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To Whom it May Concern:

Please find enclosed the Final Technical Report and SF 298 for N00173-12-2-C001 for your records. Feel free to contact me directly should you need anything further during the closeout process of this award.

Sincerely,

A handwritten signature in blue ink, appearing to read "Karen Dunn", with a stylized flourish extending from the end.

Karen Dunn
Assistant Director, Pre-award Services

***Interstitial Hardening of Stainless Steel for Enhanced
Corrosion Resistance for Naval Applications
Final Report (Contract NOO173-12-2-C001)***

Collaborative work between the Corrosion Science group at NRL and the Dept. of Materials Science and Engineering at CWRU had demonstrated that a novel low temperatures "paraequilibrium" interstitial hardening process led to a dramatic improvement in corrosion resistance of austenitic stainless steels in marine environments. This prior work had been concerned with carburization, mostly using carbon monoxide (CO) as the carbon source. Inasmuch as many commercial hardening processes involve nitridation or nitrocarburization, one of the principal aims of the program was to establish whether interstitial hardening treatments using nitrogen in isolation, or in combination with carbon, could likewise enhance corrosion resistance of austenitic stainless steels, and if so, to define the optimum treatment conditions.

Hardened corrosion-resistant "cases" could be achieved with nitrogen alone or in combination with carbon, but there were interesting differences compared to carbon alone. In particular, a larger surface nitrogen content and greater surface hardening, could be achieved at high chemical activities of nitrogen (achieved by using ammonia (NH₃) as the nitrogen source) but this led to severe surface cracking. Fortunately, it is straightforward to nitride at lower nitrogen activities by mixing NH₃ with hydrogen (H₂) gas and a systematic study of nitridation was conducted at various nitrogen activities. These studies also revealed that austenite of 316 composition (18% Cr, 12% Ni) became ferromagnetic when the nitrogen content exceeded 14 at %. Early theoretical work had predicted that when the lattice parameter of face centered cubic (fcc) iron (e.g. austenite) was expanded, a paramagnetic to ferromagnetic transition should occur. The nitridation studies revealed substantial lattice parameter expansion and confirmed that expanded austenite could indeed become ferromagnetic. This has implications for naval applications of interstitially hardened austenite, which may not be sufficiently magnetically "quiet".

Nitrocarburizing using either NH₃/CH₄ (methane) mixtures or gaseous urea (CH₄N₂O) was also conducted. Simultaneous and sequential nitro-carburization (nitriding followed by carburizing or carburizing followed by nitriding) was studied. Characterization of the interstitial depth profiles using scanning Auger spectroscopy revealed the non-intuitive finding that carbon enters the austenite lattice to a greater depth than does nitrogen, regardless of whether nitridation proceeds or follows carburization, or if both interstitial solutes enter the austenite lattice simultaneously. A straightforward thermodynamically based numerical model was developed that explained "simple" carburization and nitridation depth profiles, and also explained the deeper carbon profiles, based on the effects of carbon on the chemical potential of nitrogen in the steel and vice versa.

Other significant findings included orientation-dependent depth profiles developed during nitridation, and successful nitrocarburization using urea as the source for both carbon and nitrogen interstitials. Essentially all these findings have been reported in top-ranked archival technical journals.

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14. ABSTRACT Low temperature interstitial hardening using nitrogen alone or in combination with carbon was shown to be effective in improving the corrosion resistance of austenitic stainless steels in marine environments, although there were interesting differences from the more familiar carburization. In particular, higher surface nitrogen concentrations (and greater surface hardness) could be achieved but was accompanied by surface micro-cracking; this undesirable aspect could be avoided by nitriding using a lower nitrogen chemical activity. Nitro-carburizing led to a two-zone hardened "case", as carbon entered the austenite lattice to a greater depth than did nitrogen, regardless of whether nitrogen preceded or followed carburization.					
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