In Situ Ellipsometric Investigation of the Stainless Steel Corrosion Behavior in Biological Media

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Background

- stainless steel is widely used as a cheap biomedical implant material
- the stainless steel surface modification due to corrosion is one of the reasons for failure of biomedical devices in the human body
- metal ion release during corrosion causes immunologic reactions

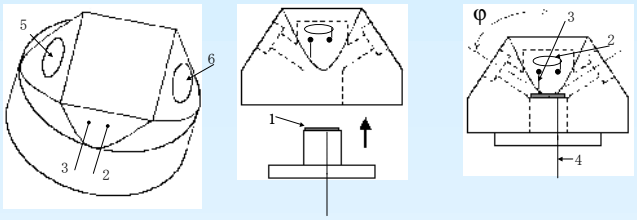
Objective

- to reveal peculiarities of stainless steel surface alteration in situ during the potentiodynamic corrosion test in biological media
- to relate these data with the corroded surface morphology studied ex situ by means of optical and atomic force microscopy (AFM)

Materials and Methods

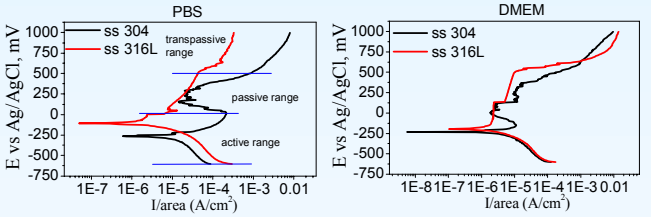
- polished discs of AISI stainless steel 304, 316 L grades
- phosphate buffered saline (PBS) and Dulbecco's Modified Minimal Essential Medium (DMEM) as the biological media (pH 7.4, T=22 ^{0}C)
- the potentiodynamic measurements were carried out in a corrosion cell that also permitted in situ ellipsometric probing of the sample surface (see right)

Ellipsometric studies: VASE (J.A. Woollam Co., Inc., USA), wavelength λ=632.8 nm, angle of light incidence φ=70 °C for in situ measurements
Potentiodynamic studies: Versastat, EG & G Instruments, Princeton Applied Research, voltage range -603 - +997 mV (vs Ag/AgCl), scan rate 2 mV/sec
AFM measurements: DualScope/Rasterscope (DME, Denmark) in the tapping mode under ambient conditions



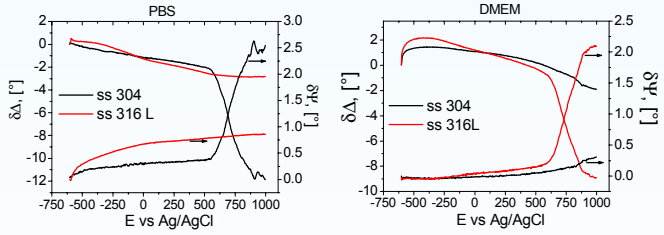
Corrosion cell for in-situ ellipsometric studies:
1: studied sample, 2: ring-like counter Pt electrode, 3: reference Ag/AgCl electrode, 4: sample electrode (Cu), 5 and 6: quartz windows for optical in-put and out-put respectively

Ellipsometry and Potentiodynamic Results



Potentiodynamic data for stainless steel grades 304 and 316 tested in PBS and DMEM

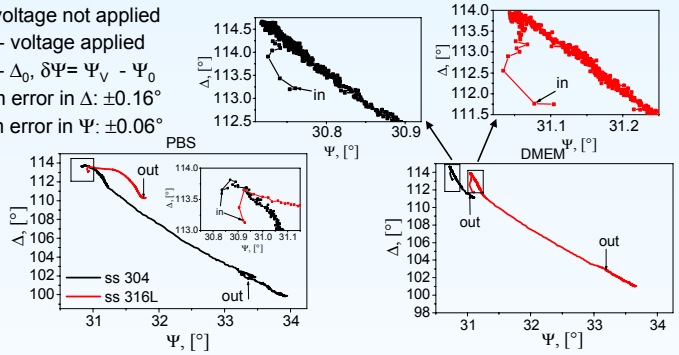
ss 304 in PBS: E_{corr}=-264.2 mV, I_{corr}=24.08 μA/cm² **ss 316 L in PBS:** E_{corr}= -108.1 mV, I_{corr}=5.821 μA/cm²
ss 304 in DMEM: E_{corr}=-232.9 mV, I_{corr}=43.71 μA/cm² **ss 316 L in DMEM:** E_{corr}=-195.2 mV, I_{corr}=4.234 μA/cm²



Change of the ellipsometric parameters Δ and Ψ during the potentiodynamic corrosion measurement of the two types of stainless steel in PBS and DMEM. The values are plotted as difference from the initial values (δΔ and δΨ) as a function of the applied potential.

Δ is the phase difference between p- and s- complex reflection coefficients
Ψ is the azimuth of the restored linear polarization, tanΨ=Re{R_P/R_S}

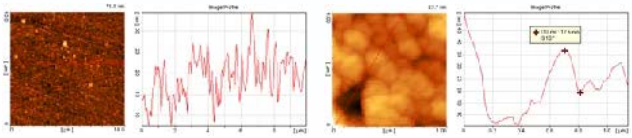
Δ_0, Ψ_0 - voltage not applied
Δ_V, Ψ_V - voltage applied
$\delta\Delta = \Delta_V - \Delta_0$, $\delta\Psi = \Psi_V - \Psi_0$
maximum error in Δ: ±0.16°
maximum error in Ψ: ±0.06°



Δ vs Ψ plots for stainless surfaces in PBS and DMEM. The points at which the voltage was turned on and off are marked.

- sharp increase of Δ with the decrease of Ψ (both steel grades, voltage range from –603 to –390 mV, DMEM) corresponds to the surfaces layer removal;
- abrupt change in Δ, Ψ dependences *vs* applied voltage can be interpreted as a consecutive growth of two layers with faster growth of the second layer;
- the kinetics of the corroded layer growth was determined from the ellipsometry data in case of SS samples tested in DMEM samples

AFM results



SS 316 L surface after potentidynamic corrosion test in PBS RMS=7.9 nm on 1x1 μm² area

Conclusions

- Ellipsometry demonstrates a better sensitivity than potentiodynamics to surface modification of the stainless steel in the active range of voltages
- For potentiodynamic tests in DMEM the removal of surface layer within the first 2- 3 min with further repassivation was characteristic while in PBS the surface layer started to grow within the first few seconds; this layer was observed by AFM only for samples tested in PBS
- A parabolic growth of the corroded layer is determined in the case of the stainless steel potentiodynamic tests in DMEM within the voltage range from –390 to +820 mV

Acknowledgments

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