Cryogenics is the continuation of heat treatment and is the last step that completes the thermal treatment processing of metals. After ferrous steel part/s are heat-treated and tempered, the part’s grain structure can be improved by subjecting the part to a deep cryogenic temperature (–320°F) soak. The process involves taking the parts down from room temperature to –70°F to –100°F using dry nitrogen gas.

**NOTE:** The slow cool down over a couple hours is to avoid thermal shock which can shatter the parts. A slow return to room temperature is used to prevent stress which could also cause parts to crack.

This is a relatively slow process (perhaps 60 minutes, depending on processor size and mass) that conditions the parts and wards off any chance of thermal shock. With the parts well chilled, the liquid nitrogen can be safely allowed to flow into the chamber and fully immerse the parts for an 18–30 hour soak (time dependent on the load mass and part spacing).

**WARNING:** Not all processors are capable of holding the weight of the parts plus the weight of the liquid nitrogen. Several processors are only used with gaseous forms on nitrogen, which greatly affects their efficiency in the transformation process.

The result of the deep –320°F subcold produces a 99.9 to 100% transformation of retained austenite to martensite. That is the rich, fine grain structure that increases wear resistance. During this transformation a precipitation of microcarbides (if carbide forming elements are present in the chemistry) will also occur and add additional wear resistance to the parts.

**POINT:** Heat treatment isn’t really complete until the metal is treated using deep cryogenic treatment.

Followed by a 300°F temper for two hours per 1” of thinness will stabilize any freshly created martен-
site and continue to refine the grain structure. Remember as we discussed in Chapter 20, the metal should be fully tempered after the quench and then tempered again after the cryogenic process is completed. The steel must be tempered directly following the quench to stabilize the structure, then cryogenically treated followed by the last temper to stabilize all the newly formed martensite. That means no other tempering processes are needed or required.

If for example, you are heat-treating a high speed steel, which typically calls for three tempers that promote a greater, finer grain transformation, the third temper is no longer needed since cryogenics transforms 99.9% of the remaining austenite; this greatly improves the tempering attempts to get a few more percent of austenite transformation.

**POINT:** Since all or nearly all the remaining austenite is completely transformed to martensite, the process completes the thermal treatment.

During the cryogenic process, the Rc hardness is set by the first temper; the grain structure is at that point as refined as it can be, and the parts are nearly stress-free because cryogenics realigns crystals that were caught out of phase. The 300 °F stabilizing temper will not have any effect on hardness but will remove the brittle structure from the freshly formed martensite. To attain the stress-free condition, the parts must be returned to room temperature from the deep subzero cold very slowly. That is the reason for the 12–20 hour return. This reduces any excess thermal stress being created in the parts and produces a very good stress-free part.

Deep cryogenics (−320 °F) is the fastest, most complete method of finishing the thermal treatment of any heat-treated steel. Thus far, we’ve taken step by step measures to detail the heat-treating process, and until a few years ago, once the tempering was completed, the task was complete.

Now we know and understand that the subzero freezing temperatures have a very positive effect on grain structure, just as heat does, but it is the next level. When heat and cold are used in combination, we can expect longer wear life, less residual stress, and completion of the thermal-treating process.

### 21.1 Cryogenic Levels

There are several levels of subzero cryogenics in use today. Mechanical freezers can achieve temperatures down as low as −150 °F. For the most part, temperatures from −100 °F to −150 °F will stabilize and remove a degree of residual stress from metals. It will also cause some additional but limited transformation of retained austenite to martensite in ferrous metals. If the metal is held at −150 °F long enough, for example, for 100–200 hours, the transformation is significant; but the economic cost and time used is poor in comparison to deep cryogenic treatment, and the metal still does not receive a complete transformation.

Deep cryogenics uses liquid nitrogen in either a gaseous or liquid form to attain the −320 °F temperature. A few cryogenic firms have tried using liquid helium, which is −452.1 °F, but there is no visible gain to the metal’s structure. A 99–100% transformation is as far as one can achieve. The nitrogen used in gaseous form is not as efficient, and depending on the load, is nowhere as dependable as using it in its liquid form. Many claim that using it in liquid form will cause cracking and severe problems from thermal shock. The reasoning is usually because their processor is not built to handle liquid, so they introduce a false fear sales presentation. The key to using it in its liquid form is to use dry nitrogen gas to first lower the temperature of the parts to −50 to

<p>| Table 21.1 Temperatures of Liquefied Gases |</p>
<table>
<thead>
<tr>
<th>Liquefied Gas</th>
<th>°C</th>
<th>°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>−33.3</td>
<td>−27.9</td>
</tr>
<tr>
<td>Propane</td>
<td>−42.3</td>
<td>−44.1</td>
</tr>
<tr>
<td>Propylene</td>
<td>−47.0</td>
<td>−52.6</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>−78.5</td>
<td>−109.3</td>
</tr>
<tr>
<td>Acetylene</td>
<td>−84.0</td>
<td>−119.2</td>
</tr>
<tr>
<td>Ethane</td>
<td>−88.3</td>
<td>−126.9</td>
</tr>
<tr>
<td>Ethylene</td>
<td>−103.8</td>
<td>−154.8</td>
</tr>
<tr>
<td>Methane</td>
<td>−161.4</td>
<td>−258.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>−183.0</td>
<td>−297.4</td>
</tr>
<tr>
<td>Argon</td>
<td>−185.7</td>
<td>−302.3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>−195.8</td>
<td>−320.4</td>
</tr>
<tr>
<td>Neon</td>
<td>−245.9</td>
<td>−410.6</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>−252.7</td>
<td>−422.9</td>
</tr>
<tr>
<td>Helium</td>
<td>−268.9</td>
<td>−452.1</td>
</tr>
</tbody>
</table>
–100 °F before introducing it in the pure liquid form. That removes the possibility of thermal shocking room temperature parts and cracking them. Liquid delivers a very uniform temperature of –320 °F to all surfaces and provides a clear transformation to 99% or better.

**NOTE:** Gas dewars are used to transport liquid nitrogen to users. The dewars come with one of two connection setups. Some have just a gaseous valve to draw off straight gas. The others have both a gas and a liquid valve. This is the setup you need for cryogenic processing. One other thing you’ll find helpful; order the gas dewar with a 50 psi relief valve. Liquid nitrogen automatically slowly changes from liquid to gas and dewars are often delivered with up to 240 psi relief valves. In order to get the liquid to flow, you must release all that built up pressure before it will deliver liquid. That wastes a lot of nitrogen and costs you money and time. Dropping off 50 psi is a lot more economical and time saving. One more note. Dewars are equipped with a gauge to indicate how full the dewar is. If a gas dealer, or you, keeps the dewars on his or your dock for very long, the liquid will change to gas, blow the relief valve to release the pressure, and lose at least 3% of its volume daily. More volume is lost if stored in hot weather areas. Make sure the gauge indicates the tank is full, or very near full, on delivery or you’ll be paying for a product you’re not getting.

**Procedure for Using Liquid Nitrogen**

The procedure for using liquid nitrogen for ferrous metal transformation is:

1. After being quenched, make sure the parts have been tempered to its preferred working hardness.

2. Load the parts into a cryogenic processor capable of using liquid nitrogen. Not all processors are built to handle the weight of the liquid plus the parts.

3. Cool the parts to –50 to –100 °F using gas before introducing the liquid form. This entire cooling down can usually be done in 60–90 minutes. For years it was thought it best to lower the temperature down in an 8–10 hour ramp down. After a thorough research by the University of Alberta Metallurgical Department in Alberta, Canada, confirmed at the University in Dublin, Ireland, and plus extensive testing over a 2 year period by two professional cryogenic processing companies, the much longer slower cool down that was once used was found to be unnecessary. The slow cool down was an insurance against dropping parts directly into liquid nitrogen. In reality, 60 to 90 minutes is like an eternity compared to an instantaneous drop into freezing –320 °F liquid.

4. Introduce liquid until the parts are covered 6" deep underneath. Floating a tight-fitting styrofoam block on top of the liquid will retard the flash off of the nitrogen and prolong the soak or the need to add more liquid. Although additional liquid may be required depending on the nature of the load. The nitrogen needs to remove the BTU of heat that is stored in the metal parts, and if those parts form a heavy mass, the larger the retained heat that must be converted; this causes a much greater flash off losses.
5. The parts need to stay under liquid for a minimum of 6–10 hours then remain in the closed processor for another 10–12 hours. It will take longer than that for the parts to return to room temperature on their own and that will depend on the size and mass of the furnace load. Do not open the processor to speed up the warming process during this phase or the parts will condensate water and oxidation may occur. The processor should have an exhaust port that can be piped out of doors to avoid asphyxiation in the area. Nitrogen is heavier than air so it will sink to the floor and displace air and oxygen. Any pilot lights or open flame heating devices will be extinguished so explosive gases could fill the area. If operating correctly with a sealed closed processor, the flashing off increases the physical size of nitrogen dramatically in gaseous form and this produces a positive pressure that must be bled off to the outdoors. Thus the parts in the chamber are not exposed to atmosphere and as long as the processor remains closed, there is no condensation.

6. Once the parts are back to room temperature, put the parts into a tempering oven, making sure there are no parts on top of one another just as described in the tempering chapter. There should be air space around each part to allow uniform heating. Set the oven for 300 °F and soak for two hours per inch of thinness. Using 300 °F to temper will not change the hardness but will stabilize all the freshly transformed martensite, removing any brittleness and completing the thermal transformation. This 300 °F temper stabilizes the freshly transformed martensite that has been created. It removes the brittle chippiness of unstable martensite but 300 °F does not change the hardness. If any steel grade has instructions to run a full second or third temper and has been cryogenically treated, it only requires the single 300 °F follow-up temper. The original second or third temper is intended to trigger additional martensitic transformation and to refine the grain structure when cryogenics is not going to be used. However, by going through a thorough, deep cryogenic process, all of the retained austenite is essentially gone and all the fine grain structure has been created that is available. The structure is relatively free of residual stress and is ready for service.

7. Cool to room temperature in air.

This last step was touched on in Step 6, but is so important we want to go over it again. The follow-up temper is vitally important. Here’s why:

6. Once the parts are back to room temperature, put the parts into a tempering oven, making sure there are no parts on top of one another just as described in the tempering chapter. There should be air space around each part to allow uniform heating. Set the oven for 300 °F and soak for two hours per inch of thinness. Using 300 °F to temper will not change the hardness but will stabilize all the freshly transformed martensite, removing any brittleness and completing the thermal transformation. This 300 °F temper stabilizes the freshly transformed martensite that has been created. It removes the brittle chippiness of unstable martensite but 300 °F does not change the hardness. If any steel grade has instructions to run a full second or third temper and has been cryogenically treated, it only requires the single 300 °F follow-up temper. The original second or third temper is intended to trigger additional martensitic transformation and to refine the grain structure when cryogenics is not going to be used. However, by going through a thorough, deep cryogenic process, all of the retained austenite is essentially gone and all the fine grain structure has been created that is available. The structure is relatively free of residual stress and is ready for service.

\[ \text{POINT: The best part of this scenario is: if a tool is treated in this manner, if used properly and is in the correct service for the application, the life of the tool will exceed 200 to 300% over a noncryogenically treated tool.} \]

21.2 Cryogenics as an Aging Tool

Cryogenics answers many other needs as well. Untransformed retained austenite in any part, or tool, continues to slowly transform over an extended period of months or years. During this time the part is changing volume and the size of the part will physically grow larger. Cryogenics causes a quick aging process to take place within the metal as well as stabilizing the metal. Gauges or fixtures used to ascertain quality control must be processed with cryogenics to halt the changes in physical size or it will make the gauges useless within roughly 3 to 6 months.

21.3 Cryogenic Stress Relief

Cryogenic Stress Relief is an area often overlooked but gaining more favor every day. During machining, welding, grinding, or forming parts, stress is always building up in any and all manufactured parts. The part starts moving and it becomes harder and harder to control tolerance di-
dimensions, flatness, or shape. Critical cross sections are out of control. That’s stress. You can fight it, but you will not win. It can be stress relieved with heat at roughly 1100 to 1300 °F, but that will cause decarburization and discoloration. That again is where cryogenics wins.

Subzero cold treatment, or deep cryogenic treatment, causes the structure, albeit ferrous or nonferrous metals, to release its stored up energy. Any working of the material: reheating, rolling, drawing, welding, or shaping of the parts puts stress forces into the parts unequally. Particularly during roughing or hogging machining operations where lots of material is removed quickly. When the stress forces get strong enough, any number of outside influences can cause these forces to overpower a weaker area and the metal will move, and in some cases, crack or rip open.

Cryogenic stress relief can be used to relax these unwanted forces and make it possible to finish parts with subsequent light machining, or metal removal, and limit the effect of change on the part. The process is the same as the transformation process discussed earlier except the soak time is shortened to 8 to 10 hours if there is no transforming of grain structure involved. Heat-treated ferrous metal must be tempered at 300 °F to stabilize any freshly transformed martensite, but aluminum, titanium, brass, or any nonferrous metal should never be tempered. It would in fact ruin the temper they do possess. Titanium can benefit from a 200 °F aging, but it must not be above 200 °F.

There is more information on cryogenics, which is Step 10 in the processes for air-, oil-, and water-hardening tool steel (see Chapters 22–24).

**21.4 Nonferrous Metals**

Dry ice stress relief can be beneficial for parts that can’t be processed with deep cryogenics. In the mid-60s, a problem developed in a company that built printing presses. Print registration from one page of a business form to the next several sheets was a major headache and the product, the business form, didn’t work without proper registration. Imagine checking off a box on page one that you indicate you’re a male, but because of poor registration on page two it shows that you checked off female or vice versa. Not a good situation. After careful analysis, it was determined the problem existed in the gear train. The backlash and tolerances within the gear train were what was causing the loss of registration. It seems that as the gears were cut, the stresses built up from the machining of tooth after tooth, and that was affecting the tolerances throughout the entire gear train. A heat method of stress relief was totally out of the question as the time added to the process would be impossible to live with. Yet, something had to be done or the company’s product line would be useless. After lots of digging, discussions, and probing, it was mentioned by an old timer that dry ice stress relief was used on ship welds during WWII. After talking to some of the shipyard workers, it was confirmed and the shipyard workers explained how they did it. Questioning deeper, it was found many of these fellows also used various liquids to carry the cold to the welds.

After experimenting, and developing a process, it was found that by cutting 6 teeth equally spaced around the periphery of a gear, then packing the gears in dry ice for 6 hours, and warming them slowly back up to room temperature before cutting the next 6 teeth worked. The process of gear cutting and subzero packing, and cutting were repeated until all the teeth were cut. We knew we had licked the problem because the registration fell into tolerance form after form.

Later, the same technique was used to age castings. For years, companies stored castings outdoors in rows and stacks to be aged by the weather for improved machinability and stability. Particularly important was the winter months. The castings that went through the −30 °F weather had the least movement during machining from stress than all the others. At the time none of us understood why, but we knew it worked, and it was definitely worthwhile.
21.5 Summary

There are other products not related to heat-treated metals that show great gains in wear resistance, longer life, and less resharpening maintenance. Things such as carbide tooling (requires a special process and temper) plastics, synthetics, gun components, rubber, and more. These last five chapters conclude the individual steps involved in heat treatment and thermal treatment. It forms the basis for all heat-treating. Next we will walk through the water, oil, and air hardening grades because there are substantial differences in their processes that we want everyone to grasp.