Frozen depths

John Stowe seeks the truth about cryogenic treatment for race engine components

While researching the article for *Race Engine Technology* on isotropic surface finishing, I uncovered an increasing level of interest in cryogenic treatment. In fact, there were some companies that offered both services from a single source. Many motor sports publications now have advertisements promoting this technology, and broad claims are made for the improvements possible with cryogenic conditioning of materials. In addition, cryogenic processing has achieved a growing level of acceptance among racing engineers. RET has decided to investigate this growing field, and report on the current state of the art, and the benefits available to the racing world.

WHAT IT IS

The term "cryogenics" comes from the Greek "kryos" (cold) and "genes" (born). There is actually some debate concerning where cold refrigeration treatments stop and cryogenic treatment starts, and it should be noted that there has been a variety of terms applied, sometimes loosely, to this process. Words like "cryotempering", "cryogenating", "cryogenic stress relief", "cryogenic hardening", "deep thermal cycling", and others show up in the various advertisements and papers … a standard designation is clearly overdue.

At the National Institute of Standards and Technology, located in Boulder, Colorado, some technicians consider the cryogenic range starting at –180 degrees centigrade and below. This seems reasonable given that the boiling points of "permanent" gases such as helium, hydrogen, neon, nitrogen, oxygen and so forth are all below this value. Common refrigerants, such as Freon, have boiling points above –180C. The Cryogenic Society of America considers anything below -153C as inside the "cryo" range. Regardless of the variations in terms and definitions, all specialists in this field draw a very strong distinction between cryogenic treatment and the refrigerant-based cold treatments that are essentially considered to be an extension of standard heat-treating processes.

Cryogenic treatment involves optimizing metallurgical characteristics by subjecting material to very cold temperatures,

usually for a sustained period of time. The crystalline structure of the material is affected in such a way as to improve strength, ductility, and in some cases, surface lubricity and hardness. In addition, there appears to be a dramatic reduction in residual stresses, which can improve stability during machining.

WHAT IT IS NOT

Cryogenic processing is not a surface treatment: changes to the material occur through its entire breadth. The change is permanent and does not "wear off". Cryogenic treatment is also not a replacement for conventional heat treatment: the dramatic changes in hardness and strength that come from heating and subsequent rapid quenching do not occur with cryogenically treated material, and constituents of an alloy do not go into solution, eutectic or otherwise, as they normally do with elevated temperature methods. Cryogenic processing is, rather, a complementary process to heat-treating that optimizes the material's characteristics. While this article will be mainly confined to the effect on iron and steel alloys, it should be noted that cryogenic treatment has been applied with apparent success to other metals and even plastic materials.

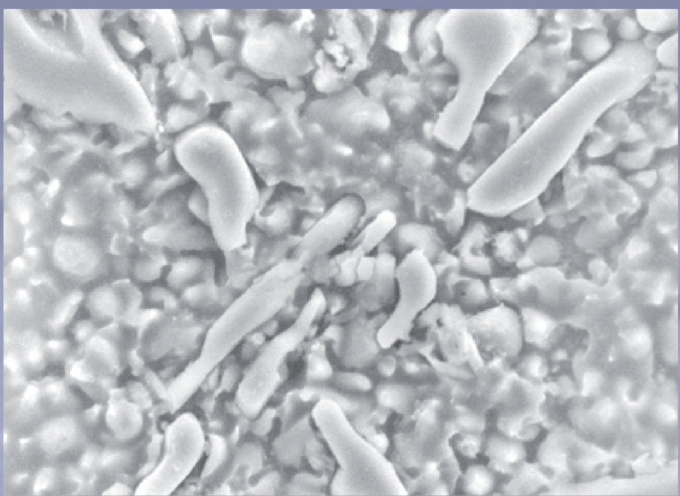
HISTORY

Various cold treatments have been with us for some time now; the well-known German Henckels cutlery company developed its "ice hardening" technology back in 1939. Before that, various heat-treating houses would refer to their "cold quenching" technology as applied to standard heat-treating, and refrigerant-based cold treatments down to –120 degrees F have been used for years. Going farther back, it is asserted that the Vikings chilled their swords in the snow to improve the toughness of these weapons. True cryogenic treatments are more recent, although there is evidence that the Junkers company in Germany applied cryogenic conditioning to components used on their "Jumo" aircraft engines as early as 1939.

Clearly, it is first necessary to be able to generate intense cold in order to implement low temperature treatments. During the late 19th century, the potential for cryogenics began to unfold largely through the work of Sir James Dewar, inventor of the Dewar flask (a thermos bottle is essentially a small Dewar flask). This container is able to hold liquids at very cold temperatures for a sustained period of time, and this development, when coupled with Dewar's work on the liquefaction of gases, made possible the generation and maintenance of the very cold environment required for industrial applications. By the 1930s, refrigeration had reached the stage where liquid oxygen (and other "permanent" gases) could be produced in commercial quantities, and at reasonable cost. All the conditions necessary for a viable cryogenic industry were now in place (at this time, the liquid nitrogen that was a byproduct of such processes was still regarded as without value, and simply vented away).

After the Second World War, experimentation with cryogenic conditioning began in earnest. In this early phase, people would simply immerse a cutting tool, gear, or similar object into an open vat of liquid nitrogen. The thermal shock resulting from this crude ►

Non-Cryogenically Treated Aluminium Piston Alloy Microstructure



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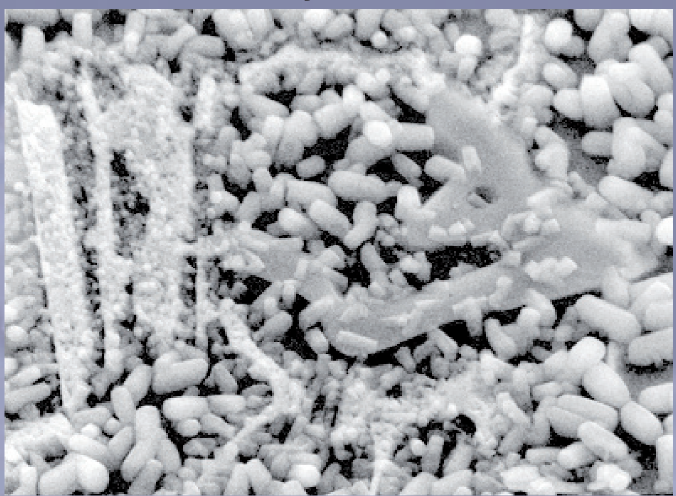

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Mark Link of Diversified Cryogenics of Burnsville, Minnesota remarks: "The cryogenically processed piston has a more wear resistant surface, higher yield and ultimate strength. This alloy will display structural, thermal and metallurgical stability not found in the untreated condition, as well as significant abrasive wear improvement. The contact and fretting fatigue will be reduced due to the tightening of the surface microstructure. In addition, the corrosion resistance to hot reactive gases and moisture in the combustion chamber will be improved."

methodology was enough to frequently cause the item so immersed to shatter, or to become so brittle that there was no useful application left for it. Nevertheless, a sufficient number of the subjected components survived to demonstrate the potential improvements to material properties. As a result, cryogenic processing began to be of real industrial interest.

One of the earliest applications was cutting tools, and very real increases in tool service life were recorded immediately. As the treatment process was refined, cold chamber equipment began to replace the simple liquid-nitrogen vat. This allowed a controlled, slow temperature reduction, a sustained period at minimum temperature, and a controlled, slow return to ambient temperatures. The process was further improved to include a subsequent holding period above ambient temperature as well.

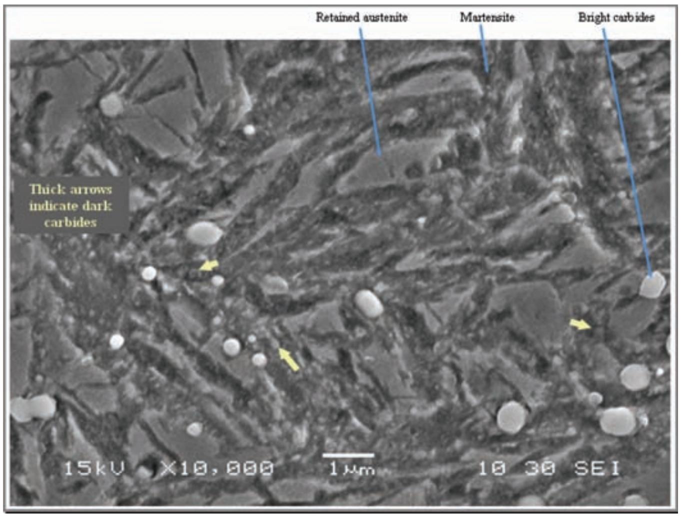
Today, most reputable cryogenic treatment houses cringe at the thought of dropping materials directly into liquid nitrogen, and almost every one of them has some horror story about "backyard" processors who continue to condition parts this way, much to the detriment of the industry as a whole. In fact, legitimacy is one of the very real issues for the industry. A review of any number of web sites maintained by cryogenic processors shows them taking pains to separate themselves from the various 'con artists' and frauds that still apparently exist in the field. In addition, they take great pains to justify cryogenic conditioning as a valid industrial process.

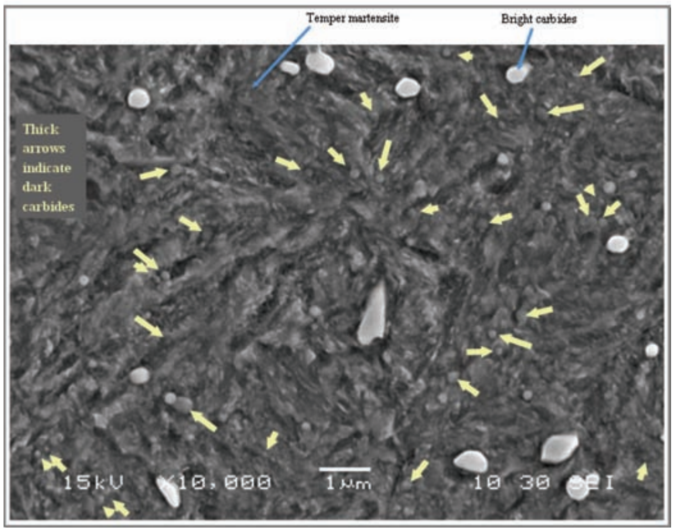
Another issue for the cryogenic industry is that the theory of how and why it works is by no means fully understood, and today there are still many doubters who believe that there are no benefits to be had from this methodology whatsoever. These people point out the lack of observed change in the molecular/chemical structure of the materials involved, and use this to make the case that there is no real improvement at all. Cryogenic experts point out that heat-treating itself was (and is) a largely empirically developed technology as well, and was successfully performed for thousands of years before there was any understanding whatsoever of how it worked. They also point out that other altered properties for ultra-chilled materials, such as superconductivity are broadly recognized, even though those materials generally do not necessarily show any observable change in structure or chemistry either.

The scepticism regarding the value of cryogenics is shifting, partly because the most important theorized change that occurs during a cryogenic cycle has been recently verified by non-empirical methods. This change is the transformation of retained austenite to martensite in steels. At high heat, carbon steel enters an austenitic phase, which is essentially a solid solution of iron and carbon (and/or other alloying materials). The conversion of austenite to martensite occurs during a rapid quench, which alters the crystalline arrangement of the material, but not its chemical composition. Martensite is harder, has higher tensile strength, and has far better wearing characteristics than, for example, non-heat-treated carbon steels. After quenching, martensitic steels are tempered to make them less brittle. Even with the best heat-treating, quenching, and tempering cycle, however, there is usually a significant amount of retained austenite left suspended in material mass, which reduces its strength, hardness, and stability. This is partly because the martensitic crystalline structure occupies a slightly different volume than does its chemically identical (but softer) austenitic counterpart; therefore, there can be significant strength-robbing internal stresses when both structures are present in the same material mass. Recently, X-ray diffraction measurements have confirmed the full austenite to martensite conversion, and there now seems to be little debate about the benefit to many martensitic alloys from cryogenic processing.

An important Japanese study found that the wear reduction frequently cited by cryogenic proponents is real, and for a very identifiable reason: cryogenic treatment increases the number of

Nitrofreeze: Before (left) and after (right) cryogenic treatment





Robin Rhodes of the Cryogenic Institute of New England, Inc. remarks: "These Scanning Electron Micrographs clearly show two of the three dramatic transformations that occur to steel that is cryogenically treated. First, the grain structure or crystal form of the cryogenically treated is pure as the flaws or imperfections of retained austenite are transformed to the desired martensite, creating a homogenous microstructure. This produces a more balanced steel that can be polished to create a reduced coefficient of friction (less drag) and has better thermal properties for improved heat dissipation. The second transformation is the dramatic increase in the population of eta-carbides in the cryogenically treated steel. These eta-carbides dramatically improve the steel's resistance to wear. The third transformation, residual stress relief, (not visible in a micrograph), reduces distortion and warping in steels and enables parts to be machined to tighter tolerances, reducing walk and creep from the machining operation. The photos were taken in the research labs at Air Products and Chemicals."

small carbides by approximately 2 ½ times. These carbides combine extreme hardness with a low coefficient of friction. The Japanese study concluded that the distribution of these carbides was more responsible for the improved wear characteristics observed than the completed conversion to martensite. This probably accounts for the improvements in durability for pearlitic components such as brake rotors, where significant amounts of either retained austenite or martensite are normally not present. There is also some discussion as to whether the increase in carbides is due to the cryo phase or the secondary tempering that occurs at the end of the full treatment.

The theoretical underpinning for the observed improvements in strength and stability in non-martensitic materials seem to be somewhat less clear. The current belief is that the extreme cold, and the slow ramp down to the cold condition, and the subsequent equally slow ramp up allows the material to fully relax, and for free carbon atoms to find their place in stable positions in the material matrix where voids would have previously existed. Proponents talk about a denser, more uniform structure, and note that during processing such as machining, far less distortion occurs in the work piece. There has been no physical verification of this belief, however, and it is this lack of a complete cryogenic materials theory that has retarded a final full acceptance of this technology in the broader engineering world.

In addition, there are those metallurgists who hold that, at the very low temperatures involved, there is not enough energy present to make any such transformation possible; in their view, all refinement is occurring during the ramp down and ramp up phases. Nevertheless, the empirical evidence for efficacy of cryo continues to build: The Cryogenic Society of America, Inc. lists dozens of technical papers and articles that have appeared in reputable technical magazines and industry trade journals; these discuss virtually every aspect of cryogenic treatment. In particular, Dr. Randall F. Barron of the University of Louisiana has conducted a broad range of tests, and authored some of the most respected reports in the area of cryogenic materials treatment. While most of these tests have been confined to the mechanical characteristics of the materials so treated, the sheer volume of the work completed, and the quality of the experiments cited, make this effort difficult to ignore.

Currently, there is a general call for more theoretical work in this field from all directions to complement the empirical research already completed. The goal here would be to develop the same kind of standardized time and temperature procedures that are prescribed for conventional heat-treating, with these specifications being correctly adjusted for particular alloys.

CURRENT PRACTICE

While each house has its own variations, there seems to be a consensus among current quality producers on how the process should be conducted. A typical cryogenic cycle has five steps:

Step One:
A slow descent to somewhere around –300F; this should take several hours. The reason for this is to make sure that the internal temperatures and surface temperatures of the object being treated do not differ significantly, thereby avoiding any possibility of cracking.

Step Two:
A holding period that might last anywhere from 8 to 40 hours. It is well known that molecular activity is vastly reduced at very low temperatures. The long "soaking" time is believed to be necessary to allow both the fine carbides to precipitate, and the crystal lattice to achieve the lowest energy state possible. This is the point where the conversion from austenite to martensite occurs.

Step Three:
The return to ambient temperature. Again, this can take from several hours to a day, for the same reasons expressed in step number one.

Step Four:
Tempering occurs at an elevated temperature. Since we now have new primary martensite from the completed conversion process, this material needs to be tempered to avoid brittleness, just as with a conventional heat treatment. Specific elevated temperatures are based on the material being conditioned.

Step Five:
The temper hold is the last step, and usually takes a few hours. Once again, depending on the material being treated, there are variations, and some metals appear to perform better with repeated temper hold cycles.

It can be seen from the preceding that the methodology has moved far away from the quick "dip and quench" method used so many years ago; now the process can take days. To support this sort of processing, one must have specialized equipment, and most houses today use "cold chamber" machines, and do not subject treated parts directly to liquid nitrogen. Producers all agree that maintaining cycles accurately is a most important part of the process, and most equipment currently being used in high quality applications is microprocessor controlled for both time and temperature.

A cryogenic cold chamber usually looks like a horizontal freezer, or sometimes, a round washing machine with a top-loading door. There will normally be one or more large Dewar containers adjacent to store the liquid nitrogen. Some systems use conventional refrigeration to get temperatures as low as possible before switching over to nitrogen. There seems to be a trend to increasingly colder temperatures: some companies are advertising their cold "soak" cycle at –320F. One saving grace is that there appears to be no degradation of material characteristics from, for example, a soak lasting longer than necessary, or at a colder temperature; in this respect, cryo seems to be more forgiving than elevated temperature processes.

APPLICATIONS AND ACCEPTANCE

It should be mentioned that there is a fairly wide acceptance of this technology in certain applications outside of racing. In particular, manufacturers of cutting tools have been using cryogenic treatment for ▶

Cryogenic treatment at Frozen Solid Ltd in the UK (picture courtesy of Matt Woods)

many years now, and their test data, while empirical, is hard to ignore, as several of them have done extensive side-by-side cutting tests, where tools are run under identical conditions until the point of failure (complete edge breakdown).

Firearms manufacturers use the stress relieving properties in steels to stabilize gun barrels, and improve the action of sliding and wearing components.

One of the first users of cryogenically processed components was the National Air and Space Administration. NASA's interest goes well back to the early 1960s, when they were trying to duplicate the conditions that materials would be exposed to in the deep cold of space. It was during these simulation experiments that changes in material behavior began to be measured carefully, and closely quantified. Measured improvements in strength, ductility, and toughness led to NASA becoming a regular cryogenic user. Many of the current cryo companies credit NASA with giving the industry a "jump start", not only because of the applications they developed, but for the improvements in equipment that resulted as well. Some of NASA's requirements are unique: in many cases, they are more concerned with the performance of materials at cryogenic temperatures, than material transformation per se.

CRYOGENIC TREATMENT IN MOTORSPORT

Virtually every part of an engine or gearbox can be treated cryogenically. Many of the web sites maintained by cryo treating houses make claims of 4-to-5 percent greater torque at any given engine speed as result of treatment and some of them have side-by-side dyno test results to justify the claim. Of course, since these tests cannot be conducted immediately after each other, it is hard to quantify with certainty that quality improvement is due to cryogenic conditioning. The belief is that the improved coefficient of friction and hardness due to the superior distribution and quantity of carbides is an important reason for the improved performance. In addition, with a reduction of residual stresses, there is less friction as result of springing and distortion of components, as well as a higher energy return through the parts themselves.

Proponents of cryogenic treating report that engine blocks are truly stress relieved after the process is completed, and that these blocks are equivalent to blocks that have been "time-seasoned" by standing for a year or more through various ambient temperature cycles.

There already is a great deal of acceptance of cryogenic treatment among "grassroots" racers. This is in part, no doubt, due to the inexpensive nature of the process. Cryogenic conditioning costs run to the "dollars per pound" range, and this makes it accessible to virtually any competition budget. Many companies have lots of anecdotal evidence and testimonials from local racers about the effectiveness of their work, and for cost-conscious teams, "cryo" takes the form of cheap insurance, especially since they cannot afford nearly as frequent tear-down and rebuild cycles as their professional counterparts.

There does seem to be something of an "it can't hurt, and it might help" attitude among many of these customers, which makes their testimonials as to the efficacy of cryo somewhat inconclusive. A growing level of acceptance is asserted for Formula One and Indy-style racing as well, but this does not yet appear to be universal. In NASCAR, the Cale Yarborough team has been cited as one of the pioneers in adopting cryogenics for its drivetrain applications, and nowadays there are some NASCAR teams that reputedly have their own cryogenic treating equipment in-house.

"Because of the extreme loads imposed by the valvetrain, all of our Top Fuel camshafts are produced from carburized steels. For these products, cryo is an integral part of the heat treating process, and is performed at the heat treater's facility," asserts a senior engineer with one of the better-known cam and valvetrain companies. "We see a measurable improvement in these components as a result." Like many others, however, he seemed less sanguine about general claims for cryogenic processing, and avoids suppliers that over-state its benefits.

"Much of our steel is comparable to steels used in the cutting tool industry. Our requirements are similar in that we need both hardness and toughness in our products. Our steel suppliers will specify cryo treatment for some alloys, but not others that are somewhat similar. This indicates that these recommendations are based on empirical experience, rather than a fully developed theoretical knowledge of precisely how the process affects these materials."

RET also contacted a well-known NASCAR engine builder, who reported that they have only used cryo sporadically on a limited number of components. "We haven't gotten into it that far yet, but we have heard some teams are using it more". He added: "We haven't considered it essential up until now but we are keeping our eyes open."

This last remark seems to summarize the current status of the technology in the racing world: that there is significant potential, and the benefits to carbon steels and martensitic high-alloy steels are reasonably well established for gears, shafts, valve springs and the like. The most effective treatments seem to be "application specific", which does not entirely conform to the general application claims made by some proponents of the process. Accordingly, it would seem that most are maintaining a "wait and see" attitude for using cryogenic treatment with other materials and applications, pending more research, and broader exposure of the results. ■