Cold Energy

Martensiting – Expansion Fitting – Delaying Age Hardening
Stress Relief – Precipitation Hardening – Dimensional Stabilizing

Table of Contents

In 1963, Cincinnati Sub-Zero Products, LLC. published a booklet entitled "Retained Austenite -Compression Block Studies Evaluate the Benefits of Sub-Zeroing". The contents were technical and attempted to update low temperature processing of steels and hardening methods being debated at the start of the 20th century.

A part of the introduction read as follows: "The timely necessity for producing superior steels has accelerated these programs. Although we have the same objectives, actually there appears to be a great duplication of effort due to the absence of adequate data retrieval and also the lack of shared information. Cincinnati Sub-Zero Products has, for a quarter century, acted as the clearing house for available disclosures involving the use of low temperatures in the field of metallurgy and. as part of our continuing effort to make available the most recent findings in this area, - - -".

We have, by necessity, abandoned efforts of categorizing and investigating in-depth analysis of such material. Heat treating, regrettably, is still something of a "black art", While we have had numerous reports of doubling or, in some cases, tripling the life expectancy of dies and tools by subjecting them to temperatures such as -120°F" supporting information has been extremely difficult to obtain. Likewise with the increase in Rockwell hardness from low temperature exposure, Or, the decreased machining time of close tolerance work from Sub-Zeroing. The contents of this booklet have been prepared in, what we hope you will find, is general guidance with accepted views. For further assistance in heat treating procedures or material selection one might contact the research and/or metallurgical staff of alloy suppliers, "The Metals Handbook" from Metals Park, Ohio is another valuable source. We know of instances where companies have given assignments to the metallurgical laboratory at local universities, for a stipend, and received some gratifying results. Frequently, the time and effort expended to research problem results in considerable cost savings and a better product.

After the material and procedure have been established, we are confident we can help in your equipment selection. We'll consider the composition, weight, temperatures, time and physical criteria to recommend the product(s) to represent your best investment.

We take this opportunity to thank you for your interest in our company and we look forward to being of service.

EXPANSION ASSEMBLY

Coefficient of expansion is a temporary change in property that can be used to advantage for requirements or service conditions of the material at ambient or elevated temperatures. Manufacturers and rebuilders of machine tools, heavy equipment, engines, off road vehicles and even low cost consumer products are realizing considerable savings through the use of low temperature for expansion assembly of parts.

When the tight fitting of two members, such as a bushing onto a shaft, is required, three basic methods are available: Press, shrink, or expansion fit. Only the latter offers the advantages of maximum results at lowest cost.

All three techniques depend upon the difference in size (interference) between the two parts to be coupled. For example, a shaft will be machined slightly larger than the I.D. of the hub into which it will be inserted. Press fit involves the use of physical force to assemble the parts. Shrink fit necessitates the expansion of the outer member through heat, and assembly is accomplished when the part shrinks on return to room temperature. Expansion fit utilizes the characteristic of metals and other materials to shrink at low temperatures and expand again on return to ambient temperature.

Each method has its advantages and limitations as depicted:

Equipment Needed	Press Fit	Shrink Fit	Expansion Fit
Physical damage in assembly	Large Press	Furnace	Low-Temp Chamber
Metallurgical change during preparation	Possible Deformaton	None	None
Change in mechanical properties of material	None	Possible recrystallization depending on temperature difference	Degree of austentic transformation
Surface finish required	16-32 Micro	Coarser finish	Coarser finish
Lubricant necessary	Yes	None	None
Importance of time at temperature		Critical	No Importance
Effect of temperature		Galling & Scaling	None
Handling & Positioning	Handling not difficult. Positioning set-up critical	Difficult	No Problem
Assembly time		Rapid & exact positioning necessary	Sufficient time for positioning
Removeability	Press out	Difficult	Less Difficult
Effect of inservice time (reliability)	Possible strain corrosion and cracking	Possible strain corrosion and cracking	None
Cost man hours, equipment etc.	High	Moderate	Low
Results	Inconsistent, varying torque	Predictable, high torque	Predictable, highest torque
Limitations	Unusually large/small parts are difficult to handle	Large parts hard to handle	Small diameters difficult

An actual example of low temperature expansion assembly will best illustrate its advantages.

The expansion fitting of large size shafts to crank gear hubs is being used at National Rubber Machinery Company, with considerable saving in time, labor and material.

The previous method of assembly involved the use of a 150-ton press and required as many as twenty man-hours. By means of a Cincinnati Sub-Zero Mechanically Refrigerated Chamber, the time required for the same assembly has been reduced to between 4-1/2 and 6 man-hours. The torque transmission factor has been increased; the problems of galling, distortion, and improper bonding have been eliminated.

Additional man-hours have been saved in the finishing of the mating parts, which originally required from 26 to 32 micro finish to obtain the proper press fit. In this case, the shaft is shrunk at -150°F, which provides concentration of .00511. The shaft is inserted to the proper depth in the hub and allowed to expand. The result is a tight and secure fit, with an interference of .01211 at room temperature.

For guideline and comparative purposes, the approximate shrinkage of rings or cylinders 2" in diameter, chilled from 70°F. to -70°F., and to -120°F. will vary with the metal as shown:

	-70°F	-120°F
Tool Steel	.0016	.0026
Phos. Bronze	.0024	.0036
Alum. Bronze	.0024	.0036
Brass	.0028	.0040
Aluminum	.0034	.0046
Magnesium	.0034	.0047

To determine the linear contraction for shrink fit:

The contraction in inches will be equal to the length, or diameter, in inches of the part at room temperature multiplied by the coefficient of linear contraction and multiplied again by the ~ temperature change.

The total temperature change is the temperature of the material in degrees Fahrenheit when loaded into the chamber added to the temperature in degrees Fahrenheit to which the material will be chilled.

For example, the linear contraction of a 3" bronze bushing chilled from 80°F. to -100°F. will be approximately .0054" (3" x .00001 x 180°) .In many shrink fit app1izations the mating part is heated below its tempering temperature to provide a tighter interference fit.

HEAT TREATING

Service conditions dictate the type of steel specified for use in the manufacture of tools, machine parts, mountings, or containers. The design engineer is concerned with the mechanical properties the metal exhibits at various operating temperatures, under changing load and stress conditions, and therefore the life expectancy of the finished product.

Speaking in broad terms, the mechanical property that is most important is "strength". This and other characteristics such as elasticity, ductility, creep, hardness, and toughness are all associated with the ability of the material to resist mechanical forces.

The mechanical properties of steel, and nonferrous metals, are dependent upon three factors; its original composition, the heat treatment or processing it received, and service conditions it must withstand. The composition may include, in addition to the base metal, carbon, manganese, phosphorus, sulfur, silicone, or many alloying elements. Combinations of these result in metals having differing properties such as hardness, ductility, corrosion resistance and other factors that will affect performance.

Regardless of the chemical composition, the physical characteristics of the metal can be altered through heat treatment, the cooling cycle, and the work treatment it receives after the first heat phase.

Initially, steel is composed of a compound of iron and carbon (iron carbide and FE3C) distributed in a matrix of iron (ferrite). These two substances when combined constitute pearlite. It is important at this point, to note that both pearlite and ferrite are soft. By tracing the processing of a typical steel it will be demonstrated that these soft substances can be transformed into a useful product.

Material	Linear Expansion (per unit length per deg. F)
Aluminum	0.00001244
Antimony	0.00000755
Bismuth	0.0000077
Brass	0.00001
Bronze	0.00001
Cobalt	0.0000683
Copper	0.00000900
Gold	0.00000778
Iridium	0.000000361
Iron, cast	0.00000655
Iron, wrought	0.0000661
Lead	0.0000163
Magnesium	0.00001294
Manganese	0.00000294
Molybdenum	0.00000700
Nickel	0.00000496
Platinum	0.00000633
Steel, carbon	0.00000361
Tantalum	0.00000361
Tellurium	0.0000093
Tin	0.00001496
Titanium	0.0000049
Tungsten	0.00000239
Vanadium	0.0000043
Zinc	0.000017

When steel is heated to about 1320°F. and above, the carbide and co-existing iron go into solid solution with each other and form a structure existing mainly at elevated temperatures, designated austenite. By this means some of the pearlite is transformed into a new phase. The austenite, like the original components, is soft.

When the metal is allowed to cool, or quenched, some of the austenite transforms to another new constituent, <u>martensite,</u> and we finally have a hard substance. At this point, on reaching room temperature, the steel is now composed of three constituents: A small amount of martensite, a large portion of the original pearlite, and all of the original ferrite.

If the initial heat temperature is increased above 1320°F. a greater percent of pearlite is transformed to austenite and ultimately into martensite. At this point the original ferrite still remains.

If the heat is increased even further, all of the pearlite is transformed and another change takes place. As the temperature of the austenite rises, it begins to enter into the ferrite and form more austenite.

After quench to room temperature the new material is composed of a large amount of martensite, no pearlite, and less than the original amount of ferrite.

At further elevated temperatures, the steel becomes wholly austenitic and, after quench, is almost 100% martensitic. The steel has now reached the maximum hardness under the conditions described, assuming rapid quench. If however, the steel is quenched slowly, the process reverses itself as the material goes through the various temperature phases and the room temperature product is once again composed of percentages of the same constituents present before heating. The amounts of martensite, pearlite and ferrite depend on the rate of cooling. The slower the process, the greater the reversal. It must be emphasized at this point that steels behave differently depending upon the carbon content and other elements introduced. Therefore, the high temperature and the quench time will vary with each type. Furthermore, complete austenitic transition is rarely accomplished and is possible only under ideal conditions.

As typical in quenched condition, hardened steels contain an amount of retained austenite, making the material softer than desired, and too brittle. These conditions can be changed to additional hardness and toughness by tempering.

TEMPERING
Tempering, or modification of the steel, may be accomplished in a number of ways. For example: By re-heating the material from 100°F to 400°F, the martensitic structure (tetragonal) may be altered and "transition carbide" (cubic structure) is precipitated; heating to 450°F to 700°F retained austenite is transformed to banite, a harder substance; elevating the temperature to 700°F to 1000°F results in precipitation of cementite form of carbide; the temperature range of 1000°F to 1300°F produces a greater cluster, or mass of cementite. This holds true for plain carbon steels; in alloy steels this temperature may possibly cause the formation of alloy carbides.

So far, this discussion has been concerned with the transformation of austenite and its influence on the hardness of the end product. One additional change occurs during the process of decomposition; that of dimensional growth.

DIMENSIONAL CHANGE
Due to differing grain structures characterizing austenite and martensite, the austenite having the greater density, transformation is accomplished by a volume increase. An increase of 1.5% may be expected.

Since most hardened steels contain between 2 and 10% retained austenite, the volume increase may then be as much as 10% of the original 1.5%, or an over- all increase of 0.03 to 0.15%.

This expansion in size is somewhat offset by the effect of tempering on martensite. Elevated temperatures cause it to contract permanently so that the actual volume change is the difference between the degree of expansion of austenite on transformation and the contraction of martensite during tempering.

Therefore, in order to predict the exact amount of dimension change that will occur during tempering, the precise amount of retained austenite must be determined. This is possible under laboratory conditions but impractical on a production basis.

NATURAL AGING

The tempering methods we have referenced are forms of artificial aging; time alone would accomplish the same change to a certain degree. Retained austenite, an unstable substance, tends to transform naturally and, after a period of time, the process will complete itself. The steel will approach a 100% martensitic condition. Because of the time required for natural aging it is an impractical means of increasing hardness and imparting dimensional stability. In fact, insufficient natural aging may be detrimental to finished products as growth may occur in service and thus shorten the useful life.

In view of the fact that the two qualities -hardness and dimensional stability contribute to the useful life expectancy of a tool or machine part, it would appear that a process more easily controlled and more predictable than the methods described would be of great benefit to industry.

We direct your attention to the section entitled Sub-Zeroing.

THE TRANSITORY EFFECT OF TEMPERATURE CHANGE

Some mechanical properties of alloys will increase as their temperature is lowered. Just as most solids become softer as the temperature is raised, a reverse of the direction has an opposite effect in many cases - basically with an increase in hardness accompanied by a decrease in plasticity. Frequently, the ability to withstand static loading, without fracture, increases. One example of the effect on yield point, percentage of elongation, tensile strength and reduction of area is shown with type 304 stainless steel. In annealed conditions, it is an example of austenitic chromium-nickel steel in common use for low temperature service.

The increase in properties often includes modulus of elasticity, and the resultant embrittlement makes many alloys unsuitable for service at low temperatures.

Temperature	Yield Point	Tensile Strength	Elongation per Inch	Reduction of Area
+70°F	32,000 PSI	85,000 PSI	75%	80%
-60°F	45,000 PSI	140,000 PSI	65%	75%
-150°F	50,000 PSI	160,000 PSI	55%	70%
-300°F	85,000 PSI	220,000 PSI	45%	60%

MODULUS OF ELASTICITY

The elastic properties of ferrous alloys change with decreases in temperature as determined by the slope of the elastic portion of the stress/strain curve obtained in tensile testing. In this evaluation the strain produced is proportional to the stress applied. The precise value depends upon the tempering, annealizing or normalizing treatment.

CONDUCTIVITY

Electrical and thermal conductivity generally increases as temperature is lowered. The electrical resistance of many metals practically diminishes when measured at near absolute zero (-459.4°F.). At this point they become superconductors.

COEFFICIENT OF EXPANSION

All metals and alloys possess lower coefficients of expansion at low temperatures and, because of the phase change, the degree varies over the temperature range. Some FE-NI alloys are inconsistent, having remarkably small coefficients of expansion, making them suitable for permanent dimensional standards.

The changes that take place as the temperature decreases are of the same order, or less, than those which occur due to an equivalent increase. For this reason, low temperature service conditions present no particular problem. The effects are predictable.

The advantages of increased strength have been referenced to static loading.

A possible disadvantage in change of property may be the diminishing of elongation values accompanied by a diminishing percentage of reduction of area. The effect of shock loading must therefore be taken into consideration.

Toughness implies the ability of a part to absorb energy, without fracture, under shock conditions. Brittleness, which is just the opposite, implies a tendency to fracture without deformation. Sub-Zero temperatures have a direct effect on the tough/brittle characteristics of ferrous alloys. The expected increase in brittleness and decrease in toughness poses no particular problem, if the alloy to be used possesses a transition temperature below that of the in-service condition.

The brittle phase is not reached and stable performance can be expected. The decrease in toughness does not hold true for all alloys. There are exceptions, such as the various grades that have been accepted as ideal materials for low temperature applications.

Although these references are not specifically concerned with materials for low temperature service, we have provided a comparative list of some typical materials and their properties at -320°F.

Material	Tensile Strength	Yield	Elongation
Aluminum Alloys			
2014-T6	82,000 PSI	73,000 PSI	14%
3003-H14	33,000 PSI	25,000 PSI	30%
6061-T6	60,000 PSI	44,000 PSI	23%
7075-T6	98,000 PSI	88,000 PSI	11%
Stainless Steels			
301 (XFH)	315,000 PSI	235,000 PSI	40%
304 annealed	220,000 PSI	60,000 PSI	20%
Alloy Steel			
9% Ni	180,000 PSI	140,000 PSI	20%
Titanium Alloys			
Ti-6A1 (ELI)	220,000 PSI	205,000 PSI	12%
Inconel			
Inconel	240,000 PSI	215,000 PSI	12%

WHAT IS HARDNESS?

0The term "Hardness, " when applied to metals is of ten confused with other physical properties which, at times, accompany a change in its relative value. In the strictest sense, hardness is the measure of resistance of material to plastic deformation and it is usually gauged by permanent indentation. It may refer also to stiffness, temper, or resistance to scratching, abrasion or cutting. The important point in the analysis of hardness rating is PERMANENT DEFORMATION.

As has been stated, other qualities may change with a change in hardness but they must not be considered as inherent or even as a necessary result of such a change.

Frequently, TOUGHNESS is used interchangeably with HARDNESS due to the fact that a material which demonstrates either quality stands up well under adverse service conditions. Toughness, however, is the ability of material to absorb energy and to deform plastically before fracturing; this may also include tensile strength. When we consider the TOUGH characteristics of rubber as compared with metal the difference becomes immediately obvious.

BRITTLENESS is the third physical property lending confusion to the subject. It is that quality of material which leads to crack propagation WITHOUT APPRE- CIABLE PLASTIC DEFORMATION.

So, in the first case we are concerned with deformation, in the second the amount of deformation before fracture, and the third is fracture without deformation.

HOW IT IS MEASURED

There are numerous methods for measuring hardness; however, three are generally accepted as standard.

BRINELL is a test for hardness of material and involves the forcing of a hard steel, or carbide ball, of specified diameter into the material under a specified load.

ROCKWELL is based on the depth of penetration of a specified fixture into the specimen under fixed test conditions.

VICKERS is an indentation hardness test employing a 136° diamond pyramid under variable loads.

The type of material to be tested determines the specific test to be used Each has advantages and the results can be converted to the scale of the other two.

FACTORS GOVERNING HARDNESS

The hardenability of steel is governed almost entirely by its chemical composition at the austenitizing temperature and the grain size of the austenite contained at the moment of quenching.

Carbon content is perhaps one of the strongest aids to hardenability, especially in the presence of other alloying elements. The percentage of carbon dictates the possible amount of austenite that can be achieved and, this in turn, through transition, is responsible for the final martensitic content. As is the case with 100% martensite, there are distinct disadvantages to the increase in carbon content beyond a point established by the end use of the material. With an increase in carbon there is also an increase in brittleness at, or below, room temperature. A high percentage of carbon may increase the hardness to a point where machining and cold working are almost impossible. With each advance in carbon content there is additional susceptibility to overheating in hot working as well as the probability of cracking and distortion during heat treatment.

In short, an increase in carbon content is not always the answer to achieving a desired hardness level.

HARDENING PROCESSES

Steel parts are subject to varying service conditions and, in order to withstand certain conditions, they are hardened to differing degrees and methods. In some cases the entire part is hardened with the shell and the core treated equally. In many cases it is important that the hardness be on the surface only and have the core retain the necessary elasticity for conditions requiring great tensile strength.

There are six predominant methods of achieving hardness:
1. Age hardening
2. Case hardening
3. Flame hardening
4. Induction hardening
5. Precipitation hardening
6. Quench hardening

 Since Sub-Zeroing has been referred to as artificial aging it shall be considered last.

CASE HARDENING

The hardening of a ferrous alloy so that the outer portion, or case, is made substantially harder than the inner portion, or core, is called Case Hardening. It is usually accomplished in one of four ways:

CARBURIZING, or the introduction of carbon into a solid ferrous alloy by holding above the temperature at which austenite begins to form during heating. (Commonly abbreviated as Ac_l.)

CYANIDING, the introduction of carbon and nitrogen into the alloy by holding at the carbonizing temperature, but in contact with molten cyanide, then quench hardened.

CARBONITRIDING is accomplished by holding the alloy above Ac_l and in an atmosphere containing hydrocarbons, carbon monozide, and ammonia, then quench hardened.

NITRIDING is the introduction of nitrogen into a solid ferrous alloy by holding below Acl and is also the case of ferric steels in contact with nitrogenous material such as ammonia, or molten cyanide. Quenching is not required. This type of surface hardening provides a marked increase in fatigue resistance in addition to the hardening effect. It makes possible the reaching of fillet areas where high stress concentration is most likely to occur.

Considerable dimensional change and distortion may be the result of nitriding and, for this reason, only parts having substantial thickness should be treated.

QUENCH HARDENING

Quench hardening is referred to as the hardening of a ferrous alloy by austenitizing and then cooling rapidly so that some, or all, of the austenite transforms to martensite. The austenitizing temperature for hypoeutectoid steels is usually above Ac_3, or the point at which transformation of ferrite to austenite is completed during heating. For hypereutectoid steels it is usually between Ac_l and Ac_{cm}, or the temperature at which the solution of cementite in austenite is completed during heating.

INDUCTION HARDENING

This is effectively a process of quench hardening, whereas the heat is generated by electrical induction following the method of Nitriding, but there is an increase in the fatigue life because of the higher surface hardness and also because of the residual compressive stresses in the outer portion of the case. Straight carbon or extremely low alloy grade steels, are most amenable to induction hardening.

FLAME HARDENING

This is another process of quench hardening but one where the heat is applied directly by a flame.

SPARK HARDENING

Spark hardening is a by-product of electrical discharge machining. When a carbide tool is used to cut hard tool steel, it has been found that a few small particles of carbide are driven into the surface of the tool.

This transfer of carbide can be accelerated to produce a thin layer of adherent carbide on the tool surface through the use of a carbide rod that is caused to make and break contact with the tool at 120 cps by means of a vibrator.

The equipment is the same as that used in spark machining, however the potential is reversed so that the work piece is the cathode. The process is best accomplished by operation in air.

The carbide rod is generally about 1/8" diameter and is composed of 12% Co (Cobalt) and 88% WC (Tungsten Carbide).

Finish	Volts	C. Microfards	Laver
Coarse	150	150	.020
Medium	80	60	.008
Fine	50	30	.004

The depth of the hardened layer is increased and the surface finish becomes poorer as the energy dissipated per unit of time increases.

In treating the tool, the vibrator is held in the hand and is traversed over the surface of the tool for about ten minutes. It is imperative that the vibrator does not come in contact with the cutting edge and the tool is not ground or lapped after treatment. Improvements in tool life from 1.5 to 63 times have been reported.

Surface hardness to 120 Vickers can be achieved by use of a graphite tool in lieu of tungsten carbide. In this case, the carbon content of the surface is increased and a layer of high beta martensite results due to the very rapid cooling rate. The martensitic transformation is accomplished even more thoroughly if the entire process is performed in a Sub-Zero chamber, due to the fact that the cooling rate is even more rapid.

This again illustrates the basic rule for hardness. Both the carbon content and the martensitic percentage have been increased and has been done without affecting the part in any way. It still retains the toughness necessary for hard service. The change has been effected only on the surface.

PRECIPITATION HARDENING

In these situations, hardening is caused by the precipitation of a constituent from a supersaturated solution and is a process where Sub-Zeroing is of special benefit. "Trapped" carbon produced in a supersaturated solution of ferrite results in achieving desired martensite. It is the ability of the steel to keep the carbon in solution enabling it to undergo the martensitic transformation that is the

important factor in this type of hardening. With precipitation hardening steels, and all austenitic steels except stainless, low temperature treatment to -120°F. is not only beneficial, but necessary.

AGE HARDENING

NATURAL AGING in a metal or alloy brings about a change in properties that occurs slowly at room temperatures.

ARTIFICIAL AGING is the speeding up of the process by holding above room temperature. This includes aging at two or more temperatures by steps, and cooling to room temperature after each (which is also referred to as INTERRUPTED AGING) and, when the temperature is increased continuously without the return to ambient, it is called PROGRESSIVE AGING.

OVERAGING occurs in either of these processes when the time and temperature are greater than those required to obtain maximum transformation. It causes the property to be altered in the direction of the initial value, or a return to a soft, unstable condition.

STRAIN AGING is aging induced by cold working at a temperature lower than the recrystallization temperature. This eliminates the possibility of over aging.

QUENCH AGING is aging induced by rapid cooling after solution heat treatment, or the heating of an alloy to a suitable temperature and maintaining that temperature long enough to allow one or more constituents to enter into solid solution. After rapid cooling, the alloy is left in a supersaturated, stable state. At this point it is ready for maximum transformation through Sub-Zero.

CONCLUSIONS

As we have seen from the methods for hardening, all techniques involve the use of heat. The degree of attained hardness depends on the amount of heat and the rate of cool down or quench.

These processes are, in effect, heat treatment. Since heat treating is properly defined as the heating and quenching of metal for the purpose of changing its properties, and with consideration for manufacturing operations which, in themselves, increase hardness, it becomes obvious that during these heating and cooling cycles there will be an alteration of properties, regardless if heat treatment was the objective.

Hardness in steel is based on the two step change which takes place when austenite is transformed. To accomplish this transformation it is necessary to fulfill two prime considerations: I. The metal must be put into austenitic condition, and 2. It must be cooled rapidly enough to suppress the precipitation of cementite while attaining the status of beta martensite.

Thus, hardness is obtained in steels which have sufficient carbon content, and have been transformed to the maximum amount of beta martensite. When striving for hardness, it is advantageous to achieve it in a manner which will not risk the reversal, or change, in basic properties. Since the carbon content

cannot be altered without a sacrifice in toughness, it is obvious that it is necessary to increase the percentage of beta martensite.

Assume that a Rc of 50 is required. It can be obtained by transforming 30% carbon steel to 99.9% martensite, 35% carbon to 95% martensite, 40% carbon to 90% martensite, 45% carbon to 80% martensite, or 60% carbon to 50% martensite. As has already been stated, the carbon content is held to the minimum required to do a specific job, and one example taken from the records of the American Society for Metals Committee on Hardenability shows that the additional hard- ness desired may be best gained by additional transformation.

Steel with a carbon content of 40% and 50% martensitic structure will have a Rockwell C rating of approximately 45, while the same steel with 80% will have a rating of 47. 90% martensitic structure results in a rating of with 95% producing a rating of 55 and 99.9% increasing to 58. Obviously the greatest percentage of Rockwell C increase occurs as the alloy approaches 100% transition.

Standard or conventional heat treat methods, when positively controlled, can produce martensite in the higher levels. However, only through the use of Sub-Zeroing, can the highest level be attained. And, there is no possible chance of reversal through chilling, regardless of how long the material is held at temperature, nor how low the temperature setpoint.

ADVANTAGES OF SUB-ZEROING

ULTIMATE TEMPERATURE

Unlike the use of heat, requiring precise temperature control in order to avoid reversal, successful transformation through Sub-Zeroing is dependent only on attaining the minimum low temperature and is unaffected by lower temperatures. So long as the material is chilled to -120°F. transformation will occur. Additional chilling will not cause reversal.

TIME AT TEMPERATURE

After thorough chilling, additional exposure has no adverse effect. In the use of heat, the holding time, as in the case of the degree attained, is critical. Here, an advantage will be found in that materials of different compositions, and of different configurations may be chilled at the same time even though each may have a different high-temperature transformation point.

RETURN TO AMBIENT

The warm-up rate of the chilled material is of little importance so long as uniformity is maintained and gross temperature gradient variations are avoided. Too slow re-warm is impossible.

The cool-down rate of the heated piece has a definite influence on the end product. The formation of martensite from solution heat assumes immediate quenching in order that the austenitic decomposition will not result in banite and cementite. In the case of a large piece consisting of thick and thin

elements, it is obvious that all areas will not cool at the same rate. Whereas the surface and thin areas may be highly martensitic, the slower cooling core may contain as much as 30% to 50% retained austenite. In addition to incomplete transformation, the subsequent natural aging induces stress and also results in additional growth after machining.

TWO ADDITIONAL ADVANTAGES

Aside from transformation, no other metallurgical change takes place as a result of chilling. The surface of the material needs no additional treatment. The use of heat frequently causes scale and other surface deformations that must be removed.

Finally, the chilled material is more easily and conveniently handled.

SUB-ZEROING

Low temperature treatment, in addition to, or as an extension of the quench cycle, continues the process of austenitic transformation. As the material is chilled to lower temperatures, a greater amount of retained austenite is decomposed until finally, on reaching -120°F. the material becomes almost 100% martensitic, attains its maximum hardness, and gains its greatest volume. In order to accomplish the same metallurgical change the material would have to be heated at a precisely controlled rate, and to some specific point between 450°F. and 600°F., dependent upon the composition and variances inherent to the alloying elements present.

TRANSFORMATION OF RETAINED AUSTENITE- THE RESULT OF TEMPERATURE ALONE

"The percentage of tempered Martensite increases as the initial quenching temperature drops toward -100°F. (-73°C.) when, for all practical purposes, it reaches 100 percent. It has been found that the amount of Martensite formed at the initial quenching temperature (below 260°F.) is independent of the holding time. In other words, the time required for transformation is so short as to be negligible. Thus transformation of Austenite to Martensite is dependent only on temperature; it is independent of time at temperature."

- L.H. Van Vlack
Dept. of Chemical & Metallurgical Engineering. The University of Michigan

"When Austenite reaches the M_s temperature (Martensite start) the beginning of transformation takes place instantly. Moreover, the small amount of Martensite formed instantly is all that will form at this temperature, in as much as holding at the temperature causes no increase in the amount."

"To cause formation of more Martensite, the piece must be cooled to a somewhat lower temperature and, at this lower temperature, an additional amount of Martensite forms instantly. Eventually, when sufficiently low temperature is reached, the transformation will be instantly completed."

- M.A. Grossman
United States Steel Corporation

PRECIPITATION HARDENING

Precipitation hardening of stainless steel, unlike carbon steels, is a function of both <u>time</u> and <u>temperature.</u> It is essentially the same as age hardening with slight variations. The effect of temperature is an acceleration of the process that would occur normally over a long period of time.

The material, containing an alloying element, is initially heated to a temperature above the solubility point. It is then cooled very quickly to room temperature so that there is insufficient time for the element to precipitate. The material is now in a supersaturated condition and the alloying element remains dissolved. The highest degree of solubility occurs at the highest temperature and this degree decreases with decreasing temperature.

At room temperature, therefore, the condition is not normal and the alien material attempts to precipitate out of solution -the material remains relatively soft until precipitation is complete.

If the material is reheated to an intermediate temperature, precipitation time is reduced. The higher the temperature the less time required for the effect to take place. Ideally, the precipitation should occur in Hardenable Martensite, rather than in a combination containing retained Austenite. In the higher carbon martensitic grades of pH steel retained austenite may run as high as 30% by volume.

This fact, combined with the possibility of a loss of hardness due to over- aging resulting from prolonged exposure to elevated temperatures, makes Sub-Zeroing a valuable treatment in the fabrication of stainless steels.

SEMI-AUSTENITIC ALLOYS

Of the three basic types of pH stainless steels, Martensitic, semi-austenitic and austenitic, only the first two benefit from low temperature treatment -the austenitic grades do not transform to martensite. The compositions of t semi-austenitic alloys are so balanced that the structure is austenitic in t solution treated condition. The unhardened, ductile material allows for easy forming by conventional techniques. Following fabrication, transformation is brought about by thermal treatment and chilling.

MARTENSITIC TYPES

In the true martensitic types, the martensite forms upon cooling. treatments develop strength and toughness. There are basically two separate mechanisms producing the desired hardness:

1. TRANSFORMATION. The allotropic transformation producing martensite.
2. PRECIPITATION. Resulting when the structure is given a simple, low temperature aging treatment that hardens by precipitation of inter-metallic compounds and simultaneously tempers the martensite.

The following is the heat treatment of pH 13-8, a typical martensitic stainless steel:

> Solution treatment at 1700°F. for one hour, hold for 8 hours; cool to -100°F. within one hour, hold for 8 hours; precipitation hardening at 950°F. for four hours.

The heat treatment of semi-austentitic grade 17-7 pH is representative.

> Solution treatment at 1900°F.; Austenite conditioning at 1750°F. for 10 minutes; cool to 60°F. within one hour, hold 30 minutes; cool to -100°F. within one hour, hold 8 hours; cold reduce 60%; precipitation hardening at 950°F. for one hour.

The rate of hardening is related to the concentration of the alloying elements and increases as the concentration increases. The final results are dependent upon the proper diffusion of the element within a solid solution.

Over aging occurs earlier for the higher concentrations because diffusion occur faster and the particles combine more rapidly into sizes unfavorable to maxi- mum hardness.

Temperature also has a bearing on diffusion. The rate of hardening increases with higher temperatures but the maximum hardness resulting is lower. Over- aging occurs sooner at elevated temperatures.

OTHER PRECIPITATION HARDENING ALLOYS

Allotropic changes do not occur in many non ferrous alloys such as aluminum, magnesium and copper based materials, and their hardenability is dependent almost entirely on precipitation hardening. In its pure state, aluminum is too soft for most practical uses. Aluminum alloys on the other hand, are superior to steel considering the strength/weight ratio.

The initial lack of hardness can be an advantage to the manufacturer. In the case of aluminum rivets, for example, the manufacturer chooses an alloy which can be quenched to a supersaturated solution but which will age harden at room temperature. Most alloys of this type will start to age harden in 16 hours after solution treatment. Since precipitation hardening is a function of time and temperature, storage at -40°F. will maintain the aluminum in usable condition almost indefinitely.

The same cold treatment is used for solution treated castings, forging and sheet metal blanks prior to cold work operation.

To promote dimensional stability and assure better-machined finishes in aluminum and magnesium castings, cold treatment is used to promote permanent growth.

STRESS RELIEF THROUGH SUB-ZEROING

The effects of Sub-Zeroing on metals for improved hardness through austenitic transformation, greater dimensional stability resulting from the increase in grain size, and improved machinability through precipitation hardening, are not the only benefits to be achieved. The metallurgical engineer can take advantage of low temperature for stress relief of castings and machine parts.

Stress is perhaps the most common cause of part failure. Stress concentrations are frequently the result of volume change, which is, in turn, usually caused by temperature changes producing thermal expansion and phase change.

Under normal conditions temperature gradients produce non-uniform dimensional and volume changes. In castings, as an example, compressive stresses are developed in the areas of smaller volume that cool first; tensile stress develops in the areas of larger volume that are last to cool. Shear stresses are developed between the two. This holds true even in large castings and machined parts of relatively uniform thickness -the surface cools first and the core last. Here, stresses are developed by phase change between those layers that transform first and the center portion that transforms last.

Stresses caused by volume changes due to thermal variation are relieved naturally when all parts of the piece gain uniform temperature. Internal developed due to intermediate stages of phase change are relieved only upon completion of the transformation. It has been found that only 15% of these stresses are relieved through natural aging.

When both volume and phase changes occur in pieces of uneven cross section, normal contractions due to cooling are opposed by transformation expansion. The residual stresses resulting will remain until a means of relief is applied.

This type of stress develops most frequently during the quenching of steel. The surface becomes martensitic before the interior and, although the inner austenite can be strained to match this change, when the inner austenite transforms, the resultant interior expansions place the surface martensite under tensions. Quenching cracks in high carbon steels arise from these stresses.

The use of sub-zeroing has been proved beneficial in stress relief of castings and machine parts of even or non-uniform cross section.

1. Transformation of all layers is accomplished when the material reaches −120°F.
2. The increase in volume of the outer martensite is somewhat counter-acted by the initial contraction due to chilling.
3. Rewarm time is more easily controlled than cooldown, without tying up equipment.
4. The expansion of the inner core due to transformation is somewhat balanced by the expansion of the outer shell.
5. The chilled parts are more easily handled.
6. The surface is unaffected by low temperature.
7. Parts containing various alloying elements and of differing sizes and weights can be chilled simultaneously.

More specific information on chilling for stress relief will be found in the Handbook.

PRODUCTION CHILLING CHAMBERS

EXPENDABLE REFRIGERANTS

Some companies have attempted low temperature processes using dry ice. In many instances the results have been unsatisfactory. Dry ice has a surface temperature of -109°F. and has some inherent limitations to consider against its appeal of assumedly low cost. In order to fully utilize the temperature capability, it is imperative that there be: A) A sufficient quantity of dry ice. B) In actual contact with the materials being processed. C) For a long enough period of time to accomplish the procedure. Sometimes the air temperature may be no lower than -10°F. or -20°F. because the mass of the materials greatly exceeds the thermal capacity of the quantity of dry ice. Or, unsatisfactory results are obtained because the materials are physically isolated from the source of cold.

Temperature non-uniformity can also be a source of inconvenience. If all of the materials constituting the load don't "see" the same temperature, inconsistent results will be inevitable.

The cost of using dry ice can be significant when handling, storage and transportation are all considered. It isn't uncommon to find these charges amounting to more than $5,000.00 per year.

Liquid nitrogen has a vaporization temperature of -320°F. The cost for liquid nitrogen has risen greatly in the past couple of years. While some processes are actually performed at these ultralow temperatures, and Cincinnati Sub-Zero Products has manufactured these chambers, some have found the rapid temperature decrease unacceptable. The reduction had to be programmed for slow rates. Others, based on the configuration and composition of the materials, have discovered that the pieces became too brittle.

AIR TEMPERATURE VS. PART TEMPERATURE

This is an inexact relationship to which no manufacturer of temperature controlled products can realistically commit without having performed some experimentation into the conductance of the materials being processed. In addition, the variables associated with the application would have to be minimized in order to have consistency in results. The considerations (variables) are as follows: 1) Composition of the materials. 2) Configuration of the materials. 3) Weight of the materials. 4) Temperature of the material entering the chamber. 5) Load orientation. 6) Processing temperature. 7) Airflow quantity and velocity passing the materials. 8) Length of time in which the process is to be completed. The reference to materials includes fixtures for containment of the load.

Generally speaking, applications for mechanically refrigerated chambers are viewed with a specific time in which to re-stabilize air temperature at some setpoint. Then, a general "rule of thumb" is to allow the materials to be subjected to the air temperature for one hour per inch of largest thickness in order to have thorough stabilization at temperature.

For example, let us assume a chamber has been operating at -120°F. A load, including baskets, is inserted at a temperature of 75°F. and the total load weighs 200 pounds. Further, the pieces are solid blocks measuring 4" cubed. When the load is placed into the unit the air temperature will rise to some value predicated on the thermal capacity of the Sub-Zero chamber. Assuming that the thermal capacity is sufficient to re-stabilize air temperature within 1 hour, the load would be left for an additional 4 hours for the reasonable assurance that the pieces have been adequately soaked.

PURCHASING A SUB-ZERO CHAMBER

The acquisition of such equipment is basically the purchase of:

1. Physical size of the working area
2. Temperature range
3. Thermal Capacity
4. Reliability of the equipment

Of these four points, none has a greater effect on the purchase price than the thermal capacity which is also directly related to reliable operation.

THERMAL CAPACITY

This influence in the cost of mechanically refrigerated chambers, and their reliable operation, is detailed. Thermal capacity, the ability to accomplish a chilling objective, or the "quantity of cold," can be perceived from comparison between the heat generated by a match versus a fireplace. Even though the tip of both flames will be at about the same temperature, the energy content between each is significant.

 While there is a tendency to evaluate and relate thermal capacity to the size of the compressors for a mechanically refrigerated unit, this is only one of five separate considerations: The remainder are:

1. The types of refrigerants
2. Method of refrigeration control
3. Sizing, matching and balancing of the compressors and components integral to the refrigeration system
4. Type and quantity of insulation.

Any of these can make an appreciable difference in the chamber's performance, reliability and, of course, its cost.

As a means of appreciation to these points we will cite an example involving a single stage, mechanically refrigerated unit to be operated to -40°F. Let us assume that contributing criteria dictate a compressor rated at 3 HP. While there are more choices than indicated, we have listed a comparison between 5 compressors, all of which are rated at 3 HP.

Compressors A, B, C and D are for use with refrigerant 502; compressor E is for use with refrigerant 12.

Compressor	BTU's/hour at -40°F	Displacement (cu.ft./hour)	Ratio of STU's per hour to displacement
A	10,000	815	12.27 to 1
B	8,480	815	10.40 to 1
C	7,250	698	10.40 to 1
D	5,700	524	10.88 to 1
E	5,700	970.6	5.87 to 1

Obviously, horsepower is hardly a precise means of measuring performance. We might add that neither is displacement, or anyone single factor.

For example, proper system balance requires the condenser to dissipate the quantity of heat being removed. With a cascade refrigeration system, the low stage compressor is directly dependent on the cooling capacity of the high stage system and indirectly dependent on the high stage condenser.

If the compressor for the low stage is over-sized (an unbalanced system), its operating parameters, and its performance, must be restricted by some means to attempt re-balancing in keeping with the operating parameters of the high stage compressor. In other words, an over-sized compressor offers absolutely no benefit over a correctly sized compressor operating at its full potential.

Compressors are designed by their manufacturers to dissipate a quantity of heat through the material and configuration of the body casting. Some compressors rely completely on the design while others are intended to receive additional heat dissipation capability from airflow across them, or are rated as refrigerant cooled. There are also some compressors which employ a combination recommended by their manufacturer.

Compressor temperature affects both performance and reliable operation. Compressors, like engines and other mechanical power transmitting systems, need adequate lubrication. The lubricating oils used in these systems are affected by temperature.

The heat originating in a compressor is from its motor and from the process of compression of the refrigerant gas. If a greater quantity of heat is generated than can be dissipated, failure of the system will be inevitable. As can be seen, oversizing compressors, whether in H.P. or displacement, can produce excessive heat. Compression ratios, which are directly traceable to the overall balance of the system are a factor in how reliable the product will be.

Some processes have been performed in mechanically refrigerated units with limited success and discouragement. As we have demonstrated, thermal capacity is extremely important and freezers should not be indiscriminately applied to requirements. Assumptions such as a chamber rated to -100°F. will provide greater thermal capacity at -30°F. than a unit rated to -40°F. are not necessarily correct. The net thermal capacity at a specific operating temperature is the guide. We have emphasized two key words to preclude theoretical and irrelevant values.

THE ADVANTAGES OF SUB-ZERO CHAMBERS

A Sub-Zero mechanically refrigerated unit provides the following advantages over the use of expendable refrigerants:

1. The temperature range is variable. Many of these products have an adjustable temperature range from -40°F to -130°F. In expansion assembly processes, for example, the adequate contraction of the piece may occur at -50°F. While dry ice has the previously stated, surface temperature of -109°F, load placement or the quantity of dry ice may only lower the air temperature to -30°F. Subsequently, there is the production time of repositioning the load, or adding more dry ice, while contending with the trial of matching the parts to see if they have adequately shrunk.

2. The uniformity of temperature is usually much better. As referenced in advantage 1, if the air temperature is only -3QOF. and the dry ice surface temperature is -109°F, we have a gradient of 79°F. All of the pieces compromising the load are not being subjected to the same temperatures.

3. As air temperature is lowered, its density changes, and it becomes a better heat transfer media. At temperature of -100°F or -120°F, the uniformity of a well designed and quality chamber will be in the proximity of ~2°F. The uniformity will change based on characteristics of the loading and air- flow, with consideration for stabilization time, but the end difference is still quite substantial.

4. Convenience. A Sub-Zero Chamber is at your disposal at all hours. This usually isn't the case with expendable refrigerants.

5. The results are consistent. Since thermal capacity remains quite stable the largest variable usually associated with expendable refrigerants has been eliminated.

6. The cost savings can be appreciable. A Sub-Zero chamber represents a capital expenditure usually depreciated over a long period of time. Expendable refrigerants and their handling, storage and transportation charges don't have this benefit.

7. Safety is the final point and, while not nearly as conspicuous an advantage, it is a consideration. Burns from handling dry ice, minor injuries from positioning LN2 tanks, and oxygen displacement with gases do occur. A mechanically refrigerated chamber is safer.

Airflow

Smaller Sub-Zero chambers have air circulators available as options while they are a part of standard design in bigger units. While airflow will be inconsequential in the re-stabilization time of a chamber, it will be of benefit in minimizing temperature gradients with a load and will promote more rapid heat transfer from the load. Most of the applications with these products are production related. The slight additional cost for these two advantages is, we believe, well worth considering.

Liquids

There are some processes that are accomplished with better results using liquid as the media, in lieu of air. The big advantage is more rapid heat transfer for the load.

The initial investment is higher and attributed to controlling fluid circulation and direction, in addition to the usual need for a heftier refrigeration system. The heat content represented by the fluid is greater than that of air. While the fluid will be slower in increasing its temperature after the load is immersed into the stabilized fluid, it will require greater thermal capacity to return to setpoint temperature. The overall efficiency is also improved. That is, the heat being extracted by the refrigeration system is now more indicative of the temperature change of the load. Generally, the process is completed once the fluid temperature has re-stabilized, rather than relying on the "rule of thumb" (1 hour of exposure per inch of largest thickness) applicable to processing in air.

When using fluids it is imperative that they be kept free of contaminants. Foreign materials, such as oils and salts remaining on the load from previous production steps, will change the fluid properties and usually decreases the efficiency of the refrigeration system. There have been instances where the foreign material accumulated on the surfaces of the refrigeration evaporator tends to act as an insulator. Subsequently, the duty cycle of the refrigeration system increases and the efficiency of the unit decreases.

Fluid selection is important. One must primarily consider the compatibility of the fluid to materials being immersed, the safety of the fluid, its cost and thermal characteristics. Fluids with low ignition temperatures can be ignited by a potential spark from the electrical components of the chamber. (There are special enclosures and precautions established by electrical codes and agencies to which we can comply in such circumstances.) From the user's point of view, the toxicity level of the fluids are important as well as evaporation rates. From the chamber manufacturer's point of view we have to consider the fluid density, specific heat, freezing point, boiling point and viscosity.

CONCLUSION

We hope that these contents have been of assistance to you. Portions dealing with metals and their properties were prepared by reputable individuals to whom we express our gratitude. We think it is important to recognize that there may, on occasion, be differing opinions. We regret that we are with- out expertise in situations involving metallurgy. Experience and knowledge in refrigeration systems, and the control of temperature and environments, are our credentials.

Being oriented to providing our products to large and small businesses we strive to maintain a genuine spirit of service. We think a good example of these statements surfaces from a fairly recent set of circumstances.

An article had appeared in a monthly publication regarding wear resistance of tool steels. The paper was well written and documented; its author was obviously knowledgeable about the subject. The contents dealt with the additional wear resistance derived by subjecting the specimens to temperature of -310°F. as opposed to -120°F. (See section: Advantages of Sub-Zeroing). The article was based on comparisons of 5 different alloys. We didn't question the findings, although some of our potential customers inquired.

Whether the configuration and size of the alloys would have any bearing in comparisons; or how the comparisons relate to other production processes; or if the comparison is fairly accurate for other alloys; or if the results had a relationship to tools made from particle metallurgy are all questions beyond our ability to answer.

We have introduced these questions as typical considerations you will want to evaluate in terms of the economic benefits derived: What does additional wearability mean to you? Is the cost of purchasing a Sub-Zero chamber and the cost of further processing worth the additional wearability, economically speaking? Performing the process at -310°F. means an investment into a chamber and the continuous purchase of LN2' plus its handling and transportation. Is the wearability derived worth the larger investment into LN2? What is the premium attached to the stated wearability from work at -310°F. vs. -120°F.? The ensuing feedback information was as widespread as the original questions. We might add that a couple of Sub-Zero chambers were purchased.

We look forward to being of service.

CINCINNATI SUB-ZERO PRODUCTS, LLC.

Weiss Technik North America, Inc.—Cincinnati Facility . 12011 Mosteller Road . Cincinnati, OH 45241 . (513) 326-5252 . www.cszproducts.com

21002-0516-1