Low-Temperature Carburization of Austenitic Stainless Steels

S.R. Collins, P.C. Williams, and S.V. Marx, Swagelok Company
A. Heuer, F. Ernst, and H. Kahn, Case Western Reserve University

LOW-TEMPERATURE CARBURIZATION is a gaseous carburization process performed at atmospheric pressure, at temperatures where the kinetics of substitutional diffusion are very slow. Low-temperature carburization hardens the surface of austenitic stainless steels through the diffusion of interstitial carbon, without the formation of carbides. The surface must be activated, by modification and removal of the naturally occurring chromia layer, for the process to work. The process results in a hardened diffusional case on the surface, typically 20 to 35 µm thick, with carbon content at the surface in excess of 10 at.%. The process is conformal and can be applied to finished components without change in dimension. Property enhancements include:

- **Increased surface hardness**: Close to the surface, a microhardness value of approximately HV 1200 is obtained, which corresponds to greater than 70 HRC.
- **Residual compressive stress**: At the surface, values in excess of 2 GPa (300 ksi) have been measured by X-ray diffraction.
- **Retained ductility**: Scanning electron microscopy of surfaces of tensile bars tested to failure show deformation characteristics typical of austenite (i.e., intersecting slip bands) and the absence of cracking.

This combination of increased surface hardness, compressive surface stress, and retained ductility leads to improved performance in applications demanding resistance to wear, erosion, and fatigue. Additionally, corrosion resistance to a variety of chloride-containing media also has shown dramatic improvement, due to carbon-enhanced passivity of the resulting surface.

**Overview**

Case hardening is a widely used industrial process for enhancing the surface hardness of metal and alloy components. In a typical commercial process, a carburizing gas contacts the workpiece at elevated temperature and carbon atoms diffuse into the metal surface. Hardening occurs through the formation of carbide precipitates. Gas carburization normally is accomplished at 950 °C (1700 °F) or above, because most steels must be heated to these temperatures to transform to the high-temperature austenitic (face-centered cubic, or fcc) structure preferable for carbon infusion. This structure is preferable because it enables higher diffusivity and higher solubility limits than the ferritic (body-centered cubic, or bcc) structure.

Austenitic stainless steels are among the most ductile and most corrosion resistant of all ferrous alloys. However, they have only modest hardness compared to other steels, limiting their performance in many applications. These steels typically contain 10 to 18 wt% Cr and 8 to 14 wt% Ni; the chromium addition provides corrosion resistance, while the nickel addition stabilizes the desirable austenitic structure at room temperature. These alloys are valued for their combined corrosion resistance and ductility. In many technical applications, however, their performance, lifetime, and aesthetic appearance would be improved if their surfaces were hardened. Unfortunately, hardening by conventional carburization is carried out at elevated temperatures, where the formation of chromium-bearing carbides cannot be avoided, and chromium depletion from the austenite matrix can compromise corrosion resistance. Additionally, the levels of hardness that can be achieved are limited by the resulting microstructure of the case, a distribution of chromium-rich carbides in a chromium-depleted matrix. Hardness values of 50 to 60 HRC are achieved under these conditions, at the expense of corrosion resistance of the alloy.

Low-temperature carburization hardens the surface of chromium-containing austenitic alloys, in particular austenitic stainless steels. The process involves activation of the surface followed by a gas-phase carburization treatment, performed at temperatures low enough to avoid the formation of carbides (350 to 550 °C, or 660 to 1020 °F), for a sufficient time (typically 20 to 60 h) to allow carbon diffusion to occur.

The result is a carbon-rich, uniform (single-phase) and highly conformal compositionally graded surface layer ranging from 10 to 40 µm thick, with a near-surface hardness that can approach HV 1200 (over 70 HRC). Because the treatment occurs at low temperature and phase transformations are avoided, parts do not distort or change dimensions. Carbon concentrations at the surface of treated 316 stainless steel components have been verified by a variety of analytical methods to be in the order of 12 to 15 at.%; up to 20 at.% has been demonstrated on treated superaustenitic steels. The case remains austenitic and retains its ductility. Parts can be bulk handled, enabling processing of high numbers of parts. In this article, examples shown are results for 316 stainless steel, although a substantial body of data has been generated for other industrially important alloys, such as superaustenitic stainless steels, precipitation-hardening stainless steels, duplex alloys, nickel-base alloys, and cobalt-base alloys (Ref 1–3).

**Background and Competing Technologies**

Methods for hardening stainless steel surfaces have been researched since at least the 1980s (Ref 4, 5). These methods include liquid sodium and cyanide salt bath treatments, plasma nitridation and carburization (Ref 6, 7), ion implantation, and gaseous atmospheric heat treatments. All of these methods will provide a hardened diffusion case on stainless steels with varying performance characteristics. However, commercial scale-up has been elusive for many of these methods due to technological barriers. For example, liquid sodium activates and readily transfers carbon to the stainless steel, but a scale-up from the laboratory to a production process presents a significant hurdle for safety and handling reasons. Plasma and ion methods are line-of-sight
methods. They effectively activate the surface but are not able to provide a uniform case for workpieces with complex shapes, especially in batch processing.

Recent survey articles have reviewed the worldwide state of low-temperature nitriding and carburizing of austenitic stainless steels (Ref 1, 8). In addition, several academic conferences have been held in the past two decades on the topic of low-temperature thermochemical surface treatments of stainless steels (Ref 9–13).

On the commercial front, several entities advertise low-temperature hardening processes for stainless steels, as shown in Table 1. It should be noted that only two of these processes (SAT12 and NV Pionite) are known to be gas-phase low-temperature carburization, while the entity responsible for a third carbon-imparting method (Kolsterising) is entirely silent on how it is achieved. The process and results discussed in this article are specific to the Swagelok SAT12 treatment.

### Commercial Application

Since 1999, low-temperature carburization has been applied to the ferrules of the Swagelok tube fitting, as shown in Fig. 1. In recognition of the development and commercialization of the surface-hardening technology in the tube fitting application, Swagelok received the ASM International Engineering Materials Achievement Award in 2006 (Ref 14). Swagelok has a captive heat treating facility that batch processes and bulk handles millions of ferrules per year, in nominal sizes ranging from 6 mm to 1 inch. The process is performed in specialty-built carburization furnaces with enhanced gas handling capabilities, as shown in Fig. 2. Due to the use of dry HCl and CO in the process, the furnaces must be leak-tight to atmosphere.

### Process Considerations

Successful low-temperature carburization of stainless steels and other chromium-containing alloys depends on the alignment of several processing parameters. These include activation of the surface, proper surface preparation, selection and condition of the alloy to be carburized, treatment temperature, and carburizing atmosphere. Figure 3 shows a typical process cycle.

#### Activation

Stainless and other chromium-containing alloys obtain their “stainless” characteristic from the chromium-rich oxide that forms on the exposed surface. This oxide layer forms when a fresh surface is exposed to an oxygen-containing medium, such as air, and will form after very short time exposures. The chromium layer on the surface of stainless steel constitutes a major hurdle to low-temperature carburization because it blocks the inward diffusion of carbon. In order to diffuse the carbon atoms into the stainless steel from the surface, the chromium oxide layer must be removed, or at least modified so that the inward diffusion is not impeded. This step generally is known as surface activation or depassivation.

Several methods have been developed (Ref 15–19) that eliminate the inhibiting effects of the oxide and activate the surface for efficient transport of carbon from a conventional carburizing atmosphere into the stainless steel matrix. As noted earlier, some processes, such as plasma or liquid sodium treatments, readily activate a passive stainless steel surface by removing the oxide by sputtering. In commercial production processing, activation can be achieved by exposing the furnace load to a halide-containing gas mixture such as nitrogen trifluoride or hydrogen chloride and nitrogen at atmospheric pressure. Hydrochloric acid is effective as an activating gas for a wide range of chromium-containing corrosion-resistant austenitic alloys, including stainless steels and nickel-base alloys, such as alloys 625 and 825.

### Processing Temperature Ranges and the Concept of Paraequilibrium

Low-temperature carburization has a limited temperature processing range, usually 350 to 550 °C (1020 °F). At the lower processing temperature, the process becomes very slow and less economically feasible. Lower temperatures mean longer times for the same case thickness. At the upper end, it becomes increasingly difficult to avoid the formation of carbides, which depend in part on the thermally-assisted mobility of substitutional alloying elements, such as chromium, in the iron matrix.

Traditionally, carburization is carried out at high temperature to maximize the solubility and the rate of interstitial solute diffusion. On cooling to room temperature, however, a major part of the solute atoms will precipitate as carbide phases. Figure 4 shows the appropriate time-temperature-transformation (TTT) diagram for the heat treatment of an austenitic stainless steel with conventional carbon contents (Ref 20). After high-temperature carburization (T > 950 °C, or 1740 °F), precipitation of carbides can be avoided only by extremely high cooling rates (path A). Furthermore, it is easy to exceed the solubility limit at these temperatures and form carbides during the carburization process itself. At the cooling rates typical of industrial processes, however, the path will cross the carbide “nose” and precipitation will occur (path B). Similar problems are encountered in nitridation of these steels. Carburization at low temperatures proved capable of hardening the surface of austenitic stainless steel without forming phases that would deplete the matrix of chromium, and thereby degrade corrosion resistance. In this process, the formation of carbides is kinetically suppressed (path C). This results in an extremely high or “colossal” carbon supersaturation, in fact far higher than can be achieved by high-temperature carburization.

At moderate temperatures, substitutional solutes such as chromium and nickel diffuse much more slowly in austenitic steels than do interstitial solutes such as carbon. At 450 to 500 °C (840 to 930 °F), the diffusivity of chromium is on the order of 10⁻¹¹ m²/s (Ref 21), whereas the carbon diffusivity at this temperature is in the range 10⁻¹⁰ to 10⁻¹¹ m²/s (Ref 22–24). This factor of 10³ to 10⁴ difference in diffusion coefficients enables homogeneous carburization in austenitic stainless steels (and other fcc alloys)

---

**Table 1** Commercially available processes for low-temperature nitriding and carburizing of stainless steels

<table>
<thead>
<tr>
<th>Entity</th>
<th>Process name</th>
<th>Interstitial hardening element</th>
<th>Temperature (°C)</th>
<th>Method</th>
<th>Applications</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>University of Birmingham, U.K.</td>
<td>LTPN</td>
<td>N</td>
<td>&lt;450</td>
<td>Plasma</td>
<td>Hardware, watch cases</td>
<td>Bodycoate acquired Nutrid (France) 2010</td>
</tr>
<tr>
<td>Bodycote, U.K.</td>
<td>Kolsterising</td>
<td>C</td>
<td>&lt;550</td>
<td>Plasma</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nihon Parkerzising, Japan</td>
<td>Palsonite</td>
<td>N</td>
<td>&lt;460</td>
<td>Plasma</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Airwater Ltd., Japan</td>
<td>NV Super Nitriding</td>
<td>N</td>
<td>300–400</td>
<td>Gas</td>
<td>Flatware, hardware</td>
<td></td>
</tr>
<tr>
<td>Swagelok Company, U.S.A.</td>
<td>SAT12</td>
<td>N</td>
<td>380–550</td>
<td>Gas</td>
<td>Tube fitting ferrules, hardware</td>
<td></td>
</tr>
<tr>
<td>Nitrex Metal Technologies, Canada</td>
<td>Nitrex-S</td>
<td>N</td>
<td>380–550</td>
<td>Gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expanite A/S, Denmark</td>
<td>Expanite</td>
<td>N</td>
<td>380–550</td>
<td>Gas</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
under conditions where the formation of chromium-rich carbides is suppressed by insufficient diffusion kinetics for substitutional solutes. In other words, carburization is possible below the nose of the carbide curve on the TTT diagram shown in Fig. 4. At the relevant temperatures, the system is not able to approach a complete thermodynamic equilibrium, because local differences in the chemical potentials of the metal atoms cannot be equilibrated by transport. Only nonuniformities of the chemical potentials of the interstitial solutes can be equilibrated. Such limited equilibration of some, but not all, components in a metallic system is called “paraequilibrium.” This can occur at temperatures where substitutional solutes are effectively immobile, whereas interstitial solutes such as carbon can diffuse over appreciable distances within reasonably short times. Peraequilibrium in austenitic stainless steels allows for vastly increased solubility limits for carbon.

Carburizing Atmosphere

Several carburizing gas species will impart carbon to the active surface, with varying levels of efficiency at the processing temperatures required for low-temperature carburization. These include acetylene and carbon monoxide, among others. Pack carburization also has been demonstrated. A side effect of the high carbon potential needed for processing can be the generation of soot, which then has to be removed after processing using standard aqueous cleaning methods.

Candidate Alloys for Treatment

Several commercially-available corrosion-resistant alloys can be treated by low-temperature carburization. The process has been applied to 300 series stainless steels, in particular 316 stainless steel, with great effectiveness. Optimal treatment is obtained on single-phase fcc or fully austenitic alloys containing high fractions of chromium and nickel. Under paraequilibrium conditions chromium, with its high affinity for
carbon, enables a dramatic increase of the solubility limit of carbon (Ref 25, 26). Nickel, although not a carbide-forming element, appears to enhance the carbon levels that can be obtained by suppressing carbide precipitation (Ref 27).

Austenitic stainless steels can contain less desirable metastable phases, such as ferrite (bcc) and strain-induced martensite (body-centered tetragonal, or bct). Ferrite can be retained in austenitic stainless steels if not sufficiently hot worked or homogenized. Strain-induced martensite can occur on the surface of susceptible alloys that have been heavily worked or machined. Carburization treatment of ferrite or martensite at temperatures usually applied to austenite results in a severe loss of corrosion resistance. The mechanism appears to be the creation of surface carbides in the ferrite phase. Optimal treatment by low-temperature carburization occurs when these phases are not present; ferrite can be reduced or eliminated by annealing, and strain-induced martensite can be removed via electropolishing.

Other alloys have been treated with varying levels of success; these include superaustenitic stainless steels (AL6XN, 254SMO), precipitation-hardening iron-base superalloys (A286), nickel-base corrosion-resistant alloys (alloy 625, alloy 718, alloy 825, Hastellox C), precipitation-hardening stainless steels (17-4PH, 15-5PH, 13-8Mo), and duplex stainless steels (2205 and 2507).

Product Forms and Surface Condition

Low-temperature carburization has been successfully applied to several product forms, including plate, sheet, foil, wire, machined components, castings, forgings, powder, powdered metal (P/M) and metal injection molded (MIM) components. Surfaces must be clean and free of scale, oil, or other residues so that the activation step can proceed. The mechanical surface condition needed for a successful treatment has been evaluated based on performance characteristics of the surface after treatment. Acceptable surface roughness parameters were determined from cyclic polarization tests performed on samples with different finishes. A 120 grit finish or better hardly limits the corrosion response in cyclical polarization testing. Rougher surfaces may show metastable pitting (Ref 28). The 120-grit finish typically is much rougher than the finish obtained through standard machining practices.

The activation step illustrated in Fig. 3 is interrupted with a short carburization cycle. This processing feature enables a deeper and more uniform case, apparently because it provides better surface activation. Observations by researchers of corrosion in flue gases (Ref 29) suggest that the presence of soot enhances activation of passive surfaces. Additional research on the second carburization cycle showed that a ramped carbon potential was needed to achieve the hardness and depth required, and to minimize the formation of soot that would need to be removed in postprocessing.

**Quality Control Methods for Evaluating Treatment**

When parts are treated correctly, application of the low-temperature carburization process should be transparent to the end user. In other words, the parts should visually appear as they did prior to treatment. Because only a layer comprising the first 2.5 μm or so below the surface is affected by the treatment, it can be difficult to determine if a component has been treated without resorting to destructive methods and optical microscopy. Two qualitative methods for examining treatment have been used: scratch hardness using calibrated files, and immersion in sodium hypochlorite solutions. These methods interrogate the case by examining improvements in hardness and corrosion response to a chloride-containing environment. Although they can identify a difference between a treated and nontreated surface, they are not specific enough to be used for anything but a screening test. For detailed evaluation of case properties, quantitative methods providing enhanced spatial resolution are preferable. These include light optical microscopy of metallographic cross sections, depth profiles of nano- or microhardness, and composition-depth profiles obtained through glow-discharge optical emission spectrometry (GD-OES) or calibrated Auger electron spectroscopy (AES) using a scanning Auger microprobe (SAM) on a cross section. These methods are destructive, in that a component must be sectioned to evaluate the case. However, quantitative comparative data is obtained and can be used to develop metrics for the case.

**Microstructure of the Low-Temperature Carburized Layer**

The low-temperature carburized layer on austenitic steel has been characterized using optical metallography. On a sectioned and etched specimen, the case appears as a relatively featureless, etch-resistant surface layer of approximately 10 to 40 μm. This layer is a diffusion gradient of carbon in solid solution in the austenite matrix. The structure of the case has been evaluated by X-ray diffraction, and has been shown to be expanded austenite. The lattice parameter of the austenite expands from 0.360 to 0.372 nm after treatment (Ref 30). Other researchers, particularly those working in low-temperature nitriding processes, have called this structure S-phase (Ref 31–33). However, there is no phase transformation and the layer does not represent a new phase. Expanded austenite is formed when large amounts of either nitrogen or carbon (or both) are dissolved in the surface of an austenitic stainless steel, forming a supersaturated solid solution without the precipitation of chromium-containing nitrides or carbides. Data for treated 316L stainless steel are shown in Fig. 5 (Ref 34). The surface was electropolished for different times to progressively remove the case. The analysis used X-ray diffraction (XRD) to determine the lattice parameter and evaluate residual stresses, and to identify the possible presence of carbides arising from carburization. The shift in the peaks to lower 20 values for lesser amounts removed (higher concentrations of carbon) indicates the increasing lattice expansion. Carbon concentration profiles using Auger electron spectroscopy (AES) and energy-dispersive spectrometry (EDS) show carbon...
levels in excess of 12 at.% in treated 316. It is clear that the lattice parameter within the carburized case has expanded. No peaks associated with carbides are evident. The process achieves very high hardness values. Figure 5 also shows a microhardness profile as a function of depth, with measurements taken from multiple metallographic mounts of 316 stainless steel specimens from a single process run. As shown, hardness values exceeding 1200 HV (70 HRC) are achieved at the surface, dropping to the value of the base material (300 HV or 23 HRC) at a depth of approximately 25 μm.

Twelve at.% carbon corresponds to 10^6 times the room-temperature equilibrium solubility limit of carbon in 316 stainless steel. Side effects of this colossal supersaturation of carbon in austenite include residual compressive stresses of at least 2 GPa (300 ksi), based on lattice expansion as measured by XRD and the carbon concentration. The hardness and stress depth profiles show an excellent correlation with the carbon concentration depth profile obtained by XRD analysis of the variation of plane spacings with depth. The layer remains austenite and retains its ductility (Ref 25, 26, 30, 34). As shown in Fig. 6, scanning electron microscopy of failed treated tensile specimens shows slip bands and no decohesion of the treated layer, verifying that the layer remains ductile. This result can be counterintuitive; usually harder materials are less ductile and more brittle. However, this desirable combination of hardness and ductility is useful in enhancing damage tolerance. Conventional surface-hardening methods applied to austenitic stainless steels usually show some loss of ductility and corrosion resistance.

Figure 7 shows metallographic evidence of improved corrosion resistance; the case is not etched by the Kane’s reagent used to reveal the microstructure of the core. This image also reveals the conformal nature of the gas carburization process—treatment extends to the base of the deep pits formed by removal of manganese sulfide stringers by electropolishing prior to carburization (not a standard part of the process). These features are carburized with the same efficacy as the flat planar external surface.

The expanded austenite case is a nonequilibrium structure and represents a condition far from equilibrium. It should be noted that the temperature stability of this structure depends on minimizing exposure to temperature, because the carburized steel may undergo decarburization, or the carbon in solid solution will continue to diffuse into the matrix at temperatures approaching treatment temperatures of 350 to 550 °C (660 to 1020 °F). After extended exposure, the case may no longer be present.

**Performance Properties of the Low-Temperature Carburized Layer**

As noted earlier, only the outer 25 μm or so in the near surface of the treated component is affected by the process. It is interesting to see the effect that this surface treatment has on tensile properties. Figure 8 shows stress-strain curves for treated and nontreated 316 stainless steel specimens, using a standard flat dog-bone specimen with a cross section of 0.635 mm (0.025 in.). For the low-temperature carburized specimen, there is a small increase in yield stress—from 650 to 670 MPa (94 to 97 ksi)—and a more noticeable increase in ultimate tensile stress, from 690 to 750 MPa (100 to 109 ksi). A minor decrease in strain-to-failure, from 45 to 40%, also is evidenced, indicating the treated material is still ductile.

In combination with the increased surface hardness and compressive surface stresses, these minor changes in tensile properties have profound effects on performance characteristics, in particular, fatigue, wear, and erosion.

**Fatigue Resistance**

As anticipated, the extremely high surface compressive stresses (>2 GPa or 300 ksi—essentially the yield stress of interstitially hardened 316 stainless steel) enhance fatigue response. It should be noted that the compressive residual stresses obtained by low-temperature carburization are higher and more uniform than any that could be obtained by mechanical means, such as shot peening. Figure 9 shows the results of fatigue testing of standard round bar 316 stainless steel specimens, in tension-compression cycling (R = −1) (Ref 35). The symbols represent different sets of specimens, with nontreated specimens identified by triangles, treated specimens by squares. The effects of the thermal cycle (heat treatment without carburization) also were evaluated, and tests of these specimens are identified by circles. The thermal cycle alone did not show a significant effect on fatigue performance. Fatigue life (number of cycles) for treated 316 stainless steel showed two orders of magnitude improvement versus nontreated 316 at the same maximum stress level. In addition, the maximum stress at 10^7 cycles (considered to be the endurance stress for infinite life), improved by ~75%, from 200 to 350 MPa (28 to 49 ksi).

Low-temperature carburized components can sustain higher stresses in alternating loading conditions, or at the same stress level, have a high-cycle fatigue life that is approximately 100 times longer than that of nontreated components.

Testing was performed to determine the effect of low-temperature carburization on fatigue crack growth, distinct from fatigue crack initiation (Ref 36). In this investigation, six specimens of 316L stainless steel with machined V-notches first were subjected to fatigue loading in order to produce fatigue cracks 2.4 mm (0.09 in.) long.
Two specimens were carburized, two were given the same heat treatment as the carburization process, but with no carburizing gases flowing, and the remaining two specimens were left nontreated. All six specimens were tested in a horizontal fatigue apparatus at 10 Hz, and the crack growth rates (\( \frac{da}{dN} \), where \( a \) denotes the crack length and \( N \) the number of cycles) are plotted versus the stress intensity factor change for each stress cycle (\( \Delta K \)).

Fracture toughness testing was used to evaluate effects of hydrogen charging on 316 stainless steel compact specimens in the nontreated and treated conditions. Testing was performed under load control (no cycling) with crack length measured by the compliance method. Cracks were observed in the hydrogen-charged carburized layer. A minor decrease in the fracture toughness was also measured, although the material remained ductile.

\[ \Delta K = \frac{da}{dN} \]

\( \Delta K \), which is experienced in typical applications, low-temperature carburization will greatly increase the lifetimes of components. The difference becomes greater as \( \Delta K \) decreases. So, for small \( \Delta K \), which is experienced in typical applications, low-temperature carburization will greatly increase the lifetimes of components. More importantly, the threshold for fatigue crack growth (\( \Delta K_{th} \), defined as the \( \Delta K \) for a crack growth rate of \( 10^{-7} \text{mm/cycle} \)) is increased by low-temperature carburization from 8 MPa-m to 10 MPa-m. This indicates there are stress states under which fatigue cracks will initiate and grow in nontreated components, but not in treated components.

\[ \frac{da}{dN} = \frac{1}{\sqrt{2\pi C_1}} \]

\( C_1 \) is a function of the stress intensity factor change (\( \Delta K \)) and crack length (\( a \)). The effects of carburization on wear resistance of 316L austenitic stainless steel were investigated using the pin-on-disk method. Sliding friction and reciprocating friction tests show wear rates of treated couples (ball and disk) lowered by approximately 100 times compared to nontreated steel. An ASTM standard continuous loop abrasion test (rotating abrasive belt) showed a 30% reduction in wear volume for treated versus nontreated 316 specimens (Ref 2, 39).

Dry sliding was tested against an Al2O3 ball, using varying contact loads from 2 to 40 N, and varying sliding velocity from 0.1 to 0.6 m/s (4 to 24 in./s). The total sliding distance was kept constant at 1 km (0.6 miles). The wear of the carburized specimens varied from 0 to 2.4 mm3 for 1 km of sliding, while the nontreated specimens varied from 1.1 to 11 mm3 for 1 km of sliding, as illustrated in the wear maps (Fig. 11). Carburization reduces wear by over a factor of four under these conditions. In addition, the wear debris was analyzed and used to show that the nontreated material suffered from severe plastic deformation during the test, while the carburized material did not. The wear mechanism for
nontreated material showed large plates, indicative of contact welding and stick-slip phenomenon, while carburized material showed minor surface wear debris (Fig. 12).

The effects of carburization case depth on wear resistance of 316L austenitic stainless steel also were investigated. Dry sliding again was tested against an Al$_2$O$_3$ ball, with a 40 N load and a 0.1 m/s sliding velocity. Carburized 316L specimens, with a nominal case depth of 30 µm, were electropolished to remove 5, 10, 15, and 20 µm from the surface. While all the carburized specimens performed better than the nontreated specimen (case thickness = 0), the specimens with case depths of 15 and 20 µm performed slightly better than the specimens with 25 and 30 µm case depths. This effect could be due to improvements in surface roughness with electropolishing, without a significant reduction in surface hardness. A field service example of the effect of enhanced wear resistance is shown in Fig. 13. This 304 stainless steel wear plate for a ten horsepower pump, outside diameter of approximately 25 cm (10 in.), is used in a pulp and paper application. In regular service, it usually wears out in three months (nontreated worn plate shown on the left) and must be replaced to restore pump efficiency. A treated plate is shown on the right; this plate had been in service for over 30 months with no sign of wear. In addition to the savings associated with avoidance of replacement, maintenance, and repair, significant energy efficiencies also have been realized due to the enhanced pump efficiency.

Erosion Resistance

The combination of hardness and ductility achieved by low-temperature carburization also enhances resistance to erosion. Figure 14 shows the results of cavitation testing of treated and nontreated 316 stainless steel specimens. Cavitation tests were performed for up to six hours in duration, with a vibratory horn and mercury as the dense liquid medium. Results of these tests showed significant increases in cavitation resistance; an approximately eight-fold reduction in weight loss rate was realized for the treated surfaces as compared to the nontreated surfaces for type 316 stainless steel. These results have been replicated in other alloys and fluids, indicating that the diffusional nature of the case provides a benefit in fluid applications where cavitation can occur.

Corrosion Resistance

Electrochemical polarization curves show a 600 to 800 mV increase in pitting potential in treated (900 to 1000 mV) versus nontreated (200 to 300 mV) type 316 in chloride solutions (Ref 42). Two possible causes for the enhanced corrosion resistance have been postulated: 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 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 (Ref 43, 44).
Figure 15 shows cyclic polarization scans of treated and nontreated specimens of 316L in both 0.6M NaCl and seawater. In each environment, pitting corrosion, normally the first indication of corrosion damage in this steel, has been completely suppressed by carburization. (The apparent pitting at high potentials actually is decomposition of the NaCl solution—Cl₂ generation—as was confirmed by post-testing metallographic examination.)

On nontreated and treated 316 stainless steel specimens, ASTM G150 critical pitting temperature (CPT) tests were performed (Ref 2). The CPT for nontreated specimens was 16.9 ± 1.2°C (62.4 ± 2.2°F), while treated specimens had a CPT of 79.1 ± 6.6°C (174.4 ± 11.9°F). This CPT value closely approximates the CPT of more highly alloyed corrosion-resistant alloys.

In crevice corrosion testing, treated 316 stainless steel compares favorably with alloy 625 (Ref 45), as shown in Fig. 16. This figure shows three specimens at the end of a weeklong crevice corrosion test in natural seawater, at room temperature, under an applied potential of 300 mV. Nontreated 316 showed initiation of a crevice in under one hour. At the end of the week, a 1270 µm (0.050 in.) crevice cut with significant material wastage was experienced. Alloy 625 did not initiate crevice formation until 60 h had passed; at the end of the week, a 76.2 µm (0.003 in.) crevice cut was evident. The treated 316 specimen, however, showed no initiation in over 160 h, and no sign of etching after this weeklong test. The suppression of crevice corrosion as a failure mode for 316 is an unexpected but important result.

ACKNOWLEDGMENTS

The authors acknowledge their colleagues at Swagelok and Case Western Reserve University (CWRU) who have supported and contributed to the ongoing research effort. Gary Michal, CWRU, was instrumental in developing kinetic and thermodynamic models; his substantial contributions to this research effort over the last 15 years were pivotal and thought provoking. Preparation of this article has been supported by Swagelok Company, and the research described has been supported by the Department of Energy Industrial Materials of the Future Program, the Ohio Department of Development Third Frontier Program, DARPA, and the Office of Naval Research. The authors are grateful for the contributions of research colleagues at Oak Ridge National Labs; Vinod Sikka, Peter Blau, Jun Qu, and Dane Wilson. Thanks are also extended to research colleagues at the Naval Research Laboratory—Farrel Martin, Paul Natishan, Bob Bayles, Roy Rayne, and Diane Lysogorski—who verified some earlier findings on corrosion and erosion response, and gave a much better understanding of the mechanisms underlying the unexpected enhancements in corrosion performance.

REFERENCES

Low-Temperature Carburization of Austenitic Stainless Steels / 459

10. First Int. Symp. on Surface Hardening of Stainless Steels, Case Western Reserve University, Cleveland, OH, Oct 22–23, 2007
11. Second Int. Symp. on Surface Hardening of Corrosion Resistant Alloys, Case Western Reserve University, Cleveland, OH, May 25–26, 2010
29. J.P. Millet et al., Corrosion Behavior of 316L Stainless Steel in a Chloride Medium in Contact with Active Carbon, NACE Conf. Proc., NACE, Houston, TX, 1988, p 45–53
42. F. Ernst, G.M. Michal, H. Kahn, and A.H. Heuer, Paraequilibrium Surface Alloying with Interstitial Solutes: A New Concept for Improving the Performance of Medical

SELECTED REFERENCES

- F. Ernst, G.M. Michal, H. Kahn, and A.H. Heuer, Paraequilibrium Surface Alloying with Interstitial Solutes: A New Concept for Improving the Performance of Medical

- J. Qu et al., Tribological Properties of Stainless Steels Treated by Colossal Carbon Supersaturation, Wear, Vol 263 (No. 1–6), Sept 2007, p 719–726