'COLD' FACTS
ABOUT CRYOGENIC PROCESSING

This article looks at the science of cryogenic treating: Is it myth or fact? Research is only now beginning to unlock the secrets as to how the process works. Because the process is not technically well understood, it has not reached even a fraction of its potential.

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Cryogenic processing (processing metals below -244°F) is making serious inroads into both consumer and industrial markets. Some of its applications defy the conventional logic that the only affect it has is to convert retained austenite to martensite. A striking application that illustrates this is the treatment of automotive brakes. Common brake rotors are pearlitic cast iron, without austenitic content. Yet, test after test by independent laboratories have shown that cryogenic treatment increases the life of a brake rotor by a factor of two to four times[1]. In a similar manner, carbide cutting tools, electronics, and plastics all show interesting effects that are not supported by the conventional theories as to why the process works.

This paper summarizes some of the recent research done worldwide, and presents a database of research created and maintained jointly by ASM and the Cryogenic Society of America.

Cryogenic Processing: What Is It?

Cryogenic processing is the creation of changes in materials by exposing them to cryogenic temperatures. What are cryogenic temperatures? There is no precise defining phenomenon that characterizes the upper reaches of cryogenic temperatures. Cryogenic temperatures are defined by the Cryogenic Society of America Inc., a professional society dedicated to the study of cryogenics (Oak Park, Ill; www.cryogenicsociety.org) at temperatures below -120K (-244°F, or -153°C). An interesting article on cryogenics in general written by the National Institute of Standards and Technology (NIST) is available at http://cryogenics.nist.gov/AboutCryogenics/about%20cryogenics.htm. Notice that these temperatures preclude cold treating as practiced by heat treating companies to convert retained austenite into martensite. Cold treating is usually performed down to about -140°F. Tests and research indicate that much greater wear resistance is generated by use of cryogenic temperatures than with cold treating temperatures[2].

Cryogenic processing, cryogenic treatment, and cryogenic tempering are all names that refer to a process where cryogenic temperatures are used to modify materials. Cryogenic processing and cryogenic treatment are the preferred names for this process.

Cryogenic tempering is a name that has become popular, but is imprecise as tempering is defined by the ASM Metals Handbook, Desk Edition as ". . . reheating hardened steel or hardened cast iron to some temperature below the eutectoid temperature for the purpose of decreasing hardness and increasing toughness." Archaic English refers to tempering as the entire hardening process, as in "tempered steel." Neither definition relates to the cryogenic process. This paper will stick with the term cryogenic processing. Note that we define the process as changing materials. Contrary to much popular belief, cryogenic processing works on materials other than ferrous metals.

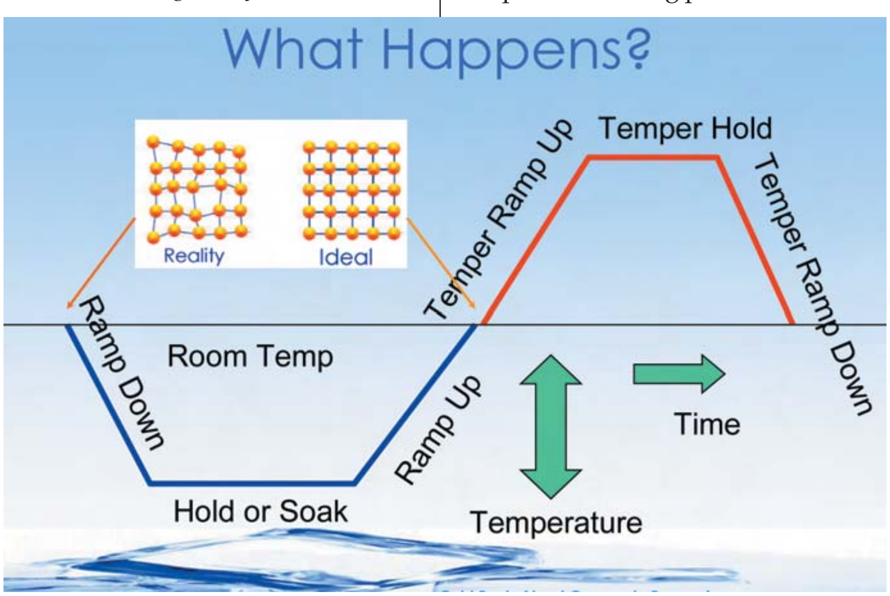

Fig. 1 — Generalized cycle of cryogenic processing.

The Cryogenic Cycle

There is a persistent idea that cryogenic processing can be accomplished by immersing a part in liquid nitrogen. Research has shown that better results are obtained by a cycle where the temperature of the component being treated is slowly reduced. A generalized cycle of cryogenic processing is shown in Fig. 1. The cycle has several steps including:

• Ramp down. In most cycles, the temperature is ramped down to 89K (-300°F, or -184°C) from ambient temperature in four to ten hours. This slow decent in temperature helps reduce the temperature gradient within the component and keeps stresses to a minimum.

• Hold. The temperature is held at 89K for a period of time, typically from six to forty hours.

• Ramp up. The temperature is brought back to ambient over a period of four to ten hours.

• Tempering. Tempering is used to temper any primary martensite that may have formed. Some materials require double or even triple tempering. The tempering cycle is not always required. Tempering temperatures and times vary with the material and the size of the part being tempered.

There is a misconception that there is no research to support the process.

Summaries of papers by legitimate researches that should dispel this notion are presented in this paper. We also present a source for more research papers, and will solicit the help of the scientific community to find more.

Cryogenic Processing Research Summaries

1. Illinois Institute of Technology (Formed Thermal Processing Technology Center under Dr. Philip Nash a Study on Effect of Cryogenic Treatment on M2 Tool Steel Masters Thesis by Rajenda M. Kelkar) gives independent verification that cryogenic processing is doing something beneficial to the metal.
2. Army Aviation & Missile Command With IITRI Study of wear resistance under Hertzian contact stresses of 9310 steel: 50% extra pitting resistance, 5% more load carrying capacity, 40 to 60°F higher tempering temperature.
3. NASA Study Effects of Cryogenic Treatment on the Residual Stress and Mechanical Properties of an Aerospace Aluminum Alloy (Po Chen, Tina Malone, Robert Bond, and Pablo Torres. 1999? NASA Marshall Space Flight Center): Reduced residual stress in HAZ 12 ksi, reduced residual stress in parent metal 9 ksi, minor increase in tensile strength and hardness, significant increases in stress corrosion cracking life.
4. University of Trento, Trento, Italy/GKN Corp.: Effect of Deep Cryogenic Treatment of the Mechanical Properties of Tool Steels (A. Molinari, M. Pellizzari, S. Gialanella, et al. 2001 *Journal of Materials Processing Technology*): Studied M2 and H13; improved hardness homogeneity, led to 50% cost reduction, increased toughness on H13, no significant changes to microstructure except reduction in retained austenite; need to study the sub-microstructure for mechanism.
5. Nanostructured Copper Is Six Times Stronger, Still Ductile (*Advanced Materials & Processes*/January 2003; Prof. En MA, Dept. of Materials Science and Engineering, Johns Hopkins University, Baltimore, Md.) A pure nanostructured copper metal is six times stronger than conventional Cu and still retains ductility. This was achieved through a combination of cryogenic treatment, metalworking methods, and heat treatment.
6. Micro Cracks Eliminated, Carbides Modified (Deep Sub Zero Processing of Metals and Alloys – Part II Evolution of Microstructure Of AISI T42 Tool Steel, C.L.Gogte, Kumar M. Iyer-Department of Metallurgical and Materials Engineering, VNIT, Nagpur, Maharashta, India; 2, R.K.Paretkar1, D.R.Peshwe1-Assab Sripad Steel Ltd., Chennai, India): There is change in the morphology of carbides, The phenomenon of merging/migration/dissolution of finer globular carbides takes place during the process leading to uniform distribution in the matrix, The microcracks present due to earlier processing are eliminated completely in the process, The stress-generated dislocations at the interface of the particles and the matrix causes diffusion, which is driven by the concentration gradient. The soaking time more than 8 and 16 hr leads to excessive contraction of the matrix thereby preventing any diffusion phenomenon. There is improvement in the tool life.
7. Copper Welding Electrodes Last Longer (Sub-zero Treatment of Steels Technology/Processes/Equipment, Linde AG, Linde Divison/82049 Hollriegelskreuth/Germany): Increases their life by a factor 2 to 9. Both durability and conductivity were increased although the mechanisms behind the improvement are being further researched. Stress relaxation through recrystallization is responsible for the property improvement.
8. Los Alamos National Laboratory, Cryogenic Treatment: The History, The Hype and The Science (Yuntian Theodore Zhu and Jianyu Huang, June 4, 2001, Illinois Institute of Technology, Thermal Processing Technology Center): Martensite is further changed during cryogenic treatment. Cryogenic treatment is real.
9. National Heat Treatment Centre, University College Dublin, Ireland (David N. Collins, *Advanced Materials & Processes*, Dec. 1998, p 23-30): A much greater number of carbide particles in the microstructure. Different partition of alloying elements between matrix and carbides. Improvement in wear resistance and increase in toughness. Little or no increase in hardness.
10. Classical Superconductors Absolute-Zero Phase Diagrams (Publication: Thermodynamics and Phase Diagram of High Temperature Superconductors; Reference: Ph. Curty, H. Beck Phys. Rev. Lett. 91, 257002 (2003) cond-mat/0401124): Superconductivity is present only below T_c (see Fig. 2).

Why Does Cryogenic Processing Work?

This is a basic question to which there is no definite answer yet. Obviously, the conversion of retained austenite is a factor for steel. But most retained austenite is converted by cold treating. Cold treating of metals has been known for many years, and takes place at around -140°F. Yet, research shows that the wear resistance of cold-treated steels is only a fraction of that of cryogenically treated metals[1].

Research also indicates the formation of very fine carbides, which is thought to increase the abrasion resistance of steels (see summaries 6 and 9). But these two factors do not explain why cryogenic processing has effects on nonferrous metals such as copper and aluminum (see summaries 3, 5, and 7). Another factor is the reduction of residual stresses caused by cryogenic processing (see summaries 3 and 7).

Cryogenic processing also has been shown to work on metals that show no austenite structure. Cast-iron brakes having a pearlitic microstructure are one very big example that is enjoying economic advantage and success. The authors have reviewed numerous tests performed for Precision Fleet Brakes Inc. (Austin, Tex.) by independent laboratories on brakes. The results show cryogenic processing increasing the life of brakes by a factor of two to four times[2].

So what else is happening at these cryogenic temperatures? The metallurgist's understanding of what happens at cryogenic temperatures is somewhat limited by several factors. There are thousands of years of experience with heating metals above ambient temperatures, but cryogenic temperatures have only been achievable since the late 1800s when the first ASUs (air separation unit) were produced. University courses for metallurgical engineering only explore phase diagrams from 0°C up. However, we know that there are definite changes at very low temperatures due to well-known phenomena such as superconductivity (see summary 5).

Most metallurgical engineering courses start with a description of crystal structures. In the book entitled *Structure-Property Relations in Non-Ferrous Metals*, the authors write: "In fact, the principal task of the metallurgical engineer could be described concisely as crystal defect engineering." They continue, "For *all temperatures above 0K (-273°C)* [italics added], there is a thermodynamically stable concentration of vacancies and interstitial atoms. Introducing a point defect into a crystal increases its internal energy vis-à-vis a perfect crystal."

Part of what we believe is the answer to what is happening is that the point defects in the crystal structure are being modified by the reduction in temperature as the crystal structure thermodynamically stabilizes to the low temperature. We also theorize that changes in solubility of the alloying elements in the crystal structure redistribute those elements.

Another theory is that the atom-to-atom spacing in the crystal structure becomes more uniform due to the removal of energy from the lattice structure. We invite those with more intimate knowledge of these factors to discuss them with us. We also invite experimentation and wish to cooperate with researchers into these subjects.

Organizational Support of Cryogenic Processing

Both ASM Cryogenic Processing Sub-Committee and the Cryogenic Society of America are working to encourage research of cryogenic processing. Both ASM and CSA have published papers and data on the process, and have taken an active interest in the issues reagarding the process.

Cryogenic Research Database

As a result of cooperation between the ASM Cryogenic Processing Sub-Committee and the Cryogenic Society of America, an online data base of technical articles about cryogenic processing has been published. This data base is available at http://www.cryogenictreatmentdatabase.org.

The Cryogenic Society of Americas states: "The purpose of the database is to encourage scientific research in the field of cryogenic treatment by providing a public and central source for information relating to the cryogenic treatment industry."

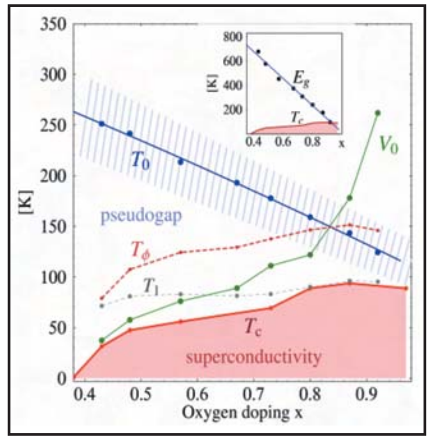

Fig. 2 — Classical superconductors absolute-zero phase diagram (from summary No. 10).

Wherever possible, CSA has acquired publications rights for papers and the entire paper is available on the web site. In some cases, important research articles are owned by publications that restrict access to visitors to their own sites, or by publishers who charge for access to the research. In those cases, we have included abstracts where available, along with information about the online location of the article or publisher.

The database is open for submission of articles and research papers. They should be mailed to:

Cryogenic Society of America
Cryogenic Treatment Database Article Submission
218 Lake St.
Oak Park, IL 60302-2609
USA

Articles and papers also can be submitted electronically via the database web site. Submitted articles are reviewed by a committee of three persons who vote on whether the article should be included in the database. Currently on this review committee are Dr. Randall Barron, Dr. Tom Siewert, and Frederick Diekman.

Conclusions

Cryogenic processing uses cold temperatures (liquid nitrogen, or in some cases helium) to make changes in materials properties. Most metals respond to cryogenic processing, and we are just beginning to understand why cryogenic processing works. The process can be used to improve performance, and it can give a company or race car enterprise a competitive advantage.

Future Work

Controlled Thermal Processing Inc. and Air Liquide U.S. LP work together in developing demonstration tests on different materials and industry applications that will continue to validate the previous work and benefits of cryogenic treating. Cryogenic processing holds huge promise to reduce production costs and increase product durability, which offers companies that use the process a means to hold a competitive edge in their markets. Cryogenic processing has proven itself with improved performance for many products including strength and wear life of all types of vehicle components, castings, cutting tools, etc. Other benefits include reduced maintenance, repairs, and replacement of tools and components, reduced vibrations, rapid and more uniform heat dissipation, and improved conductivity. A big advantage of the process is that it can often be added to components with no other engineering design changes. Research is only now beginning to unlock the secrets as to how the process works. Because the process is not technically well understood, it has not reached even a fraction of its potential. **HTP**

References

1. Numerous tests performed for Precision Fleet Brakes, Inc. by Greening Laboratories and Link Laboratories to SAE 2707 JUL 2004 METHOD B.
2. ASM Handbook, Volume 4, Heat Treating, ASM International, Materials Park, Ohio, p 205, 1991.

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