

SPECIAL EDITION

# Sub-zero Treatment of Steels Technology/Processes/Equipment

# Sub-zero Treatment of Steels

## Summary

Sub-zero treatment of steels is a relatively new process that is gaining acceptance in the United States and 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 works well for only certain alloys, and explains the variation in prior research results. The sub-zero treatment processes can be grouped into three broad categories and they impact steel in the following ways:

- Shrink fitting reduces the diameter of a steel shaft so workers can readily assemble it with other components
- Cold treatment completes the metallurgical phase transformation of austenite into martensite during the hardening of steels via quench and temper heat treatment
- Cryotreatment at liquid nitrogen temperatures 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 cryotreatment technology, safety, and cryogenic processing equipment. In addition, this document will discuss some less commonly known applications of sub-zero processing.

## Table of Contents

<b>1. Introduction</b>	<b>4</b>	<b>3. Equipment</b>	<b>11</b>
<b>2. Theory and Applications</b>	<b>4</b>	3.1. Principle Methods of Cooling	11
2.1. Shrink Fitting	5	3.2. Cryogenic Chambers	11
2.2. Cold Treatment for Retained Austenite Transformation of Steels	6	3.3. Supporting Equipment	13
2.2.1 Heat Treatment Process Description	6	3.3.1 Liquid Nitrogen Supply	13
2.2.2 Increasing Hardness by Transforming Austenite to Martensite	6	3.3.2 Liquid Nitrogen Piping	13
2.2.3 Improving Dimensional Stability	7	<b>4. Safety</b>	<b>14</b>
2.2.4 Processing Cycles for Cold Treatment	7	4.1. Oxygen Deficiency or Asphyxiation	14
2.2.5 Should Cold Treatment be Performed Before or After Tempering?	7	4.2. Frostbite	14
2.2.6 Cold Treatment Applications	8	4.3. Gas Expansion Hazard	14
2.3. Cryotreatment for Wear Resistance and Dimensional Stability	8	<b>5. Remaining Issues and Closing Comments</b>	<b>15</b>
2.3.1 Cryotreatment Introduction	8	<b>6. Appendix</b>	<b>16</b>
2.3.2 Processing Cycles for Cryotreatment	9	6.1. General Discussion of Steel Metallurgy and Hardening Practice	18
2.3.3 Successful Cryotreatment Applications	10	6.2. Hardening Practice	18
2.3.4 Unsuccessful Cryotreatment Applications	10	6.3. Austenitic Phase Transformation	18
2.4. Other Sub-zero Technologies	10	6.4. Effect of Carbon and Other Alloying Elements on Martensite Start Temperature	18
2.4.1 Welding Resistance Electrodes	10	<b>7. References</b>	<b>19</b>
2.4.2 Cryogenic Wire Drawing	10		
2.4.3 Forming Delay after Quenching Aluminum	11		
2.4.4 Uphill Quenching of Aluminum	11		
2.4.5 Stabilization/Cycling of Al and Mg Alloys	11		
2.4.6 Cryoforming of FCC Alloys	11		
2.4.7 Cryogenic Plastic Deformation of FCC Alloys	11		

## 1. Introduction

Heat treatment of metals has transformed over centuries 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

As an earlier 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  $-80^{\circ}\text{C}$  ( $-110^{\circ}\text{F}$ ), and parts cryogenically treated at  $-190^{\circ}\text{C}$  ( $-310^{\circ}\text{F}$ ) using liquid nitrogen, raised questions about the causes of the improved wear resistance. However, the overall results from these studies could not be disputed and further research has been conducted to gain a better understanding of the underlying mechanisms.

## 2. Theory and Applications

Numerous factors impact how sub-zero treatments affect an alloy. Processing factors like 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.

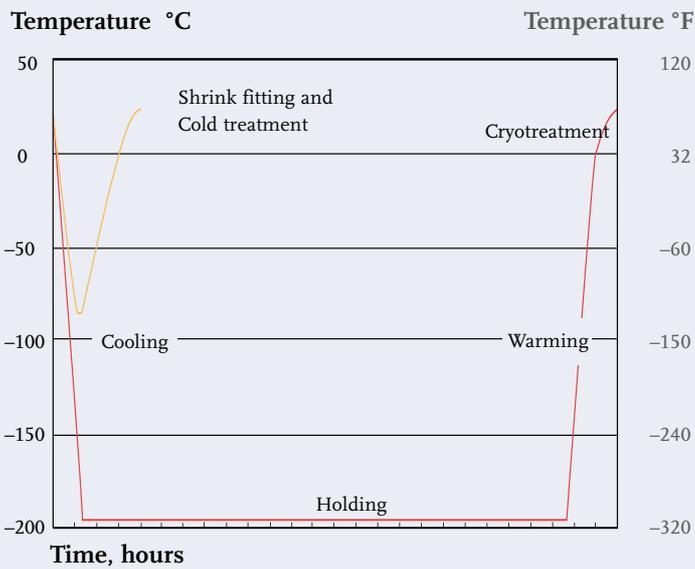
The table below discusses three sub-zero treatment applications. Sub-zero treatment falls into the broad categories of shrink fitting, cold treatment, and cryotreatment. **Figure 1** shows the differences in the basic processes as regards the time-temperature process cycle.

**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

Wear ratio is defined as  $\frac{\text{Life After Treatment}}{\text{Life Before Treatment}}$

Figure 1: Sub-zero Process Cycle Profiles



## 2.1. Shrink Fitting

Metals expand when heated and contract on cooling. The following equation describes this size change:

$$\Delta L_T = \alpha (\Delta T) L$$

Where:

- $\Delta L_T$  = change in length
- $\alpha$  = coefficient of linear expansion
- $\Delta T$  = change in temperature
- L = length

Shrink fitting is a convenient technique to assemble parts when the tolerances between pieces are very close or there is an interference fit (negative tolerances). Generally, workers cool the shaft to decrease the diameter, assemble the shaft with its related parts and allow the assembly to warm to room temperature. The coefficient of linear expansion is a physical property of a material and a listing of the values for some of the more common metals are provided in Table 4 (see p. 7).

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)	<i>Materials that showed improvement</i>	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
<i>Materials without significant improvement</i>				
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

## 2.2. 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 2.3). 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. A more detailed discussion of steel metallurgy and hardening practice is in the Appendix at the end of this document but a basic overview is provided here.

### 2.2.1 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 martensite matrix and prevent cracking of the part.

### 2.2.2 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 the steel specification sheets, heat treatment guides and standards, or metallurgical reference texts. Some austenite, designated retained austenite, is always present after hardening. Higher martensite contents and carbon percentages increase the hardness of steel as shown in Table 5. 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

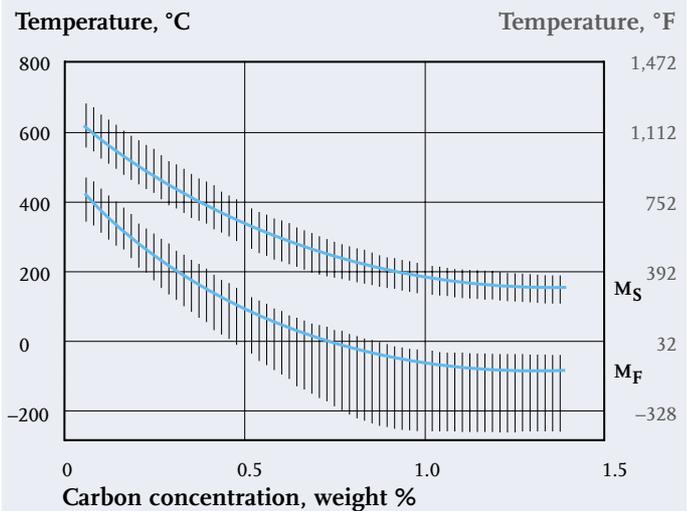


Table 3: An Overview of Sub-zero Treatment Processes for Metals

Process	Description	Parameters	Objective
Shrink fitting	Overall contraction of metals when cooled allows tight assembly of parts	$-70$ to $-120$ °C ( $-90$ to $-190$ °F) until metal is cold throughout	Temporary change in size
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	<ul style="list-style-type: none"> <li>■ Transformation of retained austenite to martensite</li> <li>■ Increase hardness</li> <li>■ Dimensional stability</li> </ul>
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

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 re-retained austenite.  $M_S$  and  $M_F$  temperatures are also depressed with increasing grain size, thus higher austenitizing temperatures can lead to higher levels of retained austenite. Cooling to sub-zero temperatures makes it possible to promote the further transformation of retained austenite to martensite to increase the hardness and strength of the steel.

### 2.2.3 Improving Dimensional Stability

Retained austenite is unstable at room temperature 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.

### 2.2.4 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 a variety of ways. Liquid nitrogen can cool the parts directly or can be used indirectly to cool air or alcohol that is used as the cooling media. 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 in.) 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. Parts are returned to room temperature by removing them from the chamber and allowing them to warm in the plant environment. A fan can be used to increase circulation around the load and reduce the warm-up time.

### 2.2.5 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 percentage 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**



**Table 4: Coefficients of Linear Expansion for Metal Alloys [11]**

Metal	a (x 10-6/°C)	a (x 10-6/°F)
Iron, pure	12	6.7
Plain Carbon Steel	12	6.7
304 Stainless steel	17.3	9.6
Aluminum, pure	25	13.9
3003 Aluminum (ASTM B221)	7.2	12.9
Copper, pure	16.6	9.2
Magnesium, pure	25	13.9
Nickel (ASTM B160, B161, B162)	11.9	6.6
Titanium, commercial	8.8	4.9
Tantalum, pure	6.5	3.6
Zinc, pure	35	19.4
Zirconium, commercial	5.2	2.9

**Table 5: Steel Hardness at Various Martensite Percentages for some Low-Alloy Steels (Reprinted Courtesy of ASM International) ASM Handbook, Heat Treatment, Vol. 4, Metals Handbook 8th Ed., 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

### 2.2.6 Cold Treatment Applications

- **Carburized steels** by their definition 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 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.

### 2.3. Cryotreatment for Wear Resistance and Dimensional Stability

#### 2.3.1. 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

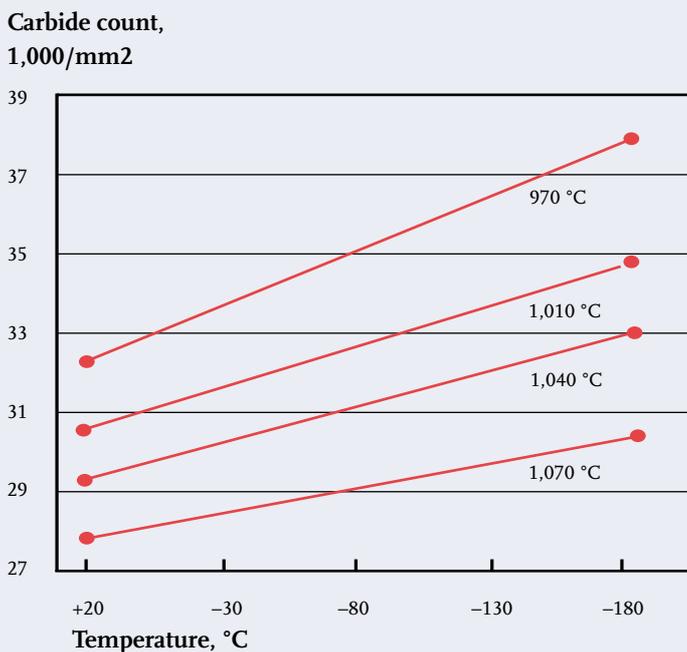
[1–9, 12–16]. Cold treatment and cryotreatment affect steels differently, as was illustrated in **Table 2** of the Introductory Section of this document. When proper heat treatment is combined with the correct cryotreatment process at liquid nitrogen temperatures, the properties can be improved beyond 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:

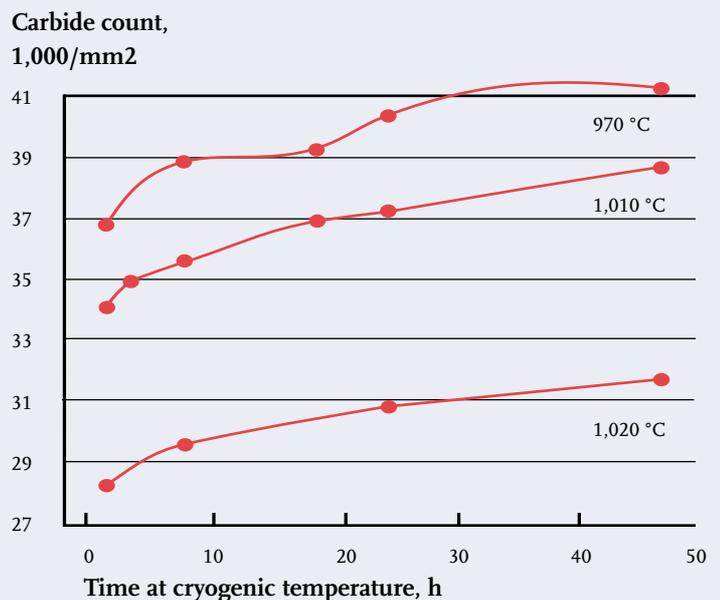
“In addition to the well-known effect of transforming retained austenite to martensite, with the consequent increase in hardness, deep cryogenic treatment, or cryotreatment, has an effect on martensite. It causes crystallographic and microstructural changes which, on reheating, result in the precipitation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

**Figure 4: Effect of Cooling to Sub-zero Temperature on Carbide Number for D2 steel. Austenitizing Temperatures 970, 1,010, 1,040 and 1,070 °C were used before Hard-ening [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]**



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 that using the lower austenitizing temperature does not offer the highest overall steel hardness; however, it does offer a significantly reduced wear rate compared to higher austenitizing temperatures, as shown in **Figure 7**.

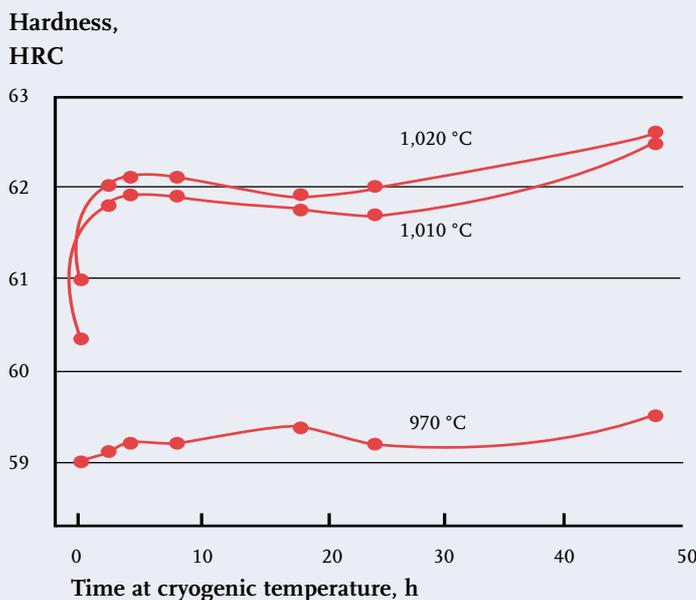
### 2.3.2 Processing Cycles for Cryotreatment

As was shown in **Figures 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 2.5–5 °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 prevent cracking of the parts. Using gaseous nitrogen as the heat transfer medium allows close control of cool-down and warm-up rates [13].

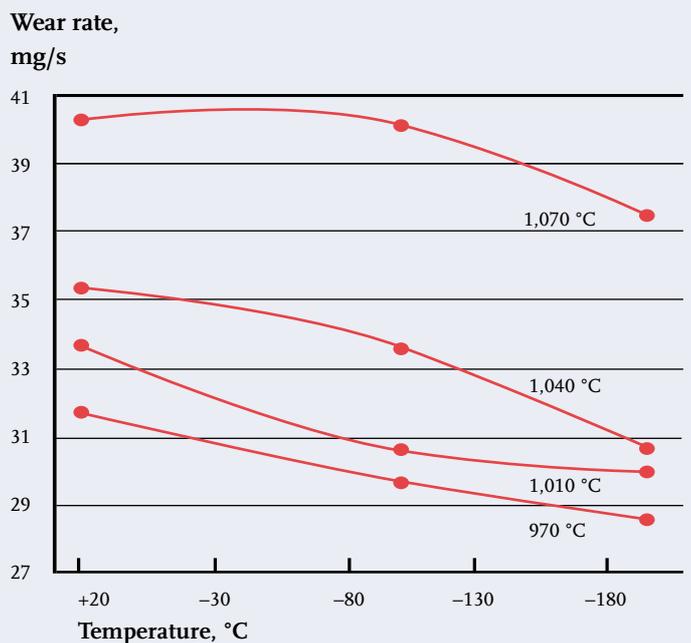
Research shows that the deep cryogenic cycle should start with a slow cooling, continue with a fairly long soak (24 to 72 hours or more hours at temperature), and finally end with a slow warming

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 some retained austenite will have converted to untempered martensite during the process [13].

**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]**



### 2.3.3 Successful Cryotreatment Applications

- **Cold-work tool steels** have been shown to respond well to cryotreatment. These steels are commonly used for tooling that will operate below 200 °C (400 °F) 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. However, cryotreatments below –100 °C (–150 °F) gave a clear improvement in toughness although the reason for this improvement was not clear.
- **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 200 °C (400 °F). They typically use these metals for forging, die-casting, and aluminum extrusion dies. H-13 showed a 50 % increase in die life in one study [9].
- **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/100 Cr 5** – Bearing steels show increased percentages of fine transition carbides with a resulting increase in wear resistance [16].

### 2.3.4 Unsuccessful Cryotreatment Applications

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

## 2.4. Other Sub-zero Technologies

### 2.4.1 Welding Resistance Electrodes

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

### 2.4.2 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].

Figure 8: Flow Stress Curves as Function of Temperature for a fcc Metal (Copper)

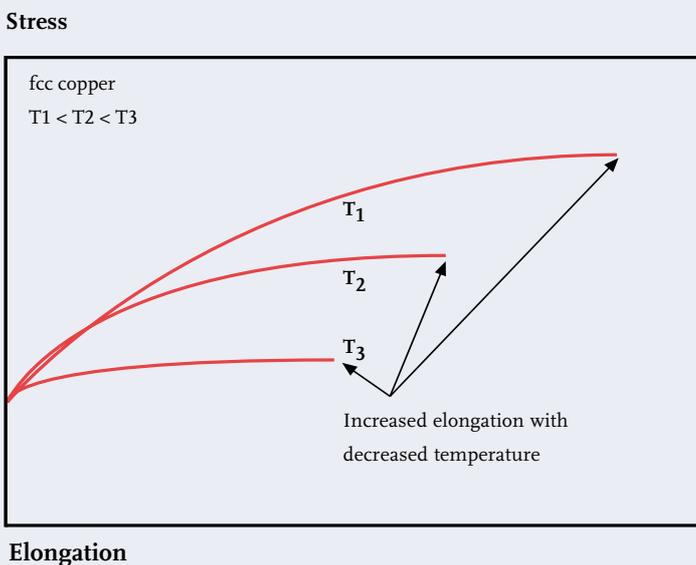
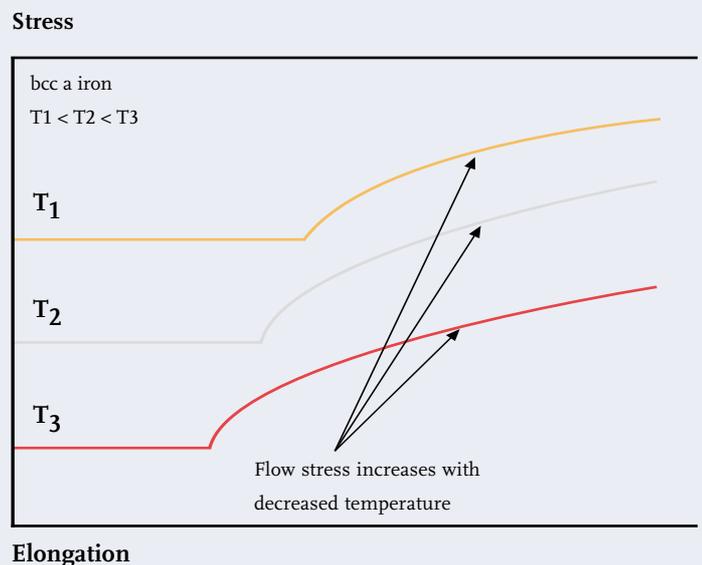


Figure 9: Flow Stress Curves as Function of Temperature for a bcc Metal (α-Iron)



### 2.4.3 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.

### 2.4.4 Uphill Quenching of Aluminum

The technique called up-hill quenching achieves a more desirable stress profile than occurs due to forming and heat treatment [18].

### 2.4.5 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  $-185\text{ }^{\circ}\text{C}$  and  $+125\text{ }^{\circ}\text{C}$  ( $-300$  to  $+250\text{ }^{\circ}\text{F}$ ). The rapid cycling of temperatures reduces residual stresses caused by dislocations and internal defects and promotes dimensional stability and machinability.

### 2.4.6 Cryoforming of FCC Alloys

Aluminum and copper are face centered cubic metals with considerable ductility even at cryogenic temperatures. The Ludwik-Hollomon equation is

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$$\sigma = k \cdot \epsilon^n$$

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where:

$\sigma$  = stress

$k$  = constant related to shear modulus

$\epsilon$  = strain

$n$  = Holloman work-hardening exponent

The work-hardening exponent,  $n$ , increases with decreasing temperature for fcc metals. Homogenous deformation,  $\epsilon_m$ , is expressed by:  $\epsilon_m = n$ . As  $n$  increases with lowered temperature it means that the 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 do the processing. This principle for a fcc metal is illustrated in **Figure 8**. For comparison the principal flow stress curve for a bcc metal is shown in **Figure 9**.

### 2.4.7 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 strain at cryogenic temperature. For austenitic steels, the strength comes in addition from martensitic transformation induced by mechanical deformation [22].

## 3. Equipment

### 3.1. Principle 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 to 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 flashes to a vapor and warms up. The LIN is directly converted to cold gas to cool the parts. Only the cold gas and not the fine droplets of LIN should come in contact with the part surface to avoid “spot martensite” formation. 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 about  $-120\text{ }^{\circ}\text{C}$  or  $-185\text{ }^{\circ}\text{F}$ , they cannot be used for cryotreatment processes.

### 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, frontloading and top loading. Just like other heat treatment equipment, the appropriate design will depend upon the production volume and part configuration of a plant. Some examples are shown below.

### Top-loaded Cryogenic Box Freezer, CRYOFLEX™-CBF

The top-loading configuration shown in **Figure 10** 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 shrink fitting, 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 the liquid or cold nitrogen gas. Some models use painted structural steel for the outer shell.

**Figure 10: Top-loaded Cryogenic Box Freezer CRYOFLEX™-CBF; the Economical Solution for Small Batch Mode Production Volumes**



### Front-loaded Cryogenic-Cabinet Freezer, CRYOFLEX™-CCF-V2

The chamber in **Figure 11** has a side-hinged door. The height of the chamber can be aligned with automated part transfer equipment such as might be part of a heat treatment processing line. Interior dimensions accommodate a standard heat treatment basket. Workers can also load the chamber with a hand truck.

**Figure 11: Front-loaded Cryogenic-Cabinet Freezer, CRYOFLEX™-CCF-V2: Accommodates a Standard Heat Treat Basket**



### Front-loaded Cabinet Freezer, CRYOFLEX™-CCF

The chamber shown in **Figure 12** can accommodate a very large number of small parts such as saw blades, inserts, or drill bits. The unit uses a programmable control system for controlled cool down, process time and warm-up. The vertical design promotes efficient cooling. Parts are loaded onto trays or shallow baskets and loaded into racks.

**Figure 12: Front-loaded Cabinet Freezer, CRYOFLEX™-CCF with Rack-Loading Capability and Features for Control Cool Down Process Time and Warm-Up**



### Cryogenic Tunnel Freezers, CRYOFLEX™-CTF use Mesh Belts to Transport Parts

Continuous process equipment like the one in **Figure 13** 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 based the design on proven technology from the frozen food industry creating a reliable processor with readily available replacement parts.

**Figure 13: Cryogenic Tunnel Freezers, CRYOFLEX™-CTF Unit Suitable for Large Production Volumes of Parts with Similar Size, e.g. Saw Blades and 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, piping, and the cooling chamber. The amount of liquid nitrogen (LIN) used determines the size of the storage vessel needed. Dewars (**Figure 14**) or pallet tanks (**Figure 15**) 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 16** is an example of a large liquid nitrogen tank.

**Figure 14: Liquid Nitrogen Storage in Nitrogen Dewars Holds Typically 50 Liters (100 Gallons) of LIN**



**Figure 15: Liquid Nitrogen Stored in a Pallet Tank Holds Typically 600 Liters (300 Gallons) of LIN**



LIN tanks operate on the same principles regardless of the size or 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.

#### 3.3.2 Liquid Nitrogen Piping

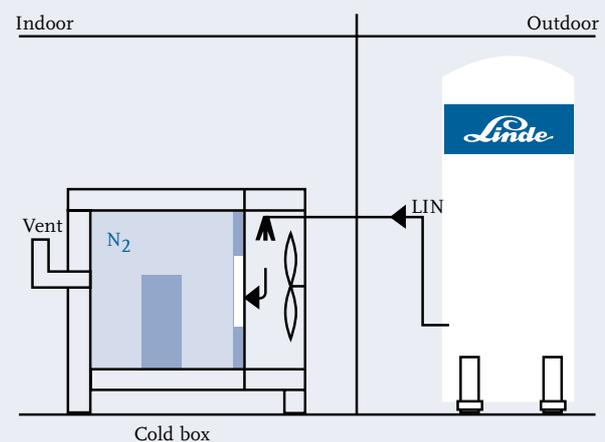
The design of liquid nitrogen storage tanks and cryogenic processing chambers promotes the efficient storage and use of liquid nitrogen. Equipment manufacturers construct the piping for the tanks and processing chambers only from copper, brass, or stainless steel.

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.

Processing plant management must balance the cost of buying and installing a specific piping system versus the cost of inefficient operation. Urethane insulated pipe offers an excellent balance between cost and efficiency for cold treatment and cryotreatment. Urethane insulation covers the rigid copper tubing and the polyvinyl chloride (PVC) shroud. Pipe fitters must silver solder the pipe joints and use special elbow fittings and valves.

For small installations operating from portable tanks, use flexible copper tubing. Check with the local gas distributor personnel for assistance in piping selection and design. Since piping availability and installation costs vary greatly in different locations, these representatives can provide a unique perspective on the project.

**Figure 16: Outdoor LIN Tank and Direct Cooled Cryo-Chamber. Tank Ranges in Size from 3,000 to 50,000 Liters or (6,000 –100,000 Gallons) Capacity**



## 4. Safety

Safety is a key concern whenever working with industrial processes. This section serves as additional information relevant to the local codes and standards. Additional safety information is available from the local gas 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 or Asphyxiation

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 cryo-treatment chamber or tunnel can harbor oxygen deficient atmosphere, it is a hazard to personnel operating and servicing the equipment. It is considered a confined space.

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  $-196\text{ }^{\circ}\text{C}$  ( $-320\text{ }^{\circ}\text{F}$ ). 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 the 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.

## 5. Remaining Issues and Closing Comments

The metallurgical community must be motivated to collect more information and technical knowledge on this important field. There have the last years been research efforts to gather this information and to build up the understanding. The **Figures 17 and 18** are examples of results obtained by research at the University of Denmark [16], partially funded by Linde Gas. This research provided the following conclusions.

- Retained austenite transforms to martensite below 0 °C (32 °F)
- The retained austenite to martensite transformation is completed on cooling before reaching -120 °C (-190 °F)
- Strain between martensite and retained austenite is relieved due to the low temperature transformation
- Sub-zero treated martensite is more stable on tempering than conventionally treated martensite. Carbon segregation and carbide precipitation was more inhibited in the sub-zero treated martensite
- The transition (ultra fine) carbides that precipitated in the sub-zero treated and conventionally treated steels differed in composition, structure and quantity
- The as-tempered hardness of the sub-zero tempered steel is slightly higher than the conventionally treated steel due to a lower percentage of retained austenite

With a better understanding of this process, a wider acceptance of cryotreatment is possible. It is unusual to find a situation in which two generally opposing properties, such as wear resistance and toughness, can be improved, particularly using steel

chemistries that are already recognized in the industry. Research and development engineers must focus their efforts on a complete understanding of the mechanisms behind the formation of the ultra-fine carbide precipitation. For applications, an understanding of the impact of balancing the properties of a particular steel will be crucial to its application.

Information specific to the effect of sub-zero treatment on tool steel and, specifically, what effects these treatments have on the percentage of retained austenite, hardness, wear, and service life must be gathered. In addition, engineers and technicians must work to standardize processing cycles including cooling and heating rates, hold times and temperatures, and temperature cycles to optimize material properties. International experts must draft standards and conduct trials to validate the processes for the more promising alloys.

Figure 17: 100 Cr 6: Dilatometry (Cooling)

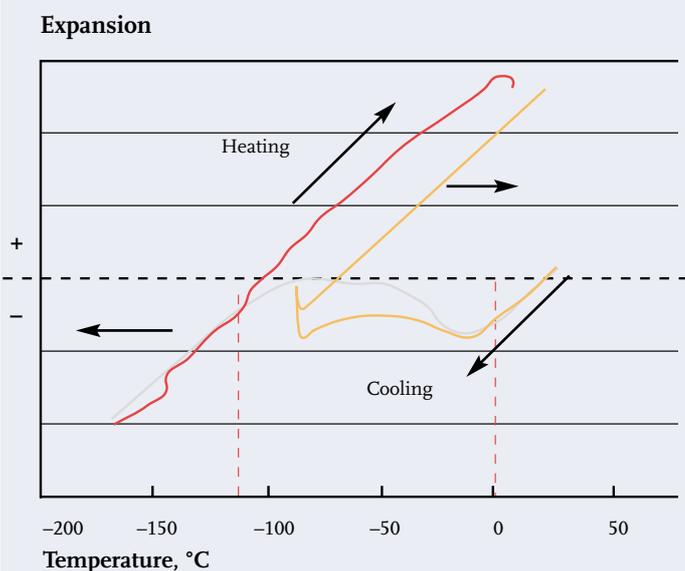
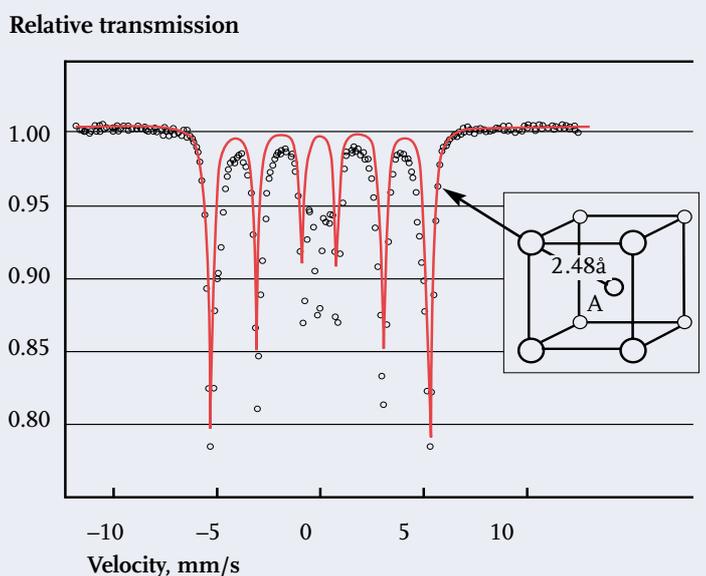


Figure 18: 100 Cr 6: Mössbauer Spectroscopy (During Cooling)



## 6. Appendix

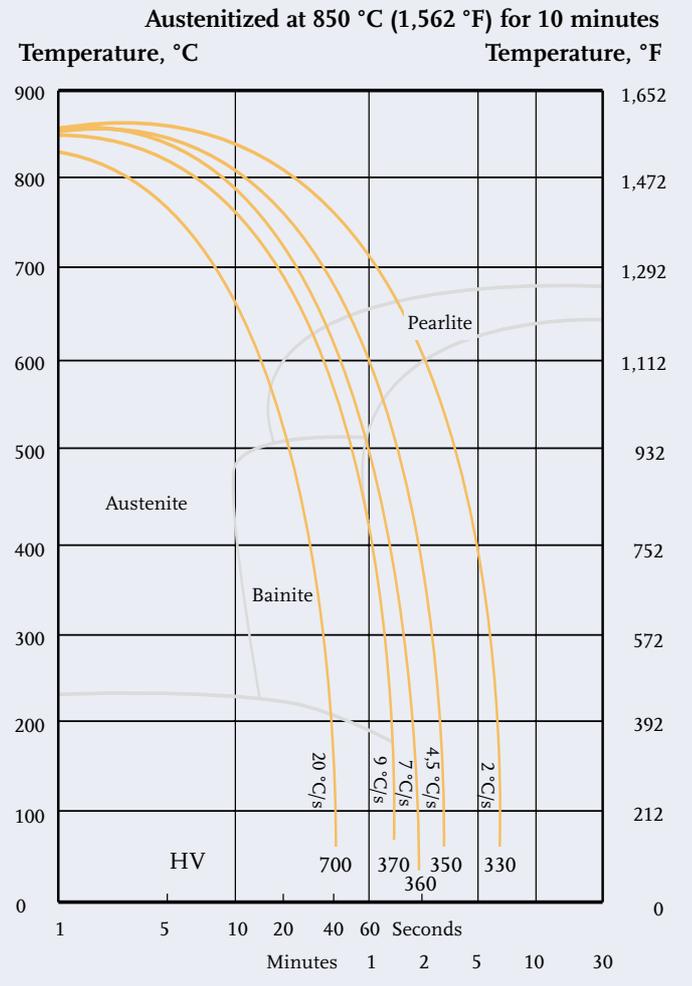
### 6.1. General Discussion of Steel Metallurgy and Hardening Practice

When steel manufacturers make steel, workers add chemical elements, such as chromium, manganese, nickel, molybdenum and carbon to the melt chemistry of iron to make the specific alloy content desired. The carbon is closely controlled since it has a very significant effect upon the final steel structure and properties. Metals and alloys transform to different phases depending on the temperature, alloy content, and cooling rate. These different phases directly affect the mechanical properties of the steel. Metallurgists use the iron-carbon diagram (**Figure A.1**) to show what structure the steel will have at different temperatures and carbon contents and a Continuous Cooling Transformation (CCT) diagram to determine what phases will form upon cooling.

The iron-carbon diagram is a useful tool to describe the phase of the metal as a function of temperature. However, it assumes that the metal is held at this temperature for an infinite amount of time. A CCT diagram is more appropriate when steel is quenched, or cooled quickly to obtain a harder structure. **Figure A.2** is an example of this process.

An overview of the properties of different steel phases is presented in **Table A.1**.

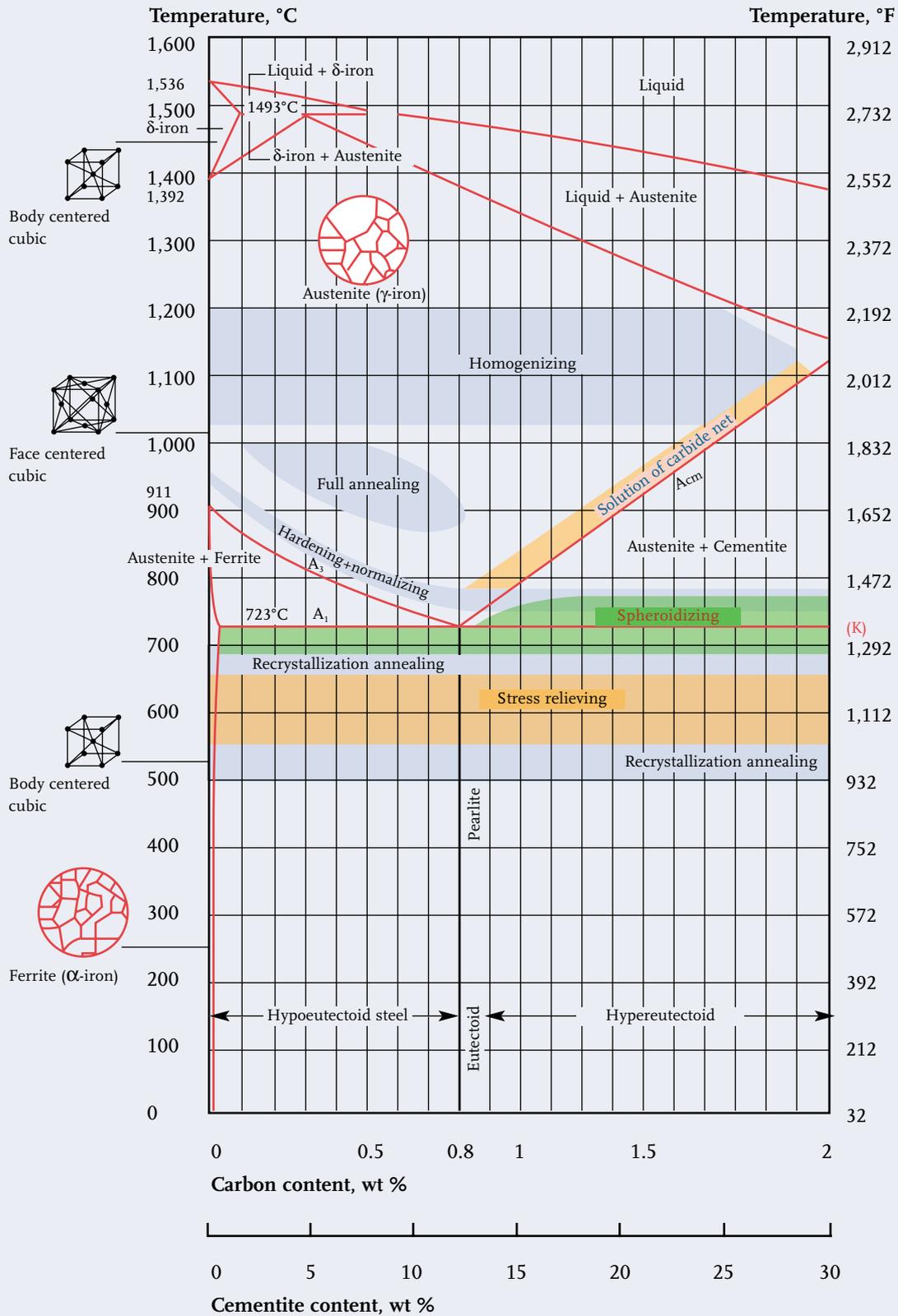
**Figure A.2: Continuous-Cooling-Transformation (CCT) Diagram for the Steel Ovako 803J corresponding to the Steel Standards AISI 52100 or DIN 100Cr6; courtesy of Ovako Steel**



**Table A.1: Steel Microstructures**

Microstructure	Symbol	Properties	Formation
Austenite	$\gamma$	Tough with generally good fatigue and impact properties	High temperature phase may be retained at low temperatures in higher alloyed steels such as tool and bearing steels. Face-centered cubic structure
Ferrite	$\alpha$		Body centered cubic structure
Cementite	$\text{Fe}_3\text{C}$	Hard and brittle	Prevalent at high carbon contents and as lamellar phase in pearlite
Pearlite		Machinable, deforms easily	Alternating layers of ferrite and cementite result of slower cooling rate allowing carbon diffusion to occur
Martensite	$\alpha'$	Hard with high yield and ultimate strength	Result of rapid cooling from austenite phase field in medium and high carbon and alloy steels. Cooling rate does not allow carbon diffusion to occur leaving it supersaturated in the matrix. Body-centered tetragonal structure

Figure A.1: The Iron-Carbon Equilibrium Diagram up to 2 wt % C



## 6.2. Hardening Practice

Steels are hardened using the heat treatment sequence of austenitizing, quenching, and tempering. The sections below detail each of the steps in the heat treatment sequence.

### Austenitizing

Austenitizing occurs at temperatures above the A3 line (See Figure A.1) in the austenitic phase field. The alloying elements go into solid solution to control the metallurgical structure upon cooling. Some carbon may be tied with alloying elements in the form of carbides that remain throughout the heat treatment cycle and can be identified in the final microstructure. These carbides are designated primary carbides.

### Quenching

Quenching is the rapid cooling of the steel using oil, polymer quenchants or water in atmospheric furnaces, or pressurized gases in a vacuum furnace. This rapid cooling transforms the microstructure of carbon and alloy steels from the austenitic structure to martensite. The differences in crystalline structure between the face-centered cubic (fcc) structure of austenite and the body-centered tetragonal (bct) structure of martensite lead to different mechanical properties. Austenite has better formability and exhibits more toughness and fatigue resistance. Martensite has a higher overall strength, but lower toughness. The speed of the transformation prohibits any change in chemical composition and since the carbon does not have sufficient time to diffuse, the martensite is supersaturated with carbon.

### Tempering

The tempering process re-heats the steel to between 200 and 600 °C (400–1100 °F). Tempering the as-quenched martensite precipitates fine carbides, which are designated transition carbides. Nucleation of these carbides relieves micro-stresses in the martensite matrix and prevents cracking of the part.

## 6.3. Austenitic Phase Transformation

The austenite to martensite transformation 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,  $M_F$ .

The  $M_F$  or even  $M_S$  temperatures can be lower than room temperature. The effect of this temperature is that the structure only partly transforms to martensite at room temperatures. The remaining structure is normally retained austenite. By cooling to sub-zero temperatures, it is possible to promote the further transformation of retained austenite to martensite.

## 6.4. Effect of Carbon and Other Alloying Elements on Martensite Start Temperature

Some constituents that inhibit the transformation of austenite to martensite include the austenite stabilizing elements of carbon, chromium, and nickel. These alloying elements remain in solution at austenitizing temperatures. There are various linear

View into hardening shop with a row of sealed quench furnaces



regression formulas to predict the martensite start temperature. One equation calculates the martensite start temperature ( $M_S$ ) for alloy steel as:

$$M_S = 539 - 423 C - 30.4 Mn - 12.1 Cr - 17.7 Ni - 7.5 Mo$$

The coefficient for carbon, 423, is an order of magnitude larger than that of the other terms in the equation which illustrates the large impact carbon has on the martensite start temperature. Changing the chemistry of the steel changes the  $M_S$  and  $M_F$  temperatures.

When higher austenitizing temperatures are used, the grain size increases and the primary carbides dissolve, thereby increasing the amount of alloying elements in solid solution. Since both increased grain size and most alloying elements depress the  $M_S$  and  $M_F$  temperatures, a higher austenitizing temperature lowers the  $M_S$  and  $M_F$  temperatures.

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