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1992

NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA

UPT SCENARIOS - IMPLICATIONS FOR SYSTEM RELIABILITY

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Contract Number:	NGT-0-002-099 The University of Alabama

OBJECTIVE

The objective of this project was to examine the corrosion resistance of 316L stainless steel in several urine pre-treat solutions. Four solutions were examined - untreated urine (control), urine pretreated with oxone (potassium peroxymonosulfate sulfate), urine pretreated with sodium hypochlorite (NaOCl) and urine pretreated with ozone (O_3). In accordance with current procedures, all solutions but the control were acidified to a pH of 2.5 using sulfuric acid - this suppresses the generation of ammonia in the solutions and is intended to limit microbial growth. Welded and unwelded coupons were exposed to each solution. In addition, Titanium coupons (welded and unwelded) were exposed to biologically active environmental control and life support system (ECLSS) water. Microbial attachment and biofilm growth were monitored. Ozone was examined as a biocide/oxidizer/corrosion preventative (simultaneous addition) and as a remediation method (added one week after exposure).

In an unrelated effort, HP 9-4-30 coupons were exposed to biologically active solutions. Corrosion rates for welded and unwelded samples were determined - results were correlated to the ongoing HP 9-4-30 weldment stress corrosion study.

INTRODUCTION

Microbiologically influenced corrosion (MIC) is ubiquitous - all alloy systems exhibit susceptibility to microbiological attack. Stainless steels are not thermodynamically resistant to corrosion - they resist corrosive attack in oxidizing solutions because they "passivate". This is a kinetic phenomena, based on a critical Cr content in the alloy system and the development of a tightly adherent surface layer that forms a barrier to further corrosive attack. In many environments, including biologically active environments, these alloys are subject to local breakdown of the of the passive layer and localized attack - pitting.

A number of investigators have reported MIC of austenitic stainless steels. In some cases investigators attribute MIC to macroscopic features (suckback, undercut, excessive reinforcement) associated with the weld. Though these features can produce stagnant water conditions which foster MIC, the more critical association is between the microbe and microscopic metallurgical features. A "typical" microbe is on the order of 2u long - undercut is typically 1 to 2mm deep, a weld crown 20mm across. Thus, the undercut is typically 500 to 1000 times the dimension of the microbe and the crown 10,000 times the dimension of the microbe! In human terms this is equivalent to a typical adult looking into a canyon 2,000 meters deep and 18 km wide from its' lip to choose a camping site - clearly there is interaction on a finer scale.

Metal oxidizing and sulfate reducing bacteria have been reported to cause corrosion in stainless steels. Several investigators have reported MIC associated with welds in fabricated components. Even stainless steels containing molybdenum, which effectively resist crevice corrosion in sea water, have been found susceptible to MIC. The case of a stainless steel tank that was not completely drained after hydrotest has been reported - subsequent through wall (8mm) pitting occurred in four weeks. Even high purity water systems are not immune. The case of a stainless steel tank storing demineralized water that failed by stress corrosion cracking - initiating at pits beneath bacterial deposits - has been reported.

The study of MIC is an inherently interdisciplinary endeavor - involving microbiology, metallurgy and electrochemistry. Though many have studied environments that promote MIC, catalogued materials that are subject to MIC, described methods of detecting MIC and found treatments to mitigate MIC problems - investigators have not yet completely correlated MIC to microstructural features. Surfaces of any kind are attractive to bacteria in aqueous environments. Surfaces, particularly metal surfaces, concentrate organic molecules crucial to microbial development. Furthermore, metal surfaces are extremely heterogeneous. Regional differences (on all scales, from submicron to macroscopic) are so well defined that local anodes and cathodes form and corrosion progresses on monolithic pieces of material. Surface condition, stress state, microstructure, chemistry and inclusion size and distribution affect local electrochemistry and MIC susceptibility. Fabrication procedure can also change MIC sensitivity. The thermal wave associated with the passage of a welding arc changes surface texture and produces local stress fields. More importantly, it alters the size, shape, amount and distribution of microstructural constituents in the fusion zone and the heat affected zone (HAZ).

PROCEDURE

Discs (15mm Diameter) of 316L stainless steel, in the as welded and as received conditions were degreased in trichloroethylene and washed with alcohol to remove surface films. Discs were used for polarization resistance studies in an EG&G Model 273 potentiostat / galvanostat. The program POLCUR, as modified by Danford, was used to estimate Tafel constants and calculate corrosion rates:

$$Icorr = B_a B_c / [2.3\ (B_a + B_c) R_p] \qquad (1)$$

Samples were exposed to raw urine as a control, and to urine with three different pretreatments - each pretreatment was acidified to a pH of 2.5 using sulfuric acid, standard practice for the Vapor Compression Distillation (VCD) subsystem. Three different oxidants were studied - oxone, hypochlorite and ozone. Oxone and hypochlorite were added to the respective test cells to concentrations specified in VCD pretreatment protocols. Ozone was produced from pure oxygen by UV irradiation and was introduced into the solution through a glass frit. The ozone was supplied to the solution for a two day period and reached a peak concentration of 60ppm. Solutions were continually stirred, corrosion rates were monitored over a three week period.

After the corrosion tests, samples were removed, fixed with formalin and dried in methanol and freon. Prior to examination by scanning electron microscopy, samples were sputter-coated with Au-Pd. Ti discs, exposed to untreated and ozonated ECLSS water, were fixed, dried and sputter-coated in a similar fashion. The effectiveness of ozone in removing established biofilms was also studied.

RESULTS AND DISCUSSION

Figure 1 shows the results of corrosion testing. The corrosion rates found in the control samples are much higher than any of the treated solutions. Corrosion rates in the treated solutions are low, however, the corrosion rates of the as welded samples are five to ten times as great as their unwelded counterparts. High corrosion rates measured early in testing are indicative of the passivation of the stainless steel in an oxidizing environment. Figure 2a-d are SEM photomicrographs of coupon surfaces. Figure 2a shows the ozone treated sample, no biofilm or microbes are present. Figure 2b shows the partially melted region of the hypochlorite treated coupon. Note the localization of microbes in the remelted grain boundaries. Figure 2c is an enlargement of this region. The surface of the weld region in the oxone treated sample, 2d, was covered with a more extensive biofilm that also showed localization at structural features produced by welding. All pretreatments limited the attachment of bacteria to the base metal surfaces. The number of colony forming units per milliliter found in the various solutions ranges from 10^9 /ml in the control solutions to near zero in the ozone. Oxone and hypochlorite have reduce the number of microbes in solution by a factor of 10^5, although figures 2a through 2d indicate they are less effective at the metal surface. The localization of the microbial colonies - and the potential for localized corrosive attack at/near these colonies pose a particularly insidious problem for the VCD system, even at low corrosion rates.

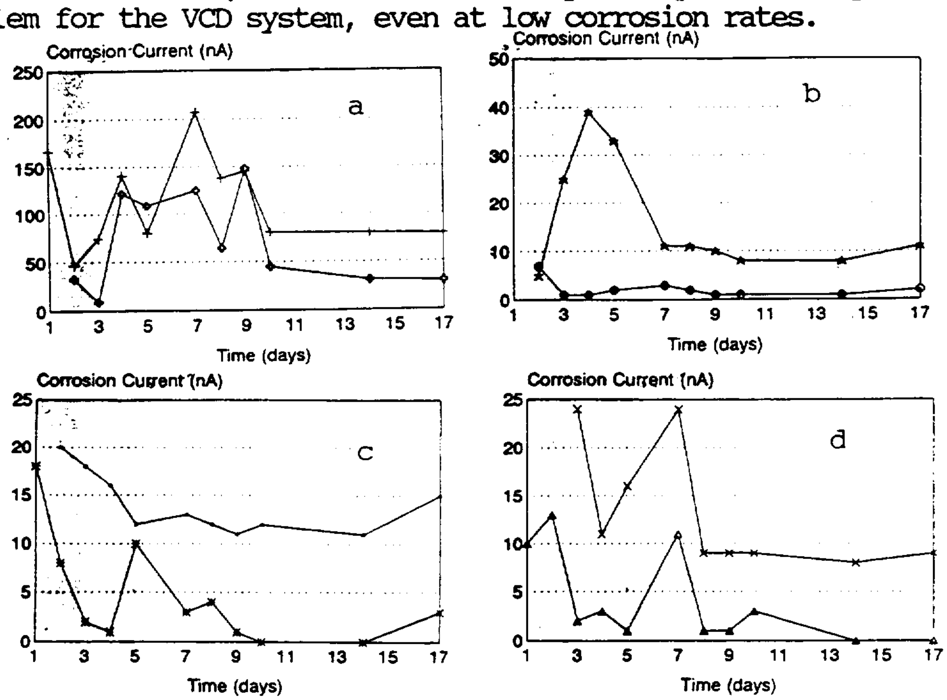

Figure 1. Corrosion rates measured over a three week period. a) control, b) ozone, c) hypochlorite, d) oxone.

The results of the film remediation study on Ti indicate that ozone is also capable of removing established biofilms - even after long term exposure.

a

b

c

d

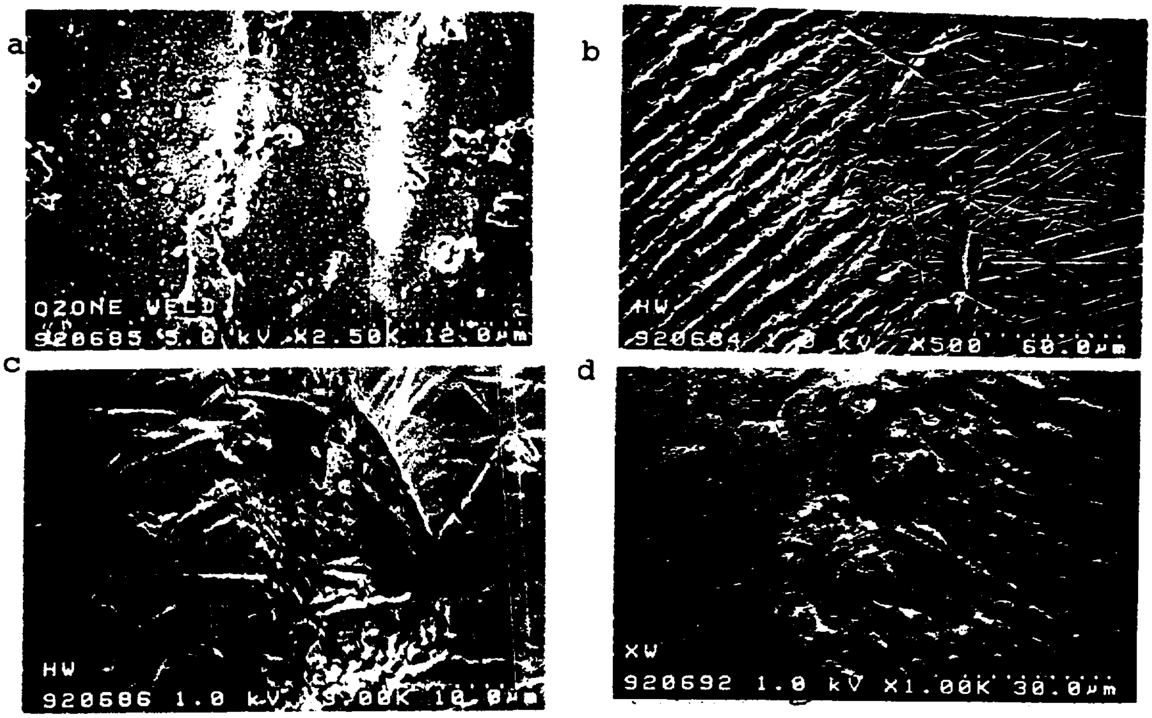

Figure 2. SEM photomicrographs of the surface of 316L coupons exposed to UPT fluid. a) ozone treated, b) hypochlorite, c) region b, higher magnification, d) oxone.

CONCLUSIONS

The results of this investigation indicate that:
- urine pretreatment diminishes the corrosion rate in 316L
- the corrosion rates in welded samples are an order of magnitude greater than corresponding base metal samples
- localized colonies of bacteria are associated with weld fusion zone and HAZ structures in all pretreatments but ozone
- localized corrosion could be damaging, even at low overall corrosion rates
- ozone removed established biofilms on Ti surfaces

ACKNOWLEDGEMENTS

I thank all the people at the M&P lab, and the Corrosion, Failure Analysis and Microbiology groups in particular - who make every trip to MSFC enjoyable and fruitful. In particular I would like to thank Merlin Danford for his patient help and interest, Tim Huff for sharing excitement and stealing coffee, Joe Montano for putting up with a paradox(c)s, Barry Moody, Mitch Mendrick, Larry Foreman, Kevin Buford, Dave Hedgepeth, Carla Hooper, Pablo Torres, Liz Rogers and Don Obenhuber. Special thanks to Jim Coston, Wendell Deweese and Jim Holly who took the time to give me help whenever needed.