5 | 42 | 46 |
| 0.28 | 36.5 | 40.5 | 43 | 44.5 | 49 |
| 0.33 | 39 | 43.5 | 46.5 | 48.5 | 52 |
| 0.38 | 42 | 46 | 49 | 51 | 54 |
| 0.43 | 44 | 48 | 51 | 53.5 | 57 |
| 0.48 | 46.2 | 52 | 54 | 57 | 60 |

The $M_F$ or even $M_S$ temperatures can be lower than room temperature, so the steel might only partially transform to martensite with the remaining structure being retained austenite. $M_S$ and $M_F$ temperatures are also depressed with increasing grain size. Therefore, higher austenitizing temperatures can lead to higher levels of retained austenite. Cooling to sub-zero temperatures makes it possible to promote further transformation of retained austenite to martensite in order to increase the hardness and strength of the steel.

### 2.1.3. Improving dimensional stability

At room temperature, retained austenite is unstable and will slowly decompose over time. For most applications, this is not a problem. However, for applications where extremely precise tolerances are required, this decomposition can cause dimensional changes resulting from the differences in crystallographic size of the phases. Dimensional stability can be improved with repetitive cold treatment cycles. This may be important where close dimensional tolerances are critical, such as in precision components and metrological standard references.

### 2.1.4. Processing cycles for cold treatment

The procedure for cold treatment cools the steel to a temperature between -70 and -120 °C (-90 to -190 °F), which is below the $M_F$ temperature for most steels. Cooling can be achieved in variety of ways. Liquid nitrogen can cool the parts directly or can be used indirectly to cool air or alcohol used as the cooling medium. Mechanical refrigeration and carbon dioxide ($CO_2$) as dry ice have also been widely used for this purpose. The process time is about 1 hour per 25 mm (1 inch) of cross section of material.

Technicians can cold-treat different alloys and part sizes together as long as the processing time for the largest part is used. Once the processing temperature is reached uniformly throughout the part, no further changes in microstructure are expected by increasing the processing time.

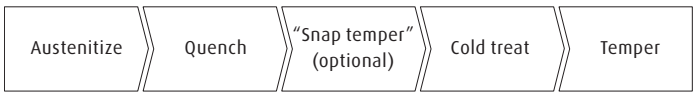
### 2.1.5. Should cold treatment be performed before or after tempering?

Research shows that to obtain the maximum percentage of transformation of austenite to martensite, cold treatment should occur after quenching and before tempering. Several researchers have reported that tempering stabilizes the retained austenite, making it more difficult to transform. So in order to achieve the highest rate of transformation, the hardening process should proceed as in figure 3 without the optional "snap-temper".

Unfortunately, some alloys cannot tolerate a delay before tempering. The freshly formed, untempered martensite is supersaturated with carbon, which makes it unstable, brittle and likely to crack. So from a commercial perspective, many higher-alloy steels are "snap-tempered" at 100 °C (200 °F) to prevent cracking, then cold-treated and tempered [13].

When precision tolerances are required, multiple cycles of cold treatment and tempering may be required to achieve the highest level of microstructural stability possible. The final processing step must always be a temper to transform any newly formed, untempered martensite.

**Figure 3: Heat treatment sequence for maximum transformation to martensite**




### 2.1.6. Cold treatment applications

- By definition, carburized steels have a carbon gradient coming from the surface. This increased carbon content will increase the amount of retained austenite and lower the $M_S$ and $M_F$ temperatures. For highly alloyed carburizing steels, these levels may be detrimental to the function of the part and need to be controlled via cold treatment.
- Precision components may rely on multiple cold treatment cycles to stabilize the microstructure and relieve internal stress so that extremely precise dimensions can be achieved.
- Improved hardness to compensate for incomplete austenite to martensite transformation may increase the hardness of a component by several points on the Rockwell C hardness scale.
- Bearings and gears may require a specific percentage of retained austenite when toughness and fatigue resistance are required.

## 2.2. Cryotreatment for wear resistance and dimensional stability.

### 2.2.1. Cryotreatment introduction

Wear resistance, toughness, hardness and dimensional stability are critical to the performance of tool steels. Wear resistance and resulting tool life of high-alloy and tool steels can be significantly increased by an appropriately applied sub-zero treatment [1–9, 12–16]. Cold treatment and cryotreatment affect steels differently, as illustrated in table 2 of the introductory section of this document.

When proper heat is combined with the correct cryotreatment process, the properties can be improved beyond those resulting from conversion of retained austenite to martensite. Experimental studies have demonstrated the effect of cryotreatment and the underlying phenomenon, but research to understand why this occurs requires sophisticated analytical equipment and extensive metallurgical knowledge.

Professor D.N. Collins at the University of Dublin has performed significant research into understanding the metallurgical effects of cryogenic treatment on tool steels. He comments:

"In addition to the well-known effect of transforming retained austenite to martensite, with the consequent increase in hardness, deep cryogenic treatment, or cryotreatment, has an effect on martensite. It causes crystallographic and microstructural changes which, on reheating, result in the precipitation of a finer distribution of carbides in the tempered microstructure, with subsequent increases in both toughness and wear resistance." [14, 15]

**Figure 4: Effect of cooling to sub-zero temperature on carbide number for D2 steel. Austenitizing temperatures 970 °C, 1,010 °C, 1,040 °C and 1,070 °C were used before hardening [15].**

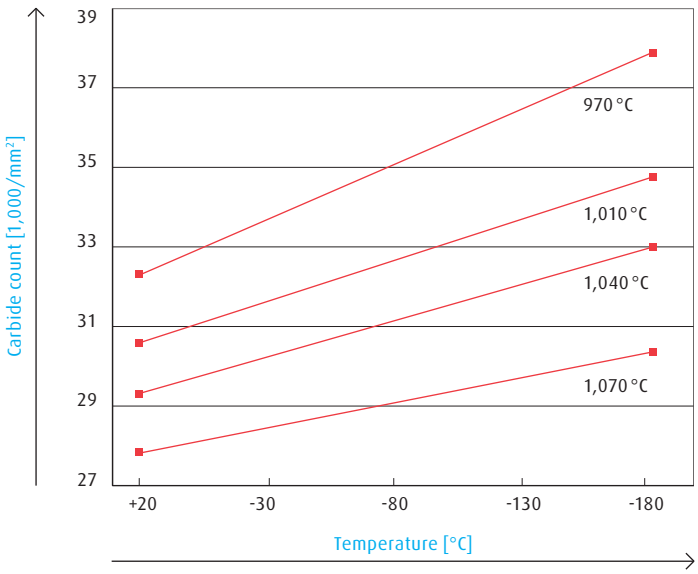
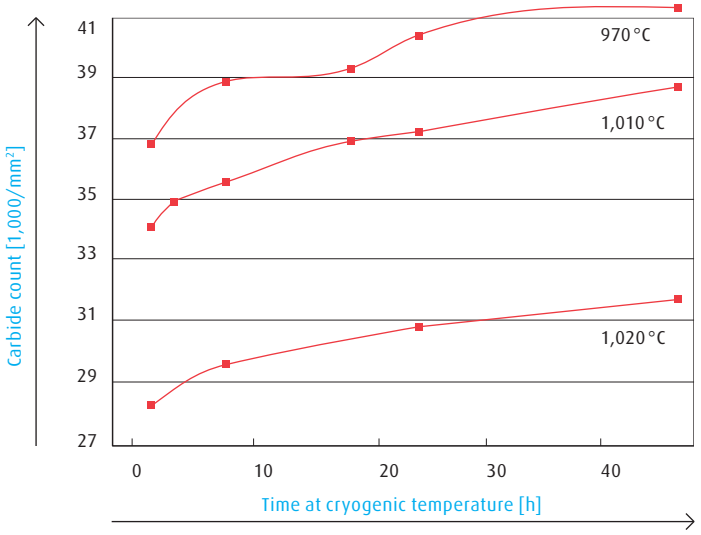



**Figure 5: Effect of holding time at -196 °C (-320 °F) on carbide number for D2 steel. Carbides were measured using optical techniques [15].**



Transition carbides that precipitate during the tempering process that follows the deep cryogenic treatment participate in the property improvement. The amount of carbides precipitated increases with decreased cryogenic temperature for D2 cold-work tool steel, as shown in figure 4. The time at cryogenic temperature significantly affects the amount of carbide precipitated, which increases with increased holding time at cryogenic temperature. This trend is shown in figure 5 [15].

The influence of holding time at temperature on hardness in figure 6 illustrates that processing times in excess of 24 hours yield a higher hardness. It is interesting to note the using the lower austenitizing temperature does not offer the highest overall steel hardness. It does, however, offer a significantly reduced wear rate compared to higher austenitizing temperatures, as shown in figure 7.

**Figure 6: Effect of austenitizing temperature and holding time at cryogenic temperature on hardness of D2 cold-work tool steel [15]**

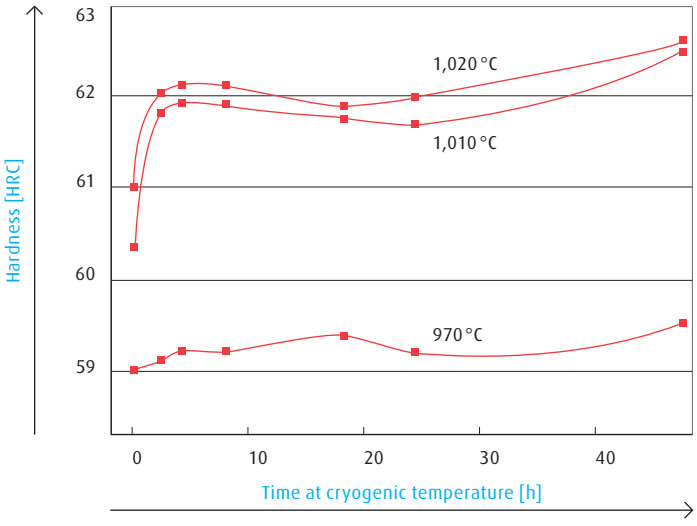
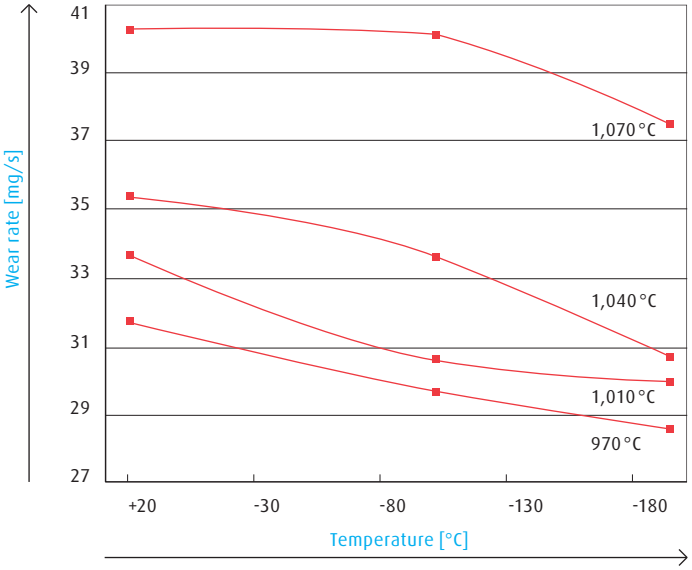



**Figure 7: Influence of temperature on wear rate for D2 steel [15]**



### 2.2.2. Processing cycles for cryotreatment

As shown in figure 4–6, steels should be hardened using the lowest austenitizing temperature possible in order to achieve the optimal structure for cryotreatment to increase wear resistance. Workers should ramp the cryoprocessing temperature slowly by 2.5 to 5 °C/min (4.5–9 °F/min) [13]. For parts with thick cross sections, it may be desirable to ramp down to an intermediate temperature and allow the temperature to become uniform before continuing with the cool-down. This procedure helps to prevent the cracking of the parts. Using gaseous nitrogen as the heat transfer medium allows close control of cool-down and warm-up rates [13].

Research shows that the deep cryogenic cycle should start with a slow cooling, continue with a fairly long soak (24 to 72 hours or more hours at temperature), and finally end with a slow warming to room temperature [1, 2, 14, 15]. The sub-zero soak temperature should be close to the liquid nitrogen temperature of -196 °C (-300 °F). The recommended heat-up process warms the material to room temperature at a rate of 1 °C/min in moving air [14]. A tempering cycle similar to that used for cold treatment follows cryotreatment since it is likely that some retained austenite will have converted to untempered martensite during the process [13].

### 2.2.3. Successful cryotreatment applications

- Cold-work tool steels have shown to respond well to cryotreatment. These steels are commonly used for tooling that will operate below 400 °F (200 °C) for applications such as cold heading, blanking and trimming. The W and D series of the cold-work steel grades were investigated by Collins and Dormer. They found that cold treatment reduced the toughness of D2 by nearly 40 %, primarily due to the transformation of retained austenite.
- Austenitic stainless steels: Cryogenic treatment may increase the strength of austenitic stainless steels. Foundries obtained excellent wear and corrosion resistance for oil pump applications using 300 and 400 series stainless steels [8]. However, they observed stress corrosion resistance to be lower after cryo-treatment of type 301 steel. In addition, the martensite formed is susceptible to stress corrosion cracking [19].
- Hot-work tool steels, including H-grade steels: Toolmakers process these metals at temperatures above 400 °F (200 °C). They typically use these metals for forging, die-casting, and aluminum extrusion dies. In one study [9], H-13 has shown a 50-% increase in die life.
- High-speed steels are used for cutting applications and include the M grades. Wear resistance increased for a variety of parts, including cutters and drills [17].
- 52100 steels/100Cr5: Bearing steels show increased percentages of fine-transition carbides with a resulting increase in wear resistance [16].
- Cemented carbide tools have shown a 2–4 times longer lifetime after cryotreatment [22]. Drawing dies, deburring tools and tool bits have been treated successfully. It is claimed that the reason for improvement is stress relaxation.

### 2.2.4. Unsuccessful cryotreatment

- Improvement is not expected for plain carbon steels or other steels that transform primarily to bainite.
- Tests on ferritic stainless steels and cast irons have not shown significant improvement.

## 2.3. Other sub-zero technologies.

### 2.3.1. Welding resistance electrodes

Cryogenic treatment of copper welding resistance electrodes increases their life by a factor of 2 to 9 [10]. Both durability and conductivity were increased. The mechanisms behind the improvement, however, are being further researched. Metallurgists suspect that stress relaxation through recrystallization is responsible for the property improvement.

### 2.3.2. Cryogenic wire drawing

When austenitic stainless steel wire is drawn at cryogenic temperatures instead of room temperature, strength improvements of 30 % in yield and ultimate tensile strength have been demonstrated. Ductility, expressed as reduction in area, was the same [18, 20].

### 2.3.3. Forming delay after quenching aluminum

Solution heat-treated aluminum can be kept soft by sub-zero soaking to prevent the room-temperature precipitation hardening that naturally occurs. This gives processors a longer delay time before the aluminum part has to be machined or undergo plastic deformation.

### 2.3.4. Uphill quenching of aluminum

The technique called uphill quenching achieves a more desirable stress profile than that which occurs due to forming and heat treatment [18].

### 2.3.5. Stabilization/cycling of Al and Mg alloys

Repeated cycles of cryogenic soaking and tempering will stabilize Al and Mg alloys [18]. Cycling occurs from 3 to 10 times between -185 °C and +125 °C (-300 to +250 °F). The rapid cycling of temperatures reduces residual stresses caused by dislocations and internal defects and promotes dimensional stability and machinability.

### 2.3.6. Cryoforming of FCC alloys

Aluminum and copper are face-centred cubic metals with considerable ductility even at cryogenic temperatures. As the Hollomon work-hardening exponent increases with lowered temperature, it means that the FCC metal can plastically deform to a greater extent by lowered temperature. So by deforming these metals at cryogenic temperatures, they can be drawn to a finer-diameter wire or thinner gauge sheet than would be possible at room temperature. However, processing at cryogenic temperatures will require more stress (force) to carry out the processing.

### 2.3.7. Cryogenic plastic deformation of FCC alloys

By plastic deformation at cryogenic temperatures, it is possible to obtain strength increases for aluminum and austenitic stainless steels. The strength increase in aluminum results from the increase in n in the Ludwik-Hollomon equation and the homogeneous stain at cryogenic temperature. For austenitic steels, the strength comes in addition from martensitic transformation induced by mechanical deformation [22].

### 2.3.8. Other metal applications and non-metal applications

Mechanical shock deformation at cryogenic temperatures is said to improve properties for stainless steels with more than 20 vol-% austenite and titanium with unstable ß-phase [20]. Sub-zero treatment has also shown to improve properties of non-metals, such as plastic bearings, wearing discs of polymer TIVAR 88, glass, plastic pellets for contact lenses, nylon gears, Teflon and golf balls [23, 24].

# 3. Equipment.

## 3.1. Basic methods of cooling.

There is a variety of methods to bring parts down to the desired processing temperature. However, all methods work on the same thermodynamic principles of heat transfer. All sub-zero equipment falls into two broad categories: direct or indirect cooling.

### Direct cooling

Processors can use liquid nitrogen effectively to achieve the temperatures necessary for cryotreatment and don't get quick cool-down rates for cold treatment. One of the most common techniques is to use a spray header system with atomizing nozzles that convert the liquid nitrogen (LIN) to very cold gas, cooling the parts as the liquid nitrogen vaporizes and warms up. The LIN is directly converted to cold gas to cool the parts. Figure 13 illustrates a direct cooling liquid nitrogen system. To avoid "spot martensite" formation, only the cold gas and not the fine droplets of LIN come in contact with the surface of the part. Technicians can control the temperature in such a box by implementing a proper nitrogen flow. Direct cooling is the most efficient means to achieve low cryogenic temperatures for controlled processing.

### Indirect cooling

Mechanical freezers are an example of indirect cooling. Nitrogen and mechanical means can both be used to cool an alcohol tank where parts could be submerged for cold treatment. Carbon dioxide in the form of dry ice has also been used to create the cooling power for cold treatment. Since the temperatures of these techniques cannot go below a temperature of about -120 °C or -185 °F, they cannot be used for cryotreatment processes.



Figure 8: Top-loading cryogenic box freezer CRYOFLEX®-B: the economical solution for small-batch-mode production volumes

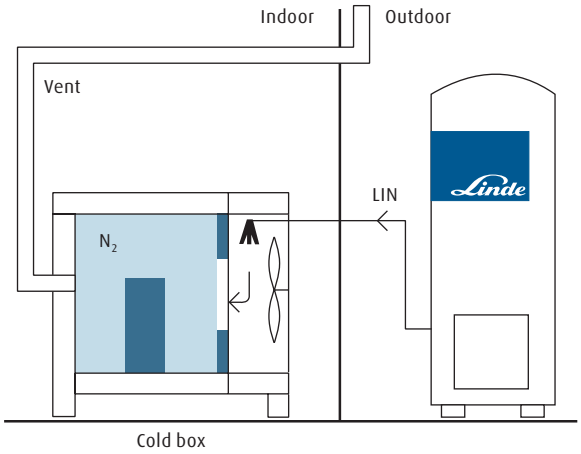



Figure 13: Outdoor LIN tank and direct-cooled cryo-chamber. Typical tank ranges in size from 500 gallons to 20,000 gallons capacity.



Figure 9: Front-loading cryogenic cabinet freezer CRYOFLEX®-C: accommodates a standard heat-treat basket



Figure 10: Front-loading cabinet freezer CRYOFLEX®-C 2800 with rack-loading capability

## 3.2. Cryogenic chambers.

Cryogenic chambers, or cryo-chambers, come in a variety of sizes and configurations. The chambers are typically designed to accommodate batch or continuous loads and come in two styles, front-loading and top-loading. Just like other heat treatment equipment, the appropriate design depends on the production volume and part configuration of a plant.

Linde offers all of these chamber types, even units with temper possibilities of up to +600 °C (1100 °F) are available.

Top-loading cryogenic box freezers – CRYOFLEX-B
The top loading configuration shown in figure 8 offers excellent use of floor space and is an economical solution for small production volumes. By using liquid nitrogen as the cooling medium, the chamber is suitable for cold treatment and deep cryogenic processing. Technicians can process different part sizes and configurations in the same load, in equipment configured to run in batch mode. The chamber is loaded manually or by using a hoist or overhead crane. The interior is made of stainless steel as is all piping and components that are exposed to liquid nitrogen and/or cold nitrogen gas.

Front-loading cryogenic cabinet freezer – CRYOFLEX-C
The chamber in figure 9 has either a side-hinged door or a guillotine door to integrate the unit into a heat treatment line. The height of the chamber can be aligned with automated part transfer equipment such as might be part of a processing line. Interior dimensions accommodate a standard heat treatment basket. Workers can also load the chamber with a hand truck.

The cryogenic cabinet freezer “C 2800” shown in figure 10 can accommodate a very large number of small parts such as saw blades, inserts, or drill bits. Parts are placed onto trays or shallow baskets and loaded into racks.

Cryogenic tunnel freezers – CRYOFLEX-T – use mesh belts to transport parts
Continuous process equipment like the one in figure 11 can accommodate large production volumes of parts with similar sizes and configurations. Easily integrated as part of a production cell, manufacturers of machined consumable items such as saw blades, knives, drill bits and end mills rely on this type of equipment to keep up with production requirements for cold treatment. Equipment manufacturers have based the design on proven technology from the frozen food industry, creating a reliable processor with readily available replacement parts.




Figure 11: Cryogenic tunnel freezer CRYOFLEX®-T: unit suitable for large production volumes of parts with similar size, e.g. knives

## 3.3. Supporting equipment.

### 3.3.1. Liquid nitrogen supply

The liquid nitrogen supply system is an integral part of any nitrogen-based cooling system. It consists of the nitrogen storage tank, the piping and the cooling chamber. The amount of liquid nitrogen (LIN) used determines the size of the storage vessel needed. Dewars or pallet tanks can supply small amounts of LIN. Dewars may be stored inside or outside. Local and national regulations require that there is adequate ventilation. Large storage vessels are always located outdoors due to their size, weight and ventilation requirements.




Figure 12: Liquid nitrogen supply and storage

LIN tanks operate on the same principles regardless of their size or the amount of LIN they store. The vessel has two walls: the inner shell made from stainless steel to accommodate the cryogenic temperatures and the outer shell constructed of structural steel. The space between the two walls contains an insulating material. Inside the tank, liquid nitrogen vaporizes to form gaseous nitrogen. This pressure drives the LIN through the piping system into the cryogenic chamber. The higher the pressure in the tank, the warmer the LIN, so the tanks should be set to the lowest practical pressure. Other processes such as vacuum heat treatment may determine the required pressure at a plant. Gaseous nitrogen rises to the top of the tank, while liquid nitrogen is drawn from the bottom. Pressure relief valves release excess pressure, and in the case of extreme pressure build-up, such as during a fire, burst disks will vent the LIN in a controlled manner. Figure 14 shows an example of a large liquid nitrogen tank and bulk delivery truck.

### 3.3.2. Liquid nitrogen piping

The design of liquid nitrogen storage tanks and cryogenic processing chambers promotes the efficient storage and use of liquid nitrogen. Equipment manufacturers construct the piping for the tanks and processing chambers only from copper, brass or stainless steel.

When designing the piping for installation, follow the most direct path with the least possible amount of bends, elbows, fittings and valves. Any valves and components must be designed for cryogenic service. Any lengths of pipe where the trapping of a rupture of the piping.




Figure 14: Outdoor LIN tank

# 4. Safety.

Safety is a key concern whenever working with industrial processes. This section serves as additional information relevant to local codes and standards. Additional safety information is available from the local Linde distributor. The main hazards working with liquid nitrogen and the cold gas it produces are:

- Oxygen deficiency
- Frostbite
- Gas expansion in a sealed pipe

## 4.1. Oxygen deficiency.

Nitrogen is a natural part of the air we breathe. As a gas, it is not hazardous until it displaces the oxygen component of air. If this happens, a person could suffocate due to lack of oxygen while still seeming to be able to breathe.

Oxygen is about 21 % of the air. If the level of oxygen drops to 15 % or less, a person will begin to feel faint or dizzy. If oxygen levels fall below 10 %, fainting can occur without warning. Oxygen concentrations below that level or sustained exposure to low levels can have permanent or fatal consequences. Liquid nitrogen expands 700 times as it converts to gaseous nitrogen. This cold gas can displace a significant amount of the air within the chamber and near the chamber doors. Since a cryotreatment chamber or tunnel is considered a confined space and can harbor an oxygen-deficient atmosphere, it is a hazard to personnel operating and servicing the equipment.

Until safety personnel have performed the appropriate air analysis and a working permit or confined space entry has been issued, personnel must not enter spaces with inadequate ventilation. Avoid breathing the cold vapors to prevent damage to lung tissue.

## 4.2. Frostbite.

Liquid nitrogen has a temperature of -196 °C (-320 °F). Skin that comes into direct contact with liquid nitrogen, the cold gas, or the transfer piping and storage vessels can suffer severe frostbite. Unintentional contact can occur due to splashing of the liquid or the severe boiling effect that occurs when technicians immerse parts into the LIN. Appropriate personal protective equipment includes well-fitting clothing with long sleeves and pants worn on the outside of boots or safety shoes, a face shield, and insulated gloves. First aid for cryogenic burns (frostbite) includes removing the victim from the source of the injury. Immerse the affected area in lukewarm water, not hot water, and wrap in a clean cloth or towel. Never rub the damaged area or apply ointments. Seek professional medical care.

## 4.3. Gas expansion hazard.

Integrate a pressure relief valve into piping systems where these systems can trap LIN. Failure to relieve the pressure build-up from the evaporating gas may rupture the supply line. Always follow the safety codes and standards when installing and operating processing equipment.

The environmental impact of this process is minimal. The release of nitrogen is generally not considered an environmental threat as it is the major component of the atmosphere.






Figure 15 & 16: Personal protective equipment.

# 5. References.


[1] R.F. Barron, Conference on Manufacturing Strategies, Volume 6, 1996, Nashville, p. 535.
[2] R.K. Barron, Tappi, May 1974, p. 137.
[3] "Dry Cryogenic Treatment Increases Machine Tool Life", Boxboard Containers, 1980.
[4] "Dimensional Tolerances and Gauging for Tooling in the Can-Marking Industry", N. Sasinowski, SME Technical paper, MR 74-945.
[5] R. Frey, Industrial Heating, September 1983, p. 21.
[6] M. Kosmowski, The Carbide and Tool Journal, Nov/Dec. 1981.
[7] Cowles superior Metal Cutting Tools Brochure, Company Literature.
[8] T.P. Sweenley, Heat Treating, Feb. 1986, p. 28.
[9] P. Paulin, Gear Technology, March/April 1993, p. 23.
[10] P.C. Miller, Tooling & Production, February 1980, p. 82.
[11] Handbook of Chemistry and Physics, 62nd edition, CRC Press, 1981-1982, pp. D161-D162.
[12] ASM Handbook, Heat Treating, Vol. 4, Metals Handbook 8th Ed. ASM International.
[13] Heat Treater's Guide: Practices and Procedures for Irons and Steels, ASM International, 1995, pp.12.
[14] "Cryotreatment – State of the art 1997 – an Update", T. Holm, AGA Internal Report.
[15] D.N. Collins, J. Dormer, Heat Treatment of Metals, 1997, No. 3.
[16] "Sub-zero Treatment of Tool Steels", A. Stojko, m.Sc. Thesis, Technical University of Denmark, DTU Department of Manufacturing Engineering and Management, 24. September 2001.
[17] "Understanding Tool-Steel Service Life", Metallurgical Services Staff of Latrobe Steele, div. Of Timken Company, Tooling & Production, December 1985.
[18] "Cryogenic Applications in Metallurgy and Related Fields", T. Holm and K.A. Orrebo, AGA Internal Report.
[19] H. Uchida et al. j. Soc. master. Sci. Jpn.; 34 (1985), p. 809.
[20] AGA Internal Research.
[21] Private communication, R. Barron, 2003.
[22] Cryoforming studies conducted at Battelle Laboratories, Columbus, Ohio USA.
[23] L. Jordansson, visit Report 830405, Projection, Stockholm.
[24] J.A. Vaccini, American Machinist and Automated Manufacturing, March 1986, p. 90.

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