

Interstitally Hardened 316L Stainless Steel: A Surface Analytical Study of the Oxide

Nicole R. Tailleart^a, Paul M. Natishan^b, Farrel J. Martin^b, Roy J. Rayne^c, H. Kahn^d, and A.H. Heuer^d

^aAmerican Society for Engineering Education, Washington, DC 20036

^bChemistry Division, US Naval Research Laboratory, Washington, DC 20375

^cMaterials Science and Engineering Division, US Naval Research Laboratory, Washington, DC 20375

^dDepartment of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH 44106

Case hardening by traditional carburization or nitridation methods has long been recognized to produce wear resistant surfaces in steels. When these methods are applied to stainless steels, corrosion performance is degraded because of carbide and nitride formation. However, low temperature gas-phase and plasma interstitial hardening (IH) processes relying on paraequilibrium kinetics have been developed (1-5) that allow substantial amounts of carbon or nitrogen to be introduced into stainless steels without formation of carbides or nitrides. Paraequilibrium refers to the concept that diffusion kinetics of substitutional solutes, such as Cr and Ni, diffuse slower than interstitial solutes, such as carbon or nitrogen. Substitutional solutes are effectively immobile, whereas interstitial solutes can diffuse into the alloy to depths of 10-30 μm . Surface carbon or nitrogen concentrations on the order of 12 at% or greater can be obtained, resulting in a hardened surface. This modified case-hardened region has been referred to as S-phase or expanded austenite. The industrial implementation of the IH treatment with carbon (IH-C) or nitrogen (IH-N) is straightforward, is a non-line of sight process, maintains sample dimensions, and is relatively inexpensive. A growing body of work on IH-C treated stainless steel alloys shows that gas phase IH-C treatment improved localized corrosion, fatigue, and wear resistance of the treated materials compared to the untreated alloys (5-9).

The origin of the hardening and the improved corrosion resistance for IH-C treated 316L stainless steels is the "colossal" supersaturation of interstitial carbon. The corrosion resistance of stainless steel involves a Cr_2O_3 -rich passive film. In previous work, grazing incidence X-ray photoelectron spectroscopy (GI-XPS) was used to determine the composition and measure the thickness of these Cr-rich passive films developed during anodic

polarization at selected potentials for both IH-C and non-treated 316L stainless steel samples. Since no Cl^- was observed in the passive oxide film of both the IH-C and non-treated samples at any of the potentials examined, and the chemical composition was the same for IH-C and non-treated samples at each potential, we suggest that passive film breakdown is of chemo-mechanical origin (8,9).

In this work, exploration into the nature of passive oxide film breakdown was extended to gas phase IH-N. The experimental work conducted follows that of our previous work on IH-C (7, 9). This includes determining the polarization behavior in 0.6 M NaCl solutions and performing potentiostatic experiments at selected potentials below the pitting potential with subsequent XPS. XPS will be used to determine the oxide film thickness and composition of the potentiostatically polarized samples. These results will then be compared to the results reported for IH-X (7, 9).

Acknowledgements

The authors gratefully acknowledge the Office of Naval Research and the Naval Research Laboratory for financial support of this work.

References

- (1) Z.L. Zhang and T. Bell, *Surf. Eng.*, 1, 131 (1985).
- (2) P.C. Williams and S.C. Marx: U.S. Patent 6,093,303, July 25, 2000.
- (3) Y. Cao, F. Ernst, and G.M. Michal, *Acta Mater.*, 51, 4171 (2003).
- (4) T. Christiansen and M.A.J. Somers, *Surf. Eng.*, 21, 445 (2005).
- (5) G.M. Michal, F. Ernst, H. Kahn, Y. Cao, F. Oba, N. Agarwal, and A.H. Heuer, *Acta Mater.*, 54, 1597 (2006).
- (6) A.H. Heuer, H. Kahn, J. O'Donnell, G.M. Michal, R.J. Rayne, F.J. Martin, and P.M. Natishan, *Electrochem. and Solid State Lett.*, 13 (12) C37-C39 (2010).
- (7) 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, *Electrochem. and Solid State Lett.*, 10 (12) C76-C78 (2007).
- (8) A.H. Heuer, H. Kahn, P.M. Natishan, F.J. Martin, and L.E. Cross, *Electrochimica Acta*, 58, 157 (2011).
- (9) A.H. Heuer, H. Kahn, F. Ernst, G.M. Michal, D. Hovis, R.J. Rayne, F.J. Martin, and P.M. Natishan, *Acta Materialia*, 60, 716 (2012).