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Carbon Surface Modification for Enhanced Corrosion Resistance

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Introduction: Case hardening by carburization has long been recognized to produce wear-resistant surfaces in steels. Historically, case hardening has not been applicable to chromium-containing alloys such as stainless steels (SS), due to chromium carbide formation that significantly degraded corrosion performance. As a result, the availability of case-hardened (and consequently wear-resistant) alloys for applications in corrosive environments was extremely limited. A new low-temperature (450°–500 °C) paraequilibrium carburization technique has been developed for introducing carbon into stainless steel surfaces without formation of carbides.[1,2] This surface modification technique has been termed Low-Temperature Colossal Supersaturation (LTCSS). Paraequilibrium refers to the concept that the diffusion of substitutional solutes (metal atoms, such as Cr and Ni in the alloy) is slower than the diffusion of interstitial solutes (atoms such as carbon, that fit between metal alloy atoms). Substitutional solutes are effectively immobile under LTCSS treatment conditions, whereas carbon can diffuse considerable distances into the alloy. These interstitially hardened surfaces constitute a new branch of engineered materials, in which improved corrosion resistance is attained alongside improvements in wear and fatigue resistance.

Improved Surface Hardness: The effect of LTCSS treatment on austenitic stainless steels has been shown to dramatically increase surface hardness through residual compressive surface stress (important for fatigue resistance and wear resistance). Figure 1 shows the surface carbon concentrations, residual surface stresses, and hardness resulting from LTCSS treatment. Carbon concentrations of up to 15 atomic percent can be generated in the near-surface region encasing the entire treated component. The large concentration of interstitial carbon induces a lattice expansion that results in surface compressive stresses greater than 2 GPa (300 ksi). These large residual compressive stresses significantly enhance the high cycle fatigue endurance limit,[2] increasing the service life of the material. Increasing the surface hardness of the material increases wear resistance. Near-surface Vickers microhardness values (HV) of 1200 HV have been obtained on LTCSS-treated 316L SS, representing a significant increase in surface hardness over the substrate material (Vickers 300 HV). To give some perspective, environmentally unfavorable hard chrome coatings are frequently used on critical aircraft components to increase wear resistance, where surface hardnesses can reach as high as 1100 HV. Thus a LTCSS-treated 316 SS has a surface hardness that rivals the best hard chrome coating. A surprising feature of LTCSS treatment is that the inherently good ductility of the base material is retained in the treated surface.[2] Additional positive attributes of LTCSS include no net dimensional changes in treated components, treatment of all exposed surfaces, and the ability to batch process large numbers of components at once.

Pitting Corrosion Resistance: Electrochemical testing at NRL to determine pitting corrosion resistance[3] has shown that that there is dramatic increase in the pitting resistance of the LTCSS-treated 316 SS when compared to the untreated material. LTCSS treatment increased pitting potential from +320 millivolts (mV) for untreated material to +950 mV for the LTCSS-treated material.[4] The pitting potential is an electrochemical parameter used in laboratory testing to compare the pitting resistance of materials; a high positive value is desired. This is a dramatic increase in pitting corrosion resistance such that under practical conditions experienced in natural seawater (NSW) environments, LTCSS-treated 316 SS is virtually immune to pitting corrosion.

Crevice Corrosion Resistance: Crevice corrosion resistance is another aspect of corrosion behavior of particular interest to the Navy. Comparison of crevice corrosion resistance for untreated 316L SS and LTCSS-treated 316L is presented in Fig. 2. Crevice corrosion damage on an untreated 316L coupon following one week of crevice exposure is shown in the center of the figure. LTCSS-modified 316L (far right) did not initiate crevice corrosion under these exposure conditions (+300 mV, ambient temperature seawater) during the one-week test. Figure 2 also includes results published for Alloy 625 (left photo, an exotic Ni-22Cr-9Mo superalloy) for the same test conditions and crevice cell design.[3] These results indicate that the corrosion resistance of LTCSS-treated 316L was greatly increased compared to the untreated 316 and the more expensive, high-grade Ni alloy.

Summary: Low-Temperature Colossal Supersaturation is a process for introducing carbon in excess of 15 atomic percent into stainless steels without formation of carbides. The results of the NRL work show that LTCSS treatment dramatically improved the localized corrosion resistance (both pitting and crevice corrosion) of 316L austenitic SS in ambient temperature seawater. LTCSS treatment has the potential to be applied to a multitude of alloys already used by the Navy. This

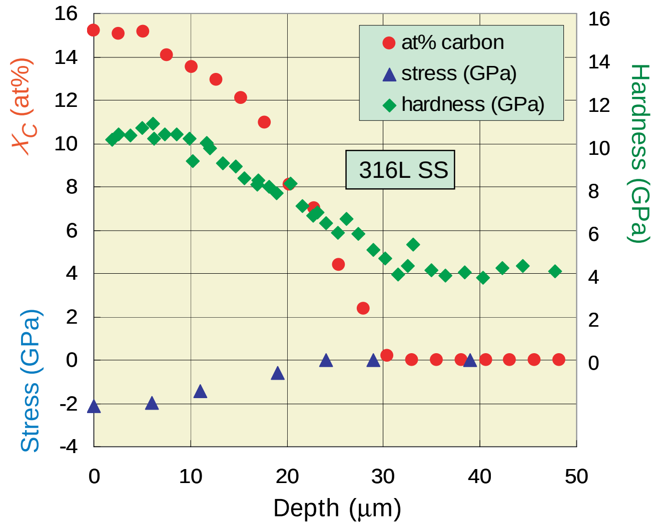

FIGURE 1
Carbon concentration, surface hardness, and residual stress profiles for LTCSS-modified 316L stainless steel (from Ref. 2).

Alloy 625 in NSW, 1 week RT 300mV | 316L in NSW, 1 week RT 300mV | LTCSS-316L in NSW, 1 week RT 300mV

- Initiation < 60 hrs
- Etching and cutting
- 3 mil crevice cut

- Initiation < 1 hr
- Etching and cutting
- 50 mil crevice cut

- No initiation in 160+ hrs
- No signs of etching

FIGURE 2
Photographs of crevice corrosion specimens after testing (RT = run time). Unmodified 316L SS (center) and LTCSS-modified 316L SS (right) after week-long ambient seawater (NSW) crevice corrosion testing at +300 mV. At left, Alloy 625 (high-grade Ni-Cr-Mo alloy) exposed to similar conditions (from Ref. 3).

in turn would increase the service life of components and increase readiness and availability of naval assets. In addition, LTCSS-treated surfaces, in most cases, have hardness values greater than hard chrome and thus present a potential alternative to this environmentally undesirable, toxic, wear-resistant and corrosion-resistant coating.

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References

[1] P.C. Williams and S.V. Marx, Swagelok Company, Low-Temperature Case-Hardening Processes, U.S. patent 6,093,303 (July 25, 2000).

[2] G.M. Michal, F. Ernst, H. Kahn, Y. Cao, F. Oba, N. Agarwal, and A.H. Heuer, "Carbon Supersaturation due to Paraequilibrium Carburization: Stainless Steels with Greatly Improved Mechanical Properties," *Acta Materialia* **54**, 1597-1606 (2006).

[3] F.J. Martin, P.M. Natishan, K.E. Lucas, E.A. Hogan, A.M. Grolleau, and E.D. Thomas, "Crevice Corrosion of Alloy 625 in Natural Seawater," *Corrosion* **59**, 498-504 (2003).

[4] F.J. Martin, E.J. Lemieux, T.M. Newbauer, R.A. Bayles, P.M. Natishan, H. Kahn, G.M. Michal, F. Ernst, and A.H. Heuer, "Carburization-Induced Passivity of 316 L Austenitic Stainless Steel," *Electrochemical and Solid-State Letters* **10,** C76 (2007). ★