Deep Cryogenic Treatment for Marine and Oil-and-Gas Applications

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Cryogenic treatment of metal offers breakthrough reductions in wear and corrosion to users of marine components – lowering maintenance and capital replacement cost and increasing operational uptime. The technology has languished in the starting gate since WWII, however, and only recently emerged as a way to address wear and corrosion in post-heat-treated items.

This article will explore the benefits of deep cryogenics, why the technology stalled and where it can be next used by the oil-and-gas (O&G) and marine communities.

The Problem

Increasing the tensile and yield strength of carbon-steel wires and fasteners without increasing hardness is a constant challenge faced by heat treaters who support marine, wind and O&G industries. Subsea bolts, risers and umbilicals used on Christmas trees, BOPs, offshore platforms and tethers are constantly exposed to salt-water corrosion and wear. Although these items often fail due to assembly over-torquing or manufacturing defects, insufficient mechanical strength and stress corrosion cracking (as a result of hydrogen embrittlement) are frequently the root cause.[1]

A common solution to improve ultimate tensile strength is to increase the hardness of carbon-steel wire and fastener hardware via the austenitizing and quenching process. This assumes that higher hardness is beneficial to carbon steel operating at high temperatures, where it generally fractures in a high-toughness, ductile manner. But carbon steel operating in low-temperature marine environments fractures in a low-toughness, brittle manner. Therefore, increasing hardness is counterproductive to deep-water material longevity.

Exotic-alloy substitutions help, but the higher price and limited supply chain present barriers. Carbon steel is cheaper and widely available, but the alloy is often entrained with hydrogen, which is diffused along grain boundaries and can't meet longevity or performance requirements in subsea environments.

The Solution – Deep Cryogenics

Deep cryogenic treatment (DCT) is a cold-temperature process that reduces corrosion, wear, fracture and fatigue in most metal items by 20-70%. Thermo-kinetic exchange occurs during a prolonged time and temperature exposure to -310˚F dry-nitrogen vapor (Fig. 1) and imparts mechanical improvements.

The resulting metallurgical changes are retained austenite to martensite conversion (ferrous materials) and a non-reversal precipitation of primary and secondary eta carbides at the grain level. Despite multiple attempts using scanning electron microscopy, TEM, EBSD and nano-characterization, the mechanistic origins of the deep cryogenic phenomena behind

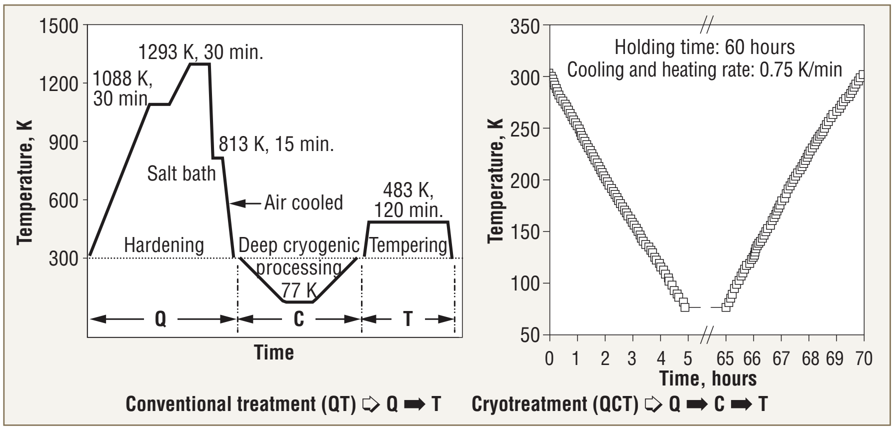

Fig. 1. Sample deep cryogenic treatment process. Each material requires a different procedure.

this improvement are unknown.

What standard ASTM destructive and nondestructive testing does show is that DCT:

- Increases tensile and yield strength in carbon- and bearing-steel alloys by 10-20% (Fig. 2)
- Reduces corrosion in high-carbon steel by 20-60% (Figs. 3 & 4)
- Reduces low- and high-carbon wear effect on some steels by a minimum of 30% (Figs. 5 & 6)

Industrial applications include oil and gas, marine, turbine, almost all additive-manufactured items, automotive, electric vehicles, wind and tidal energy. DCT addresses the greatest challenge facing all manufactured items — extending operational life.

How it Works

Items are placed in a specially designed tank and slowly cooled from ambient temperature down to -310˚F, cold soaked in a dry atmosphere over an 18- to 60-hour period and then slowly returned to room temperature before one to three annealing steps (needed to eliminate hydrogen embrittlement). The entire process takes three to four days, costs approximately 5% of the original item to double the wear and corrosion life, can be performed in bulk and can treat parts weighing up to several thousand pounds. The DCT process is nontoxic, uses no chemicals and generates no hazardous or environmental waste.

Effective on raw material, castings, forgings, and additive-manufactured and fully machined parts, it affects the entire through-core material, as distinct from surface treatments or applied coatings – maintaining wear protection even after coatings have eroded. The process generally (but not always) follows heat treatment and improves steel, aluminum, copper, titanium, refractory alloys and metal-matrix composites. The effect is more pronounced in single- versus dual-phase steels. DCT is fast, effective, low-cost and green. It is supported by over 25 years of quantitative scientific research from leading international universities. The process is currently at TRL 3-5 and is scalable to large industrial use.

History and Equipment

DCT has evolved greatly since WWII, when liquid nitrogen was experimentally poured on aircraft forging dies in primitive attempts to increase wear life. This often initiated fatigue cracking and fracture in those die sets when exposed to thermal shock. Between 1980 and 2000, technology advancements

	Yield KSI	Peak % strength		Strain stress	Reduction elong. @ break
		KSI	%	%	%
No cryo 52100, baseline	268	359	2.5	3.9	6
Cryo 52100, cryo then tempered	317	382	1.6	3.5	1
Cryo 52100, tempered then cryo	320	376	1.8	3.8	4.5
No cryo 4340, Baseline	221	295	15.3	12.5	51.7
Cryo 4340, cryo then tempered	240	300	14.2	11.6	51.3
Cryo 4340, tempered then cryo	221	287	15.9	12.3	51.6

Fig. 2. Deep cryogenic treatment of 52100 and 4340 steels showed a 20% increase in yield strength for cryo-treated steel.

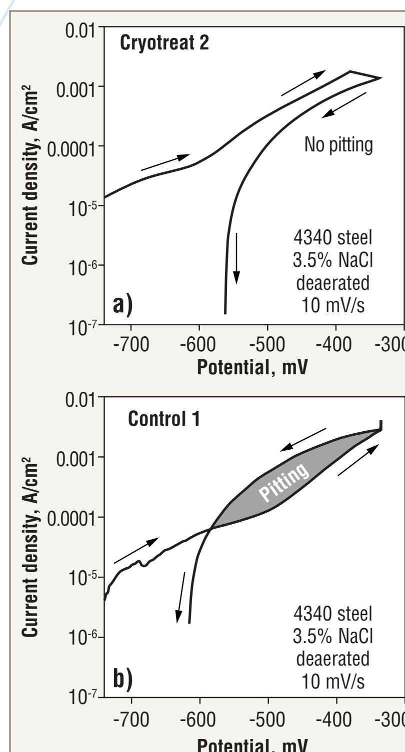

Fig. 3. Potentiodynamic pitting-resistance test of 4340 for 36 hours in 3.5% NaCl for three cryo-treated coupons (a) and three non-cryo coupons (b).

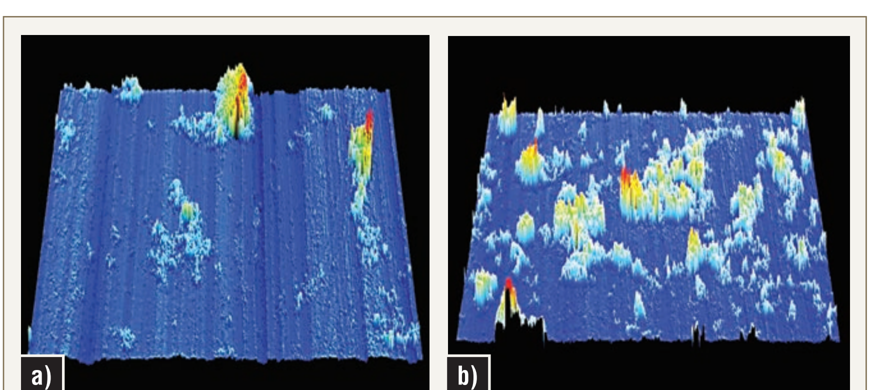

Fig. 4. Uniform surface-corrosion test of 4340 steel. Test was 18 hours in 3.5% NaCl with a result of 64% (volumetric) reduction in corrosion with cryo (a) vs. non-cryo (b).

including digital-controlled liquid N_2 supply, use of dry-nitrogen vapor, PID optimization and in-situ annealing capability vastly improved DCT processing results. However, small-size tanks are the norm – the largest commercially available being 3 x 3 x 6 feet. Among other reasons, small equipment size has effectively throttled industrial use.

Barriers to Entry

Until recently, widespread adoption of deep cryogenics has been hampered for the following reasons:

- No known test or qualification methods
- No engineering-based standards for deep cryogenic qualification or acceptance
- No large-capacity DCT tanks available to treat industrial size or quantities of parts
- No providers of scale-up treatment tanks or treatment services

Out of approximately 130 DCT captive or job-shop providers in the world, no facility offers on-site test, validation or certification documenting authenticated DCT of parts or actual measurement of the wear/corrosion improvement.

Unlike heat treating, which performs in strict accordance with hundreds of ASTM, Nadcap, AMS and MIL-STDs, nothing of the kind exists in the deep cryogenic industry. Instead, customers must rely on the DCT service provider's word and a receipt for payment as anecdotal proof of treatment, hence the lack of industry acceptance when no formalized test, qualification or acceptance occurs. Imagine the outcry if parts in an airplane, car or power plant were not built to standards or process testing never occurred!

As a result, almost all end users are individuals with small-size parts and small-scale demands – not military or industrial companies that drive large R&D efforts or downstream commercialization. Consequently, scale-up equipment has only recently emerged, and these large tanks almost certainly require on-site liquid-N_2 production as well as test equipment to be effective in remote locations. These barriers to market entry are high.

Qualification

Qualification agencies DNV-GL and Lloyds have both issued proposals charting the future application of this technology within the O&G community. Because use of DCT doesn't change sources of supply, material type, manufacturing method, dimensional tolerance or even end use, qualification time can be compressed in the traditionally conservative energy industry.

A key benefit is that DCT can be added to existing manufacturing processes without changing, modifying or eliminating any of the prior steps. A recent USPTO patent issuance may further change acceptance protocols by advancing both destructive and nondestructive testing of artifact coupons that accompany each DCT lot, the use of established ASTM tribology and corrosion procedures to qualify the proxy coupons,

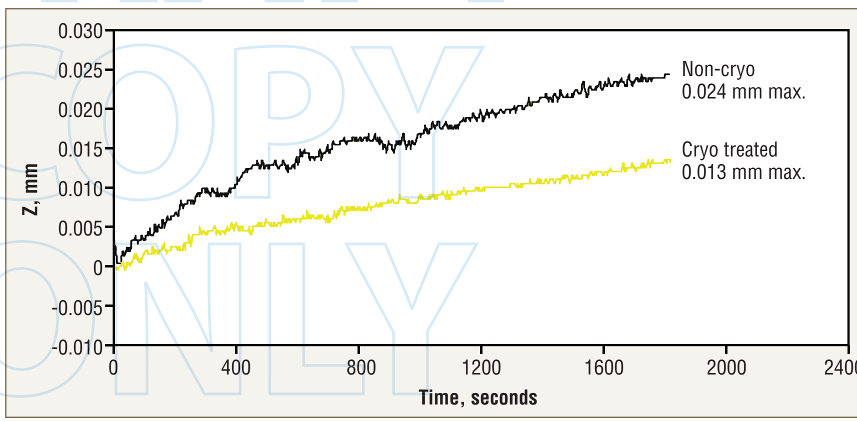

Fig. 5. Pin-on-plate wear-depth comparison. Test showed 84% reduction in wear depth during 30-minute self-mating test.

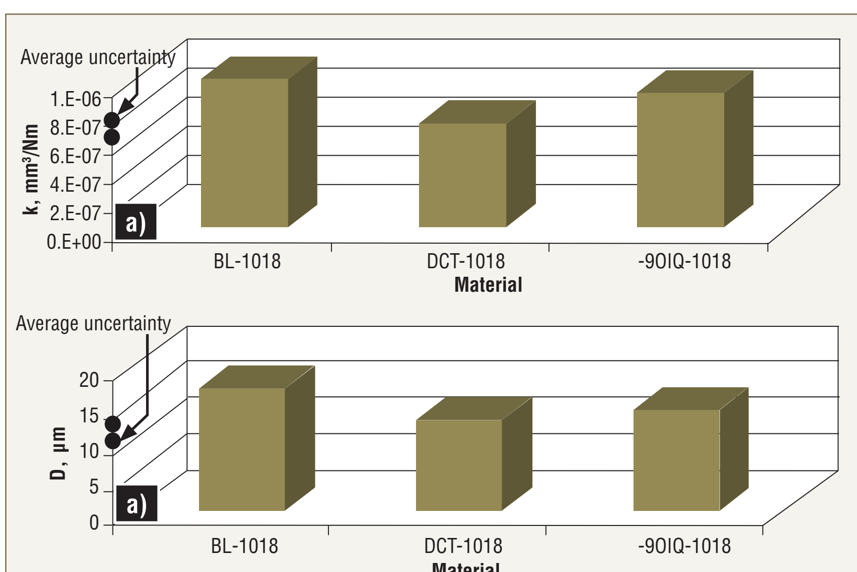

Fig. 6. High-load ball-on-disk tribological testing for 1018 steel showed an average wear rate (a) reduction of 30% for cryo vs. non-cryo. Similar trends were observed for average wear depth (b).

and reliance on high-quality optical profilers and tribology testers to provide absolute and parametric certification data.

Opportunities

Numerous marine assemblies – such as power plants, transmissions, subsea risers, umbilicals, drill string and pipe – are an excellent match for improvement by deep cryogenics. But DCT of abrasive wear components including drilling bits, valve and erosion sleeves, thrust bearings, injector nozzles and gears are even better insertion points because they allow the substitution of low-cost carbon steel for expensive superalloys and tungsten-carbide products.

Mining operations can expect significant uptime increase and maintenance decrease by DCT of crusher teeth, mill liners, pump-box nozzles and slurry pipe – items that often fail due to erosion corrosion, rolling-contact fatigue, mechanical-induced fatigue or gouging/high-stress abrasion.

Summary

Deep cryogenics will allow heat treaters and end users to sharply reduce wear and corrosion effect on marine and industrial items. The technology has now come of age with the introduction of engineering-based acceptance standards, known destructive/nondestructive testing, large-size tanks and certification protocols.

The first companies to purchase and implement a scale-up DC tank and test/certification protocols will likely gain the first-mover advantage. This step-change in thermal treatment of metals will pass on to customers reduced operational downtime, lower maintenance/capital-replacement cost and increased net profitability. A disruptive technology that has finally arrived.

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Reference

1. "QC-Fit Evaluation of Connector and Bolt Failures - Summary of Findings," BSEE Office of Offshore Regulatory Programs, Aug. 2014