ENGINEERING MATERIALS ACHIEVEMENT AWARD

Low-Temperature Colossal Supersaturation

Swagelok won the 2006 Engineering Materials Achievement Award for its surface treatment that both hardens the surface of stainless steel and improves corrosion resistance.

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Low-temperature colossal supersaturation (LTCSS) is a novel surface hardening method for carburization of austenitic stainless steels without the precipitation of carbides. The formation of carbides is kinetically suppressed, enabling extremely high or colossal carbon supersaturation. As a result, surface carbon concentrations in excess of 12 at.% are routinely achieved. This treatment increases the surface hardness by a factor of four to five, improving resistance to wear, corrosion, and fatigue, with significant retained ductility.

LTCSS is a diffusional surface hardening process that provides a uniform and conformal hardened gradient surface with no risk of delamination or peeling. The treatment retains the austenitic phase and is completely non-magnetic. In addition, because parts are treated at low temperature, they do not distort or change dimensions.

To make the process work, the naturally forming Cr_2O_3 surface passive layer on the stainless steel has to be removed to "activate" the surface for carburization. Without this activation step, carbon diffusion into the surface is blocked. This is solved by placing the part in an atmosphere of carbon-assisted gaseous HCl, which removes the Cr_2O_3 from the surface.

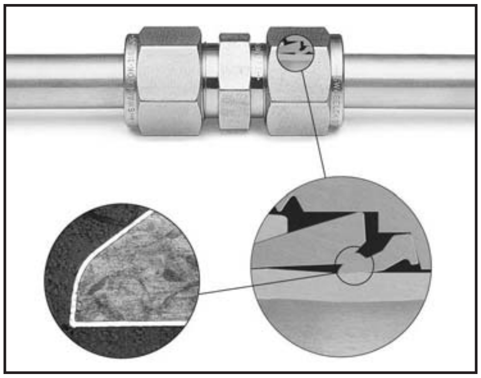
The LTCSS process

After initial activation in the carbon-assisted gaseous HCl, as shown in the diagram, the metal alloy is heated in a mixture of carbon monoxide, hydrogen, and nitrogen at a temperature of 470°C for three hours. A carbon solid-solution case begins to form at temperatures high enough to promote carbon atom diffusion from the surface, but low enough to prevent carbide formation.

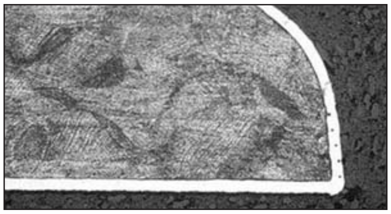
The surface is then activated once again, this time with carbon assistance, and carburized again at 470°C for 20 to 30 hours. At the end of this treatment, the amount of carbon in the interstices of the alloy crystals has been elevated in excess of 12 at.%, and the alloy is cooled.

During this treatment, carbon diffusion proceeds into the metal at temperatures that constrain substitutional diffusion or mobility between the metal alloy elements. Though immobilized and unable to assemble to form carbides, chromium and other metal elements nonetheless draw enormous amounts of carbon into their interstitial spaces.

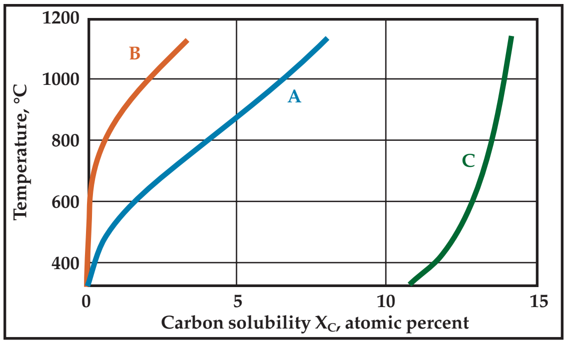
The carbon in the interstitial spaces of the alloy crystals makes the surface harder than ever achieved before by more conventional heat treating or diffusion process. The carbon solid solution manifests a Vickers hardness often exceeding 1000 HV (equivalent to 70 HRC), with an associated expanded metal lattice and resultant compressive stress.



This image shows a Swagelok tube fitting cutaway. The back ferrule is treated by LTCSS, enabling a gas-tight seal, tube grip, and vibration resistance on makeup of the fitting.



The hardened surface layer is at least 25 µm thick. Close to the surface, a Vickers hardness of ≈HV1200 is measured — this corresponds to four to five times the hardness for bulk 316 steel. The thickness of the hardened layer can be increased further by additional carburization treatments at the same temperature. Hardness depths of 10 to 50 µm are routinely achieved.



Low-temperature colossal supersaturation. Line A, for pure iron, assumes the absence of ferrite. The presence of chromium (a strong carbide former) in Type 316 SS reduces the carbon activity coefficient in iron, and hence the maximum solubility of carbon (line B). Absent carbide formation, however, the maximum para-equilibrium solubility of carbon is greatly enhanced (line C).

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*Member of ASM International

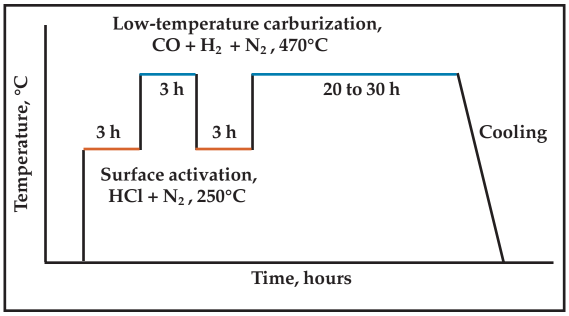
Recent developments

In January 2004, Swagelok, Case Western Reserve University (CWRU), and Oak Ridge National Lab started on a $2.5 million three-year research project, funded in part by the Department of Energy through the Energy Efficiency and Renewable Energy Industrial Technologies Program. The project objective is to extend the LTCSS treatment to other alloys, and to quantify improvements in fatigue, corrosion, and wear resistance. Highlights from the research include the following:

- **Microstructural characterization:** XRD evaluation of treated materials at CWRU verifies expanded austenite, with no evidence of carbide precipitation. Carbon concentration profiles via Auger and EDS show carbon levels in excess of 12 at.% in treated Type 316 stainless steel. Scanning electron microscopy of pulled-to-failure treated tensile specimens shows slip bands and no de-cohesion of the treated layer, verifying that the layer remains ductile. Compressive stresses in excess of 2 GPa have been calculated at the surface of the case, based on the XRD lattice expansion and the carbon concentration.
- **Thermodynamic modeling:** CALPHAD (Thermo Calc) and Wagner dilute solution thermodynamic models have been developed at CWRU. These models calculate the solubility of carbon in austenite as a function of alloying content for the process time and temperature. Elements considered in the model include Fe, Cu, Ni, Co, Cr, Mn, Si, Mo, W, Al, V, Nb, Ti, Zr, and N. Special efforts were made to determine the necessary carbon-matrix element interaction parameters relevant to LTCSS. Several commercial alloys have been modeled, and the model has been used to design experimental alloys with enhanced affinity for carbon solubility at treatment temperatures.

At Oak Ridge, four of the experimental alloys have been melted, rolled, and manufactured into test specimens, and initial LTCSS treatment indicates successfully enhanced results.

- **Corrosion resistance:** Electrochemical polarization curves determined at Swagelok, CWRU, and the Naval Research Lab show a 600 to 800 mV increase in pitting potential in treated (900-1000 mV) versus non-treated (200-300 mV) type 316 in chloride solutions.



After activation in the gaseous HCl, the metal alloy is heated in a mixture of carbon monoxide, hydrogen, and nitrogen at a temperature of 470°C for three hours. A carbon solid-solution case begins to form at temperatures high enough to promote carbon atom diffusion from the surface, but low enough to prevent carbide formation. The surface is then activated once again, this time with carbon assistance, and the alloy is heated again at 470°C, this time for 20 to 30 hours. At the end of this treatment, the amount of carbon in the interstices of the alloy crystals achieves and often exceeds 12 at.%, and the alloy is cooled.

Two possible causes for the enhanced corrosion resistance were posited: the concentration of carbon at the surface, or the enormous surface compressive stress. An electrochemical polarization curve was prepared for the plastically deformed gage length of a pulled-to-failure treated tensile pull specimen, to remove the effect of the residual compressive stress. This curve showed the same enhanced corrosion behavior, indicating that the enhancement is due to the high carbon concentration.

Polarized crevice corrosion tests at the Naval Research Lab showed five orders of magnitude improvement in crevice-corrosion resistance for treated vs. non-treated type 316L. Treated 316L showed crevice-corrosion behavior similar to that of Ti-6Al-4V and Hastelloy C22.

- **Erosion resistance:** Cavitation tests up to six hours in duration at Oak Ridge, with a vibratory horn and mercury as the dense liquid medium, show that treatment on Type 316 specimens reduces weight loss by a factor of about 5.5 times. This finding is particularly important for slurry and corrosive pumping applications.
- **Wear resistance:** Wear tests at Oak Ridge also indicate significant enhancement in wear properties, important for bearing applications. Standard ASTM pin-on-disk sliding friction and reciprocating friction tests show wear rates of treated couples (ball and disk) lowered by approximately 100 times compared to non-treated. An ASTM standard continuous loop abrasion test (rotating abrasive belt) showed a 30% reduction in wear volume for treated vs. non-treated 316 specimens.
- **Fatigue resistance:** Fatigue testing at CWRU shows an order of magnitude improvement for treated versus non-treated Type 316 at the same maximum stress level (R = -1). The maximum stress at 10^7 cycles, the endurance stress for infinite life, improved by approximately 50%, from 30 to 45 ksi.

In short, LTCSS is a paradigm-shifting technology: applied to stainless and corrosion resistant alloys, it significantly enhances performance characteristics, and extends the use of these alloys into applications currently served by more expensive materials.

Other alloys

In addition to austenitic stainless steels, we have been pleasantly surprised by the ability to treat chromium-containing precipitation-hardening stainless steels, duplex alloys, nickel-based alloys, and cobalt-based alloys. At present, Swagelok uses the technology for treatment of tube fitting rear ferrules, mostly manufactured in type 316 stainless steel. Swagelok intends to make the technology available commercially to third parties, and will set up a new business unit to support these efforts.

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