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CHARACTERIZATION OF THE CORROSION RESISTANCE OF BIOLOGICALLY ACTIVE SOLUTIONS - THE EFFECTS OF ANODIZING AND WELDING

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The study of microbiologically influenced corrosion (MIC) is an inherently interdisciplinary effort. An understanding of fabrication processes, metallurgy, electrochemistry and microbiology is crucial to the resolution of MIC problems. The object of this effort was to use AC impedance spectroscopy to characterize the corrosion resistance of Type II anodized aluminum alloy 2219-T87 in sterile and biologically active media and to examine the corrosion resistance of 316L, alloy 2219-T87 and titanium alloy 6-4 in the welded and unwelded conditions. The latter materials were immersed in sterile and biologically active media and corrosion currents were measured using the polarization resistance (DC) technique.

MIC is recognized as a major problem in many industries. MIC is ubiquitous; all alloy systems exhibit susceptibility to microbiological attack. MIC of water treatment and delivery systems is particularly insidious, MIC can occur during construction, testing, operation or shutdown periods. In fact, extended periods of shutdown can be particularly damaging. Researchers have developed some understanding of environments that promote MIC, materials susceptible to MIC, methods to detect MIC and rudimentary approaches to treat and prevent MIC. However, little understanding of the metallurgical basis for these processes has developed. Furthermore, little "hard data" on corrosion rates of material systems in biologically active environments exists. In even fewer cases have researchers examined the effects of fabrication processes on the MIC susceptibility of metals.

Microbes are living agents of corrosion. Their size provides them access to material inhomogeneities at the microstructural level. Microbes are motile, and able to move away from toxic chemicals and toward food - they have specific chemical receptors for target chemicals in the environment. Surfaces of any kind are attractive to most waterborne bacteria. Surfaces, particularly metal surfaces, concentrate scarce resources. The surface concentration of protein and polysaccharide molecules is much greater than that in the bulk solution. Microbes able to attach and establish themselves on such surfaces will be at a competitive advantage in their environment. Microbes are hardy, different varieties can withstand temperature variations from -10°C to 99°C, pH variations from 0 to 10.5 and oxygen concentrations from 0% to 100%. Microbes are prolific and able to exist in large colonies. Many are able to produce extra-cellular slime layers. The slime layer is used by the microbe to protect it from toxins, collect food and anchor to the surface. It also is critical to the development of complex microbial ecosystems, consortia of many different microbes on the surface. These synergistic consortia are able to accomplish complex chemical reactions at the material surface and create aggressive chemical environments. The slime layer is involved in the formation of oxygen depletion cells, it can sequester metabolic byproducts (bacteria found in ECLSS waters are known to produce organic acids and hydrogenase), it can harbor microbes that depolarize cathodic sites (SRB have been found in large numbers in ECLSS waters), thus it will accelerate corrosion. SRBs flourish in anaerobic environments at the film-metal interface, rendering the environment more chemically aggressive and providing several mechanisms to depolarize the rate limiting cathodic reaction. Furthermore, many bacteria can directly oxidize metal ions. At a minimum this will lead to a passive co-accumulation of negative ions (typically Cl^-). This may produce an acidic ferric chloride, cuprous chloride or magnesium chloride solution at flaw tips, producing an <u>in-vivo</u> stress corrosion cracking environment more severe than many <u>in-vitro</u> tests.

Slime layers produce a crevice like anaerobic environment in which passivating films damaged by abrasion or halide ion attack go unrepaired. The biofilm can consume oxygen, and prevent oxygen in the environment from reaching the metal surface and restoring passive films. In addition, the lack of oxygen may also promote cathodic reactions that do not involve oxygen.

Metal surfaces are extremely heterogeneous. Regional (on all scales - from submicron to macroscopic) differences are so well defined that local anodes and cathodes form and corrosion takes place on individual pieces of metal. Surface condition, stress state, microstructure, chemistry and inclusion size and distribution affect local electrochemistry and MIC susceptibility. Welding changes the surface texture, and produces local stress fields. More importantly, it alters the size, shape, distribution and amount of microstructural constituents in the fusion zone and in the heat affected zone. In our study welding accelerated and aggravated corrosive attack.

Corrosion implies the existence of anodic sites on a metal surface, where oxidation of insoluble metal atoms to soluble metal ions takes place. Cathodic regions on the metal surface balance the reaction. In systems where external current is not supplied, anodic and cathodic currents must be equal. Reactions at the anode and the cathode can be treated as "half-reactions" whose sum is the total corrosion reaction. Corrosion potentials are thermodynamic quantities, measured at equilibrium, and as such indicate what reactions are possible. Corrosion currents are kinetic values and reflect dynamic, nonequilibrium processes at electrodes. Typically there is a single anodic reaction, the dissolution of metal ions. However, there may be several cathodic reactions; which is favored depends on the chemistry of the environment. In our systems, the pH is near neutral and the oxygen and water reactions are possible. In biologically active media, other reactions are possible, the chemistry at the metal-film interface is drastically different from the bulk chemistry.

Polarization resistance techniques were used to study the uncoated samples, AC impedance techniques were used to study the anodized materials. These methods have been described by Danford (Ref. 1,2,3). The corrosive media used was mild corrosive water for the bare Al 2219 samples and 3.5% NaCl solutions for all other samples. All media were sterilized in an autoclave. Bioactive solutions were made by inoculating these sterile media with 20 ml of ECLSS water. Samples I_{corr} and E_{corr} were monitored over a four week period. Samples were examined by scanning electron microscopy and optical microscopy. Water chemistry and microbial ecology were monitored.

Figure 1 shows the corrosion current measured in Al 2219 over a three week period. Note that initial measurements do not indicate the average current over longer periods. The Al 2219 (welded and unwelded) corrodes at a much lower rate in the sterile media. Similar results were observed in parallel tests with 316L and Ti 6-4. Figure 2 shows the charge transfer resistance measured for anodized samples over a four week period. This value is inversely proportional to the corrosion current. Note the precipitous drop in the resistance for the bioactive solution after several days exposure. The morphology of corrosive attack for the bioactive solutions was also different, microbes aggregated at weak spots in the coating (Fig. 3) and grossly enlarged pits. Figure 4 shows microbes located between weld ripple marks on 316L material. Microbes also aggregated at pores and flaws in oxide coatings. The microbial attachment density was lower on the unwelded base material.

The results of this testing indicate that ECLSS waters are microbe rich, it contains large numbers of SRBs, Enterobacter, Pseudomonas and Klebsiella - that the AC impedance technique and the DC polarization resistance techniques are well suited to MIC investigations - that microbes attach to <u>all</u> materials studied - that microbes increase I_{corr} and decrease E_{corr} in all samples for all treatments (in the media studied Al 2219 was most susceptible, Ti 6-4 least susceptible) - that anodized materials in sterile media maintain coating integrity for longer periods than typically measured - that ECLSS rich media aggravate corrosive attack of anodized materials and change the morphology of attack - that microbes localize corrosion and fix anodes at microstructural features - that welding increases I_{corr} - that microbes randomly attach to a surface, proliferate at opportune locations, develop a biofilm and form complex consortia on the material surface that inhibit subsequent colonization by other bacteria - that microbes are at a minimum catalysts for the corrosion reaction, but are often directly involved in the corrosion process - that enhanced corrosion in Al 2219 is caused by the promotion of the more rapid hydrogen evolution reaction at the cathode, anaerobic films and SRBs foster this reaction.

The list of people who have helped me this summer reads like the Huntsville phone directory. Thanks to all in the corrosion, micro, FA and metallography groups. Special thanks to Merlin Danford whose quietly correct and kind approach makes working and learning so easy and to Jeff Sanders for field emission effects. Special thanks to Joe Montano, Barry Moody and Carlla Hooper. Special thanks to Tim Huff for all his help and interest. Finally thanks to Kevin Buford - good luck next year at school.

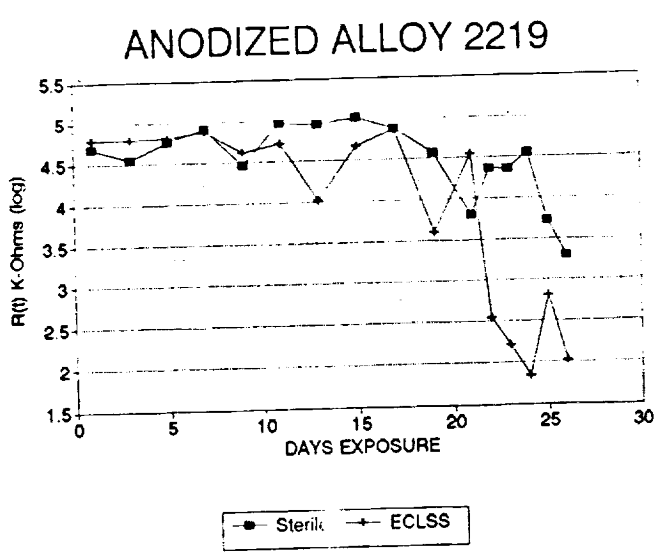

Figure 1.

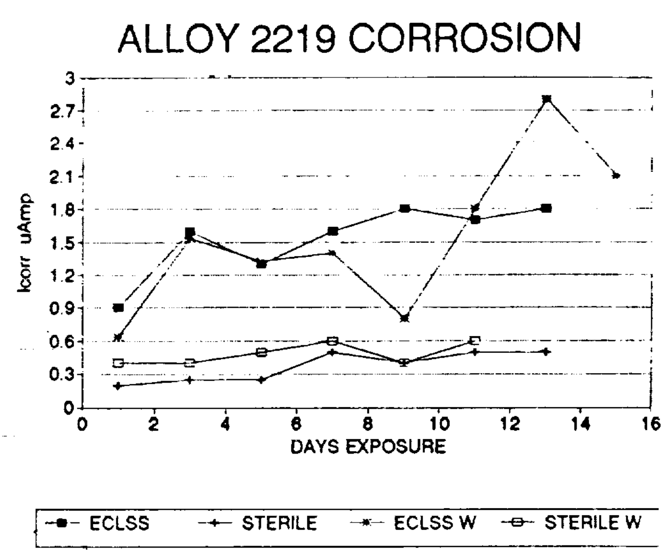

Figure 2

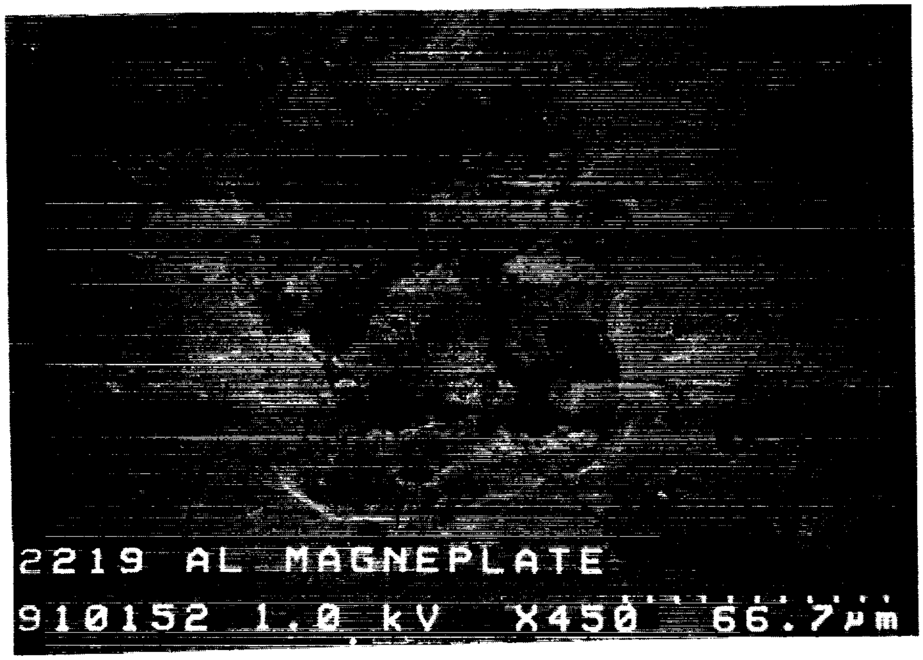

Figure 3. Localized MIC attack at weak spot in anodized coating.

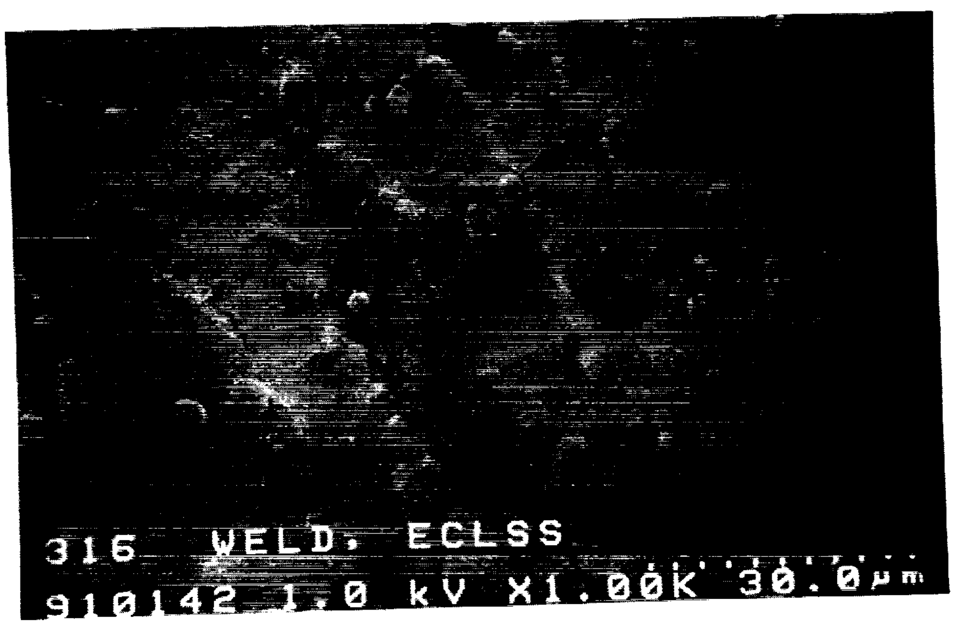

Figure 4. Microbes at weld ripple marks on 316L

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