

Ennoblement Response During a Warm-to-Cold Seawater Transition

F. J. Martin¹, C. S. Yentsch², D. A. Phinney²,
W. E. O'Grady³ and P. M. Natishan³

¹ GEO-Centers, Inc.
FT. Washington, MD 20749

² Plankton Research and Instrumentation
Boothbay Harbor, ME

³ U. S. Naval Research Laboratory
Washington, DC 20375

The corrosion behavior of stainless steels and other corrosion-resistant metals immersed in seawater can be influenced by the microbiology of surface films. Corrosion potential ennoblement in seawater is one such phenomenon where the corrosiveness of seawater to passive alloys is amplified by formation of a highly oxidative surface film(1). Several authors(2-5) have proposed that the oxidative character of this surface biofilm is governed by manganese-related oxygen reduction.

Ni-Cr-Mo alloys such as Alloy 59 (UNS N06059) are widely recognized for excellent seawater corrosion resistance, although these alloys are susceptible to seawater crevice corrosion. Ennoblement at neutral temperatures has been linked to the initiation of seawater crevice corrosion on Ni-Cr-Mo alloys(6). It is known that seawater ennoblement ceases in elevated temperatures (approaching 65°C), but to-date there is no body of information indicating the lower bounds of temperature where ennoblement is viable.

Experimental

The present research measured open circuit potentials (E_{CORR}) for three Ni-Cr-Mo alloy coupons in temperate waters extending from summer into winter. The coupons and reference electrodes were suspended from adjacent positions on a floating dock in coastal waters off Boothbay Harbor, Maine. The location is a semi-enclosed bay having little wave action that is tidally flushed, with a mean salinity of 33 parts per thousand. Weather-ruggedized data storage units collected semi-continuous E_{CORR} measurements every 15 minutes. Discrete measurements surface temperature and salinity were made almost daily for one month and weekly after that for four months. The observations commenced in late summer when temperatures were at a seasonal high (around 18°C), and ended in the winter when temperatures were lowest (around -2°C).

Alloy 59 (UNS N06059) coupons were hot-rolled, solution annealed (HR/SA) plates, 75mm X 75mm X 5mm thick, cut from neighboring locations on the Alloy 59 parent material. Electrical and mechanical connection to each plate was maintained by welded contact with a 2mm dia. X 300mm long Alloy 59 rod. Reference electrodes were seawater service silver/silver chloride (Ag/AgCl) of our own manufacture. All potentials are reported versus seawater Ag/AgCl at the immediate ambient seawater temperature (ranging between -2°C and 18°C) at the time of measurement. At the conclusion of marine exposure studies, surface analytical chemistry was performed using X-ray absorption near-edge spectroscopy (XANES).

Results

Initial E_{CORR} for each of the three Alloy 59 coupons were around -100mV. The time required to enoble each of the three specimens to +300mV varied widely (19, 29, and 60 days, respectively), despite the apparent similarities in exposure conditions. Figure 1 shows a time-history trace of semi-continuous measurements for the specimen taking 29 days to enoble, and an overlay of seawater temperature for this timespan. The maximum daily corrosion potential occurs between midnight and 4:00AM, with the highest recorded E_{CORR} (+354mV) occurring on day 83 at 2:30AM. E_{CORR} values dropped precipitously every morning at sunrise, supporting the notion that direct sunlight has a mitigating effect on ennoblement(7).

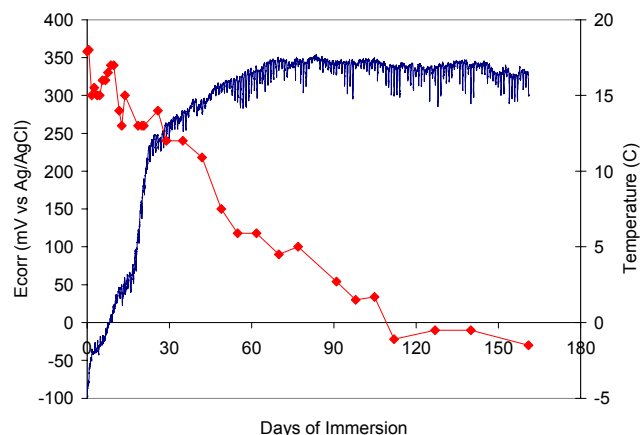


Figure 1 - Ennoblement of Alloy 59 in Boothbay Harbor during summer-winter transition

The transition to cold seawater temperatures did not appear to have major influence on ennobled specimens, indicating that the processes driving ennoblement are viable even in near-zero temperatures. Ennoblement persisted despite heavy macrofouling with algae, hydroids and bryozoans.

Surface analytical chemistry revealed the presence of Mn(IV) and Mn(III) compounds in the biofilm.

References

1. V. Scotto, R. Di Cintio, and G. Marcenaro, *Corrosion Science* **25** (3), 185 (1985).
2. W. H. Dickinson, F. Caccavo, and Z. Lewandowski, *Corrosion Science* **38** (8), 1407 (1996).
3. P. Linhardt, *Biodegradation* **8** (3), 201 (1997).
4. D. T. Ruppel, S. C. Dexter, and G. W. Luther, III, *Corrosion* **57** (10), 863 (2001).
5. G. Salvago and L. Magagnin, *Corrosion* **57** (9), 759 (2001).
6. F. J. Martin, P. M. Natishan, K. E. Lucas, E. A. Hogan, A. M. Grolleau, and E. D. Thomas, *Corrosion* **59** (6), 498 (2003).
7. M. Eashwar, S. Maruthamuthu, S. Palanichamy, and K. Balakrishnan, *Biofouling* **8** (3), 215 (1995).