Corrosion Resistance and Biological Response to Nitinol

Christine Trepanier

Nitinol Devices & Components, Fremont, CA

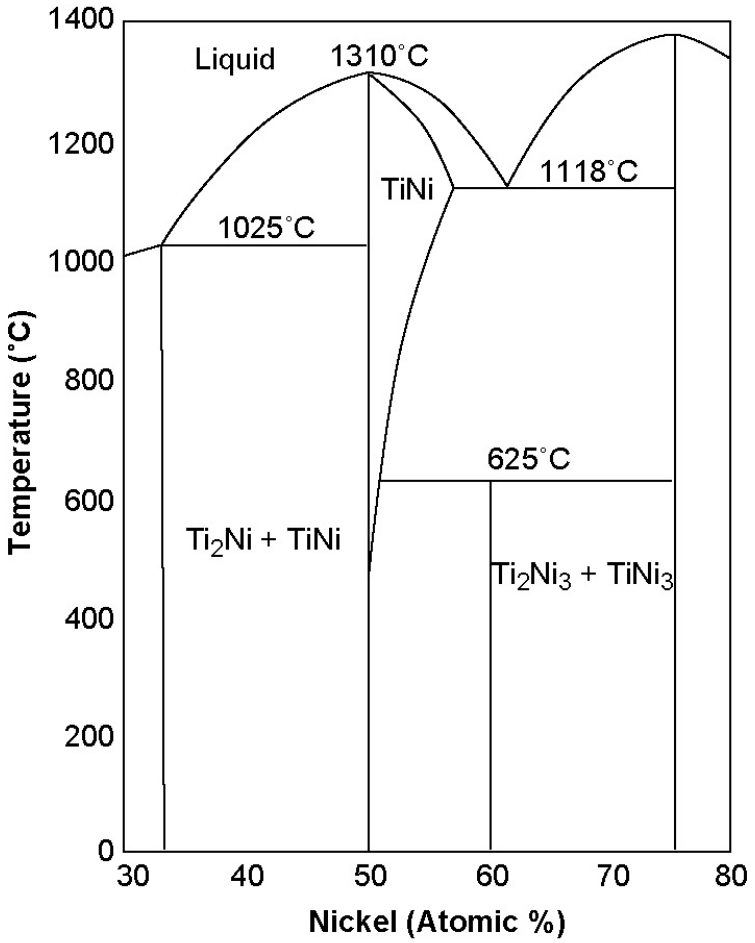
Outline

1. Background
2. Surface properties
3. Corrosion resistance
4. Biocompatibility
   Case Study: Effect of oxide layer composition on corrosion resistance and biocompatibility
5. Summary

Nitinol

Composition

50.8% at. Nickel, Titanium



Biocompatibility

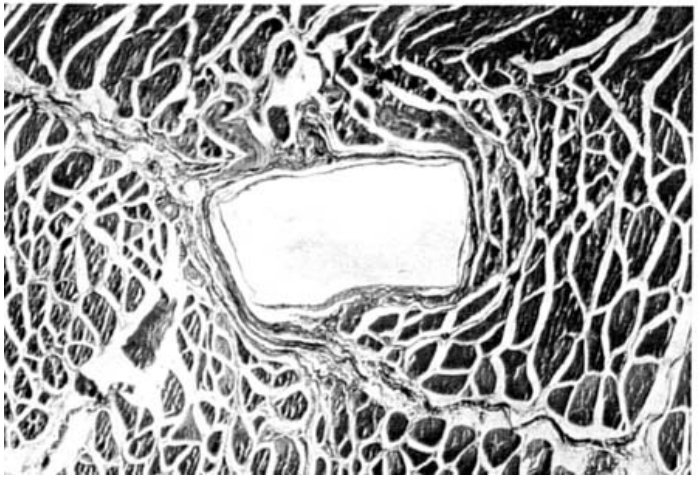
- Titanium

–Well accepted by the body. No clinical toxicity observed (Hildebrand, et al. 1998)

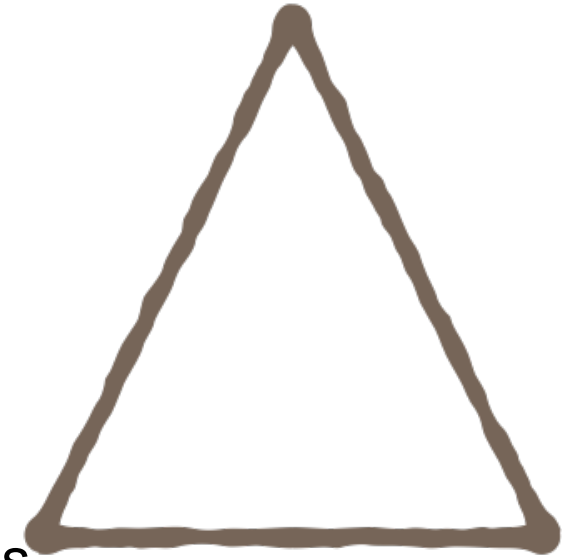
- Nickel

–Observed to be toxic (Denkhaus, et al. 2002 and Barceloux, et al. 1999)

–Can trigger contact allergies ~ 10% ww population (women > men) (Schafer, et al., 2001)



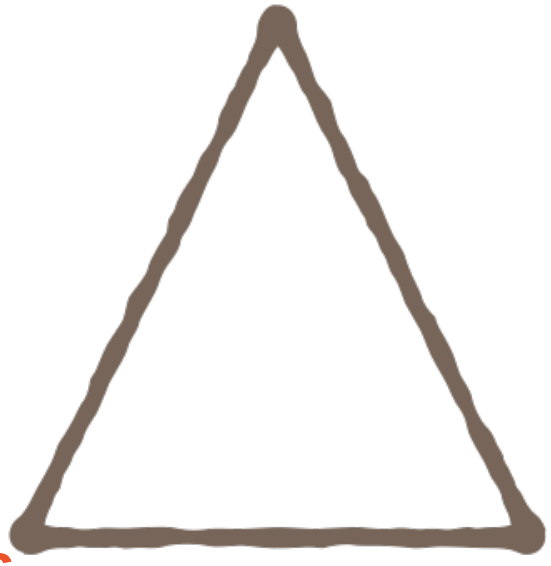
Biocompatibility



Surface properties

Corrosion resistance

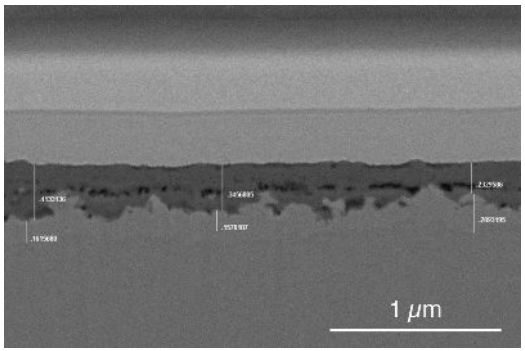
Biocompatibility

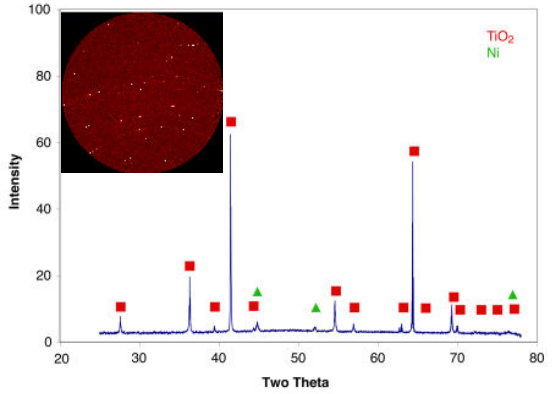


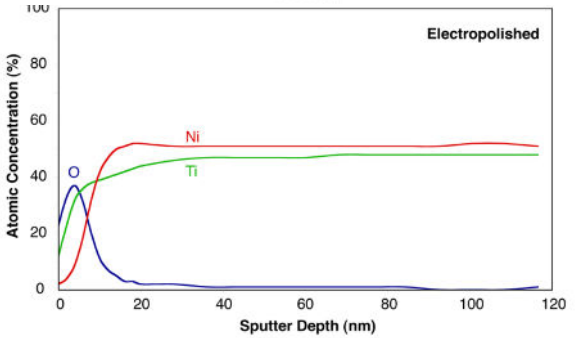
Surface Properties

Corrosion resistance

Thermal Oxidation of Nitinol

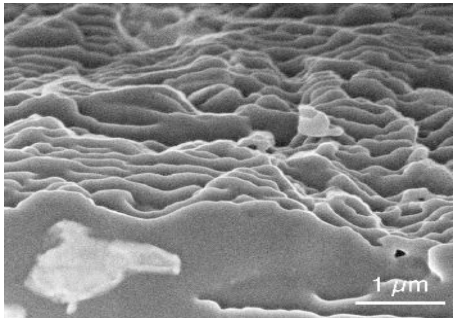


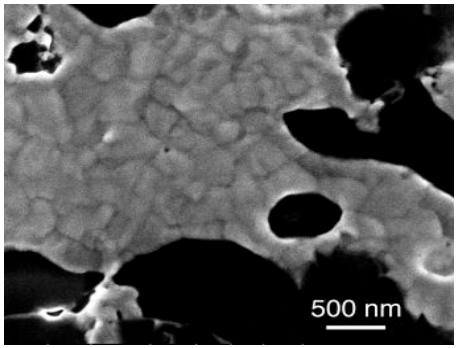


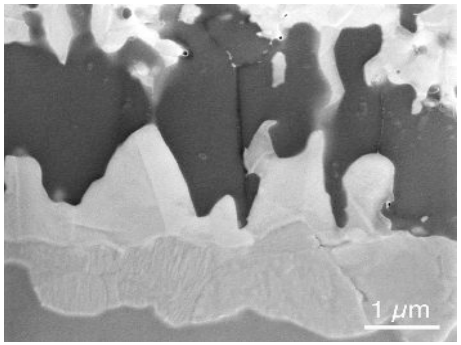


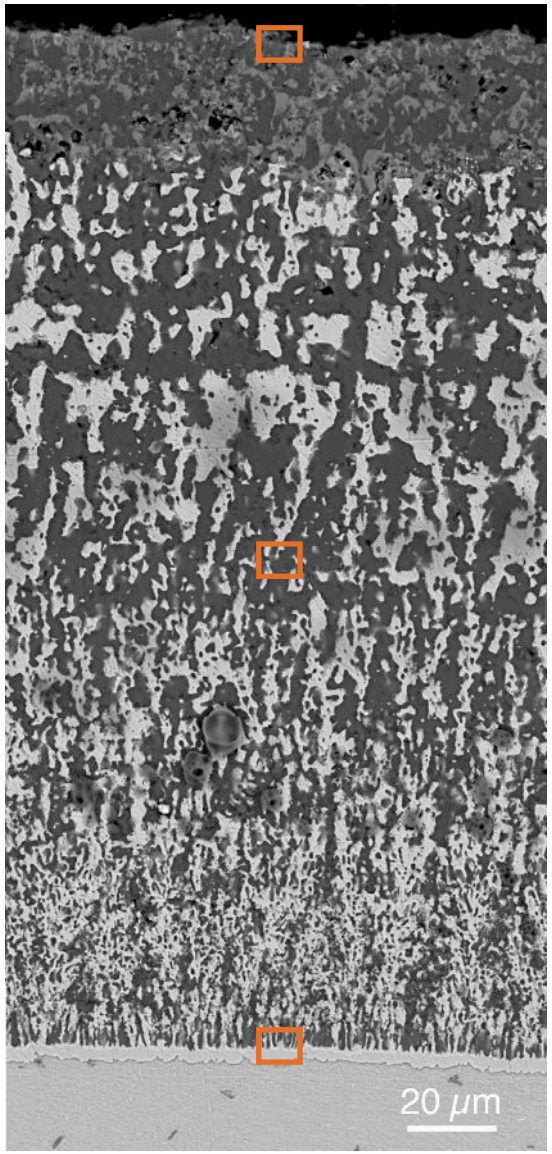
Zhu, *et al.*, Trepanier, *et al*, SMST 2003;
Pelton, *et al.,* Solid-to-Solid Transformations 2005

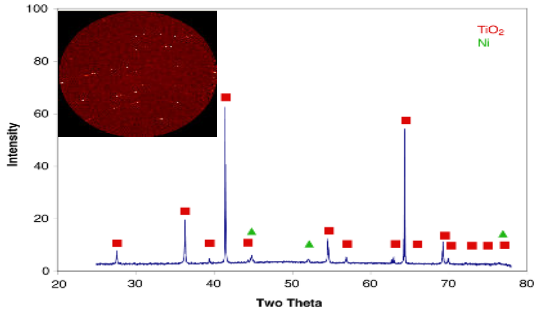
Surface Properties of Thermally Oxidized Nitinol

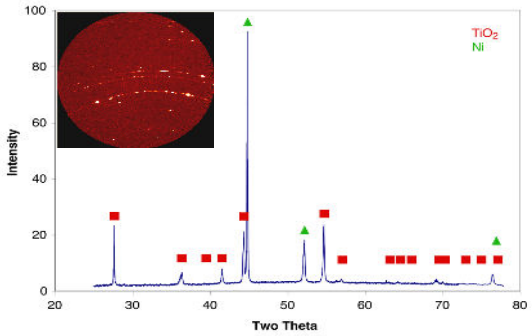


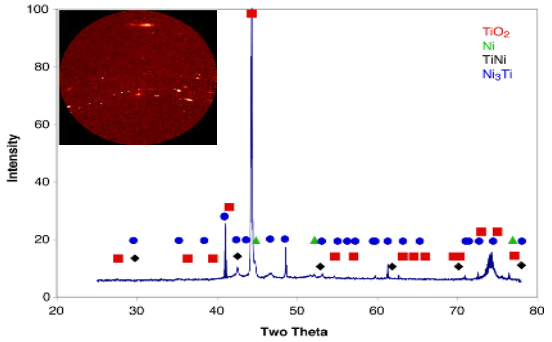




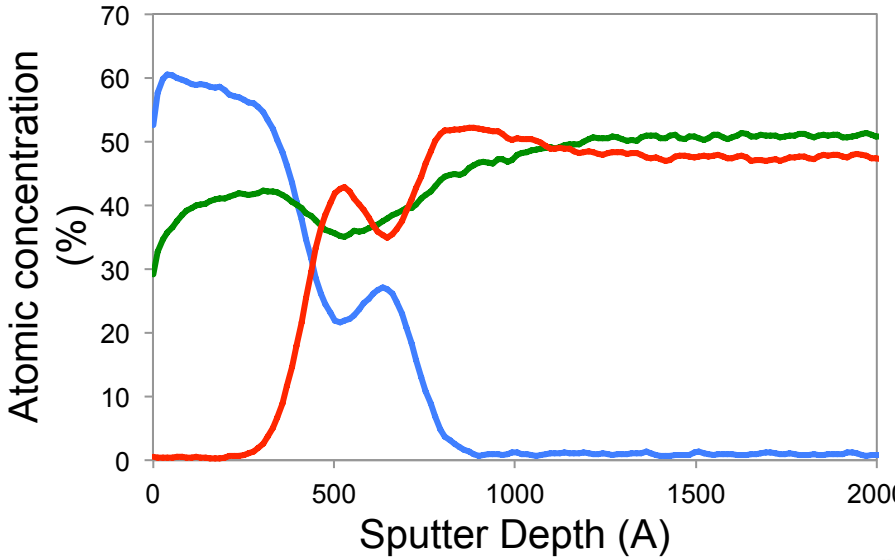






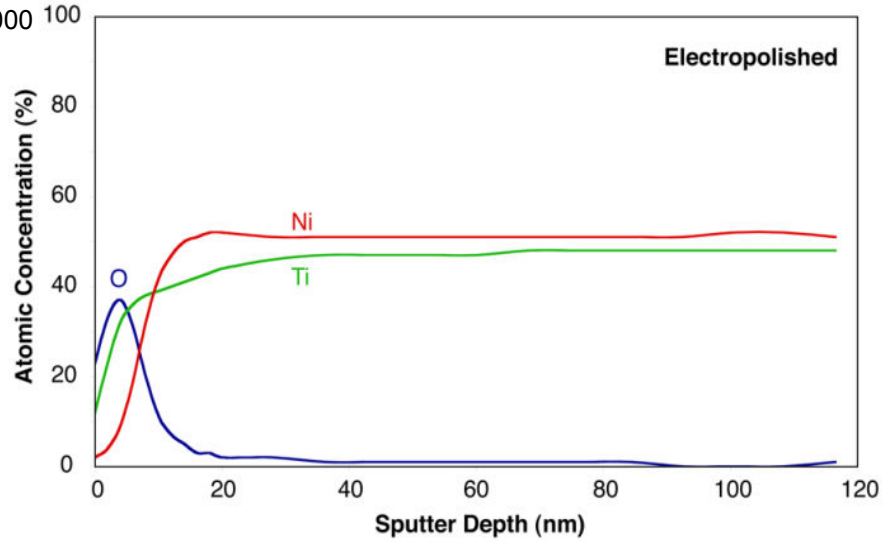


Surface Composition – AES

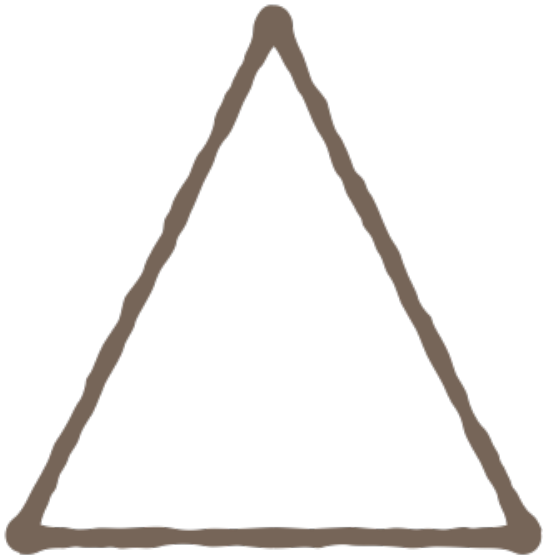


Heat treatment 500°C, 5 min

Electropolished



Biocompatibility



Surface properties

Corrosion resistance

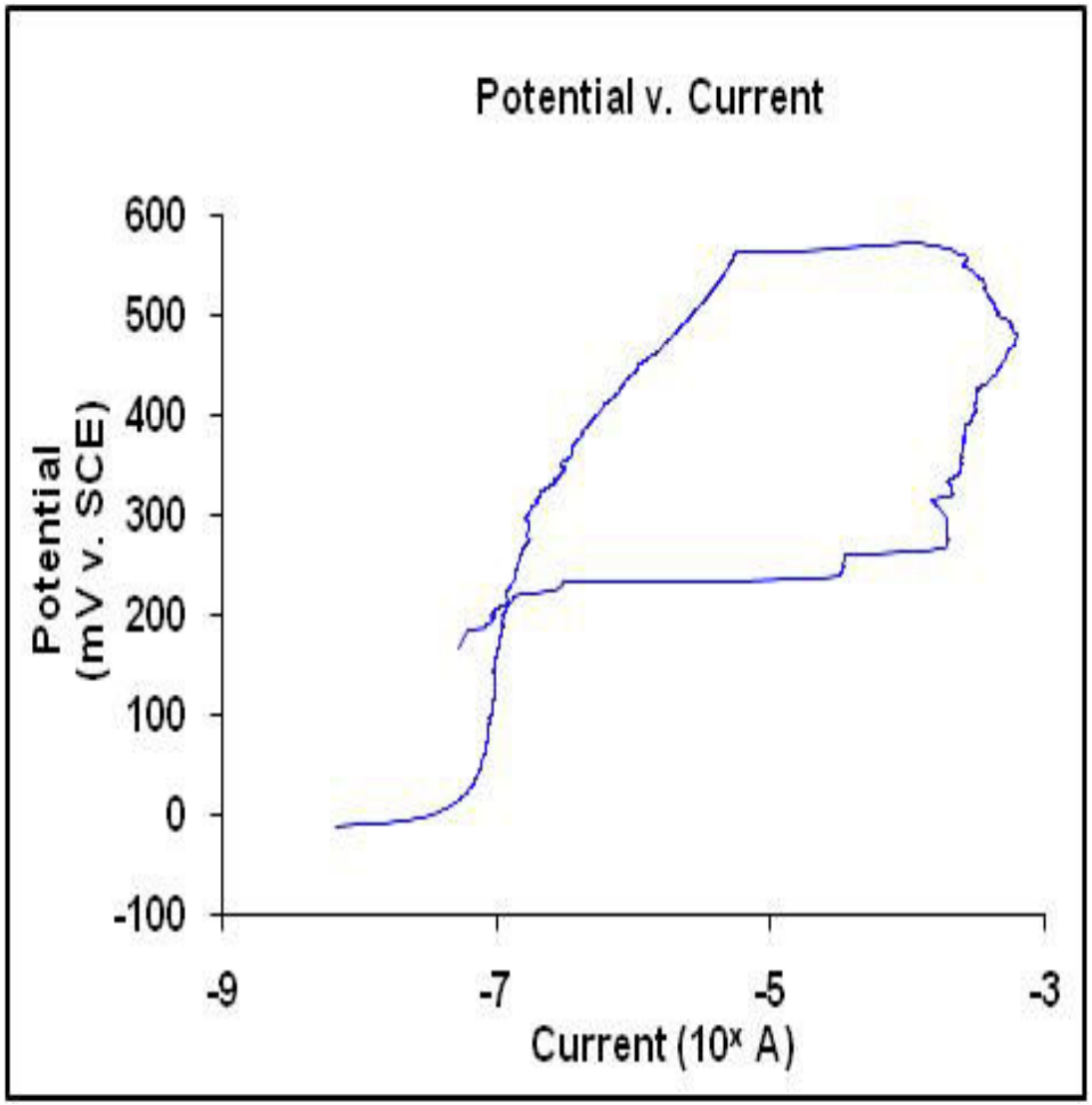
Localized Corrosion Resistance

Designation: F 2129 – 08

Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements to Determine the Corrosion Susceptibility of Small Implant Devices[1]

This standard is issued under the fixed designation F 2129; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

Localized Corrosion Resistance

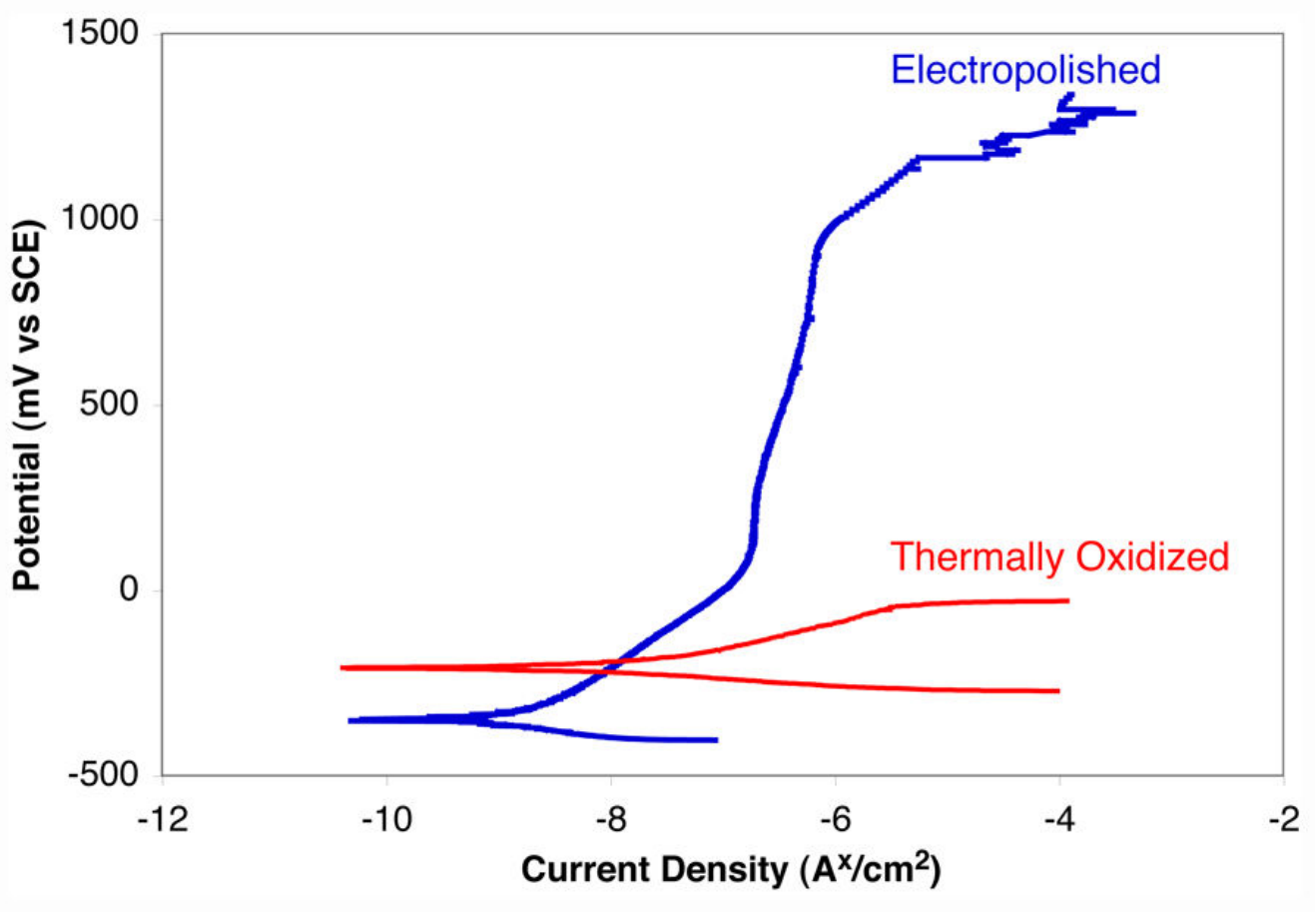


Localized Corrosion – Acceptance criteria

- Predicate device
- Literature reference
  - Corbett, 2003. Breakdown potential >600 mV vs SCE.

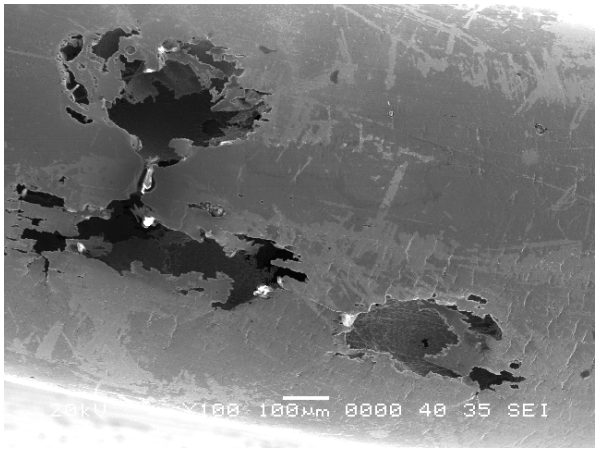
- E_b vs E_b-E_r
- Tool to compare corrosion performance
- Tool to predict biocompatibility?

Localized Corrosion Resistance



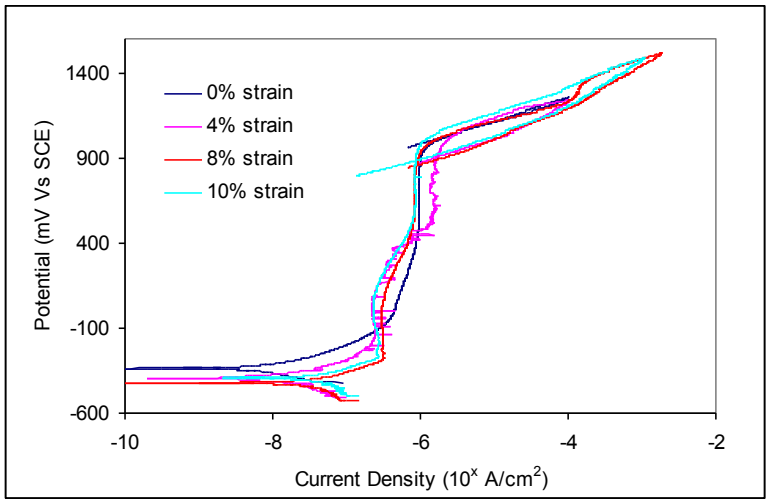
Effect of Strain

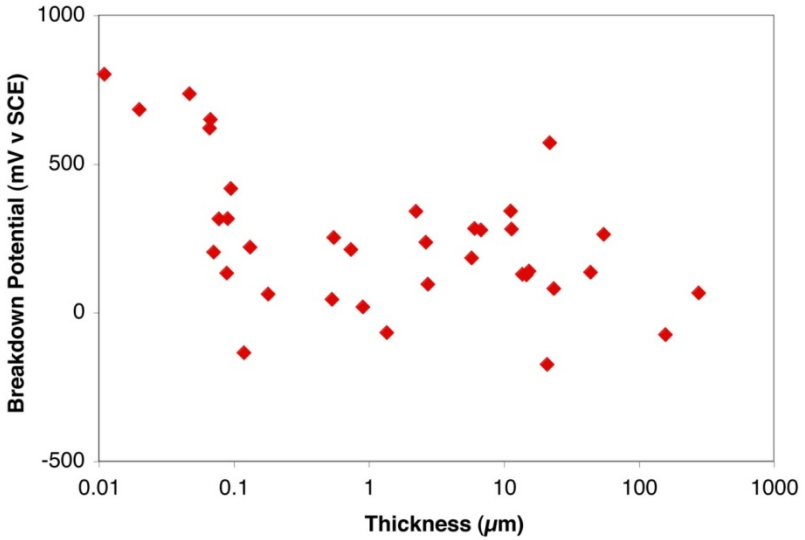
- Strain Range up to ~10% during constrain
- *In Vivo* Strain Range Nitinol Implants ~1-2%



Thermally Oxidized NiTi

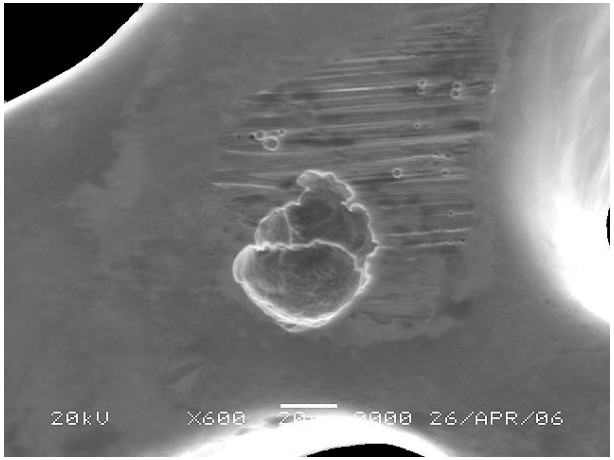
Electropolished NiTi



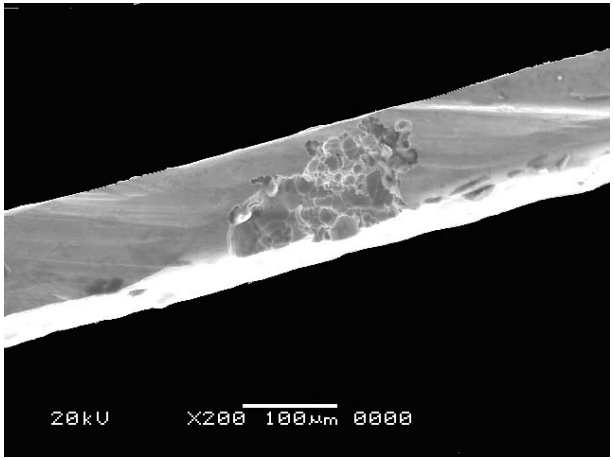


Trepanier, et al., SMST 2003

Effect of Fretting on Localized Corrosion

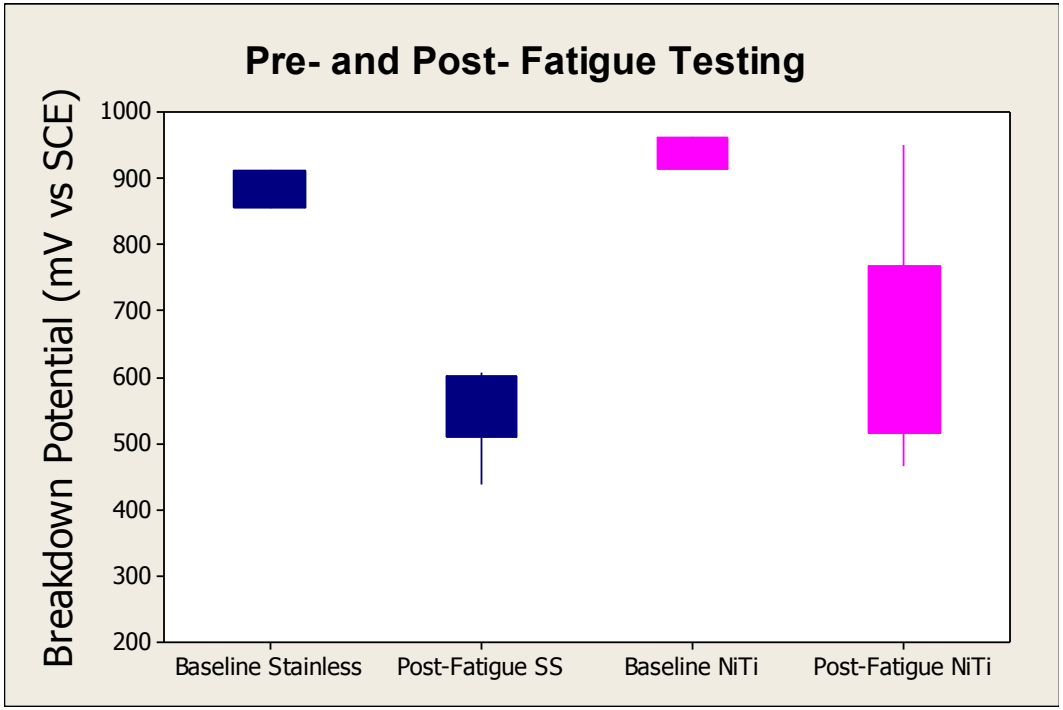


316L stent post-fatigue & corrosion

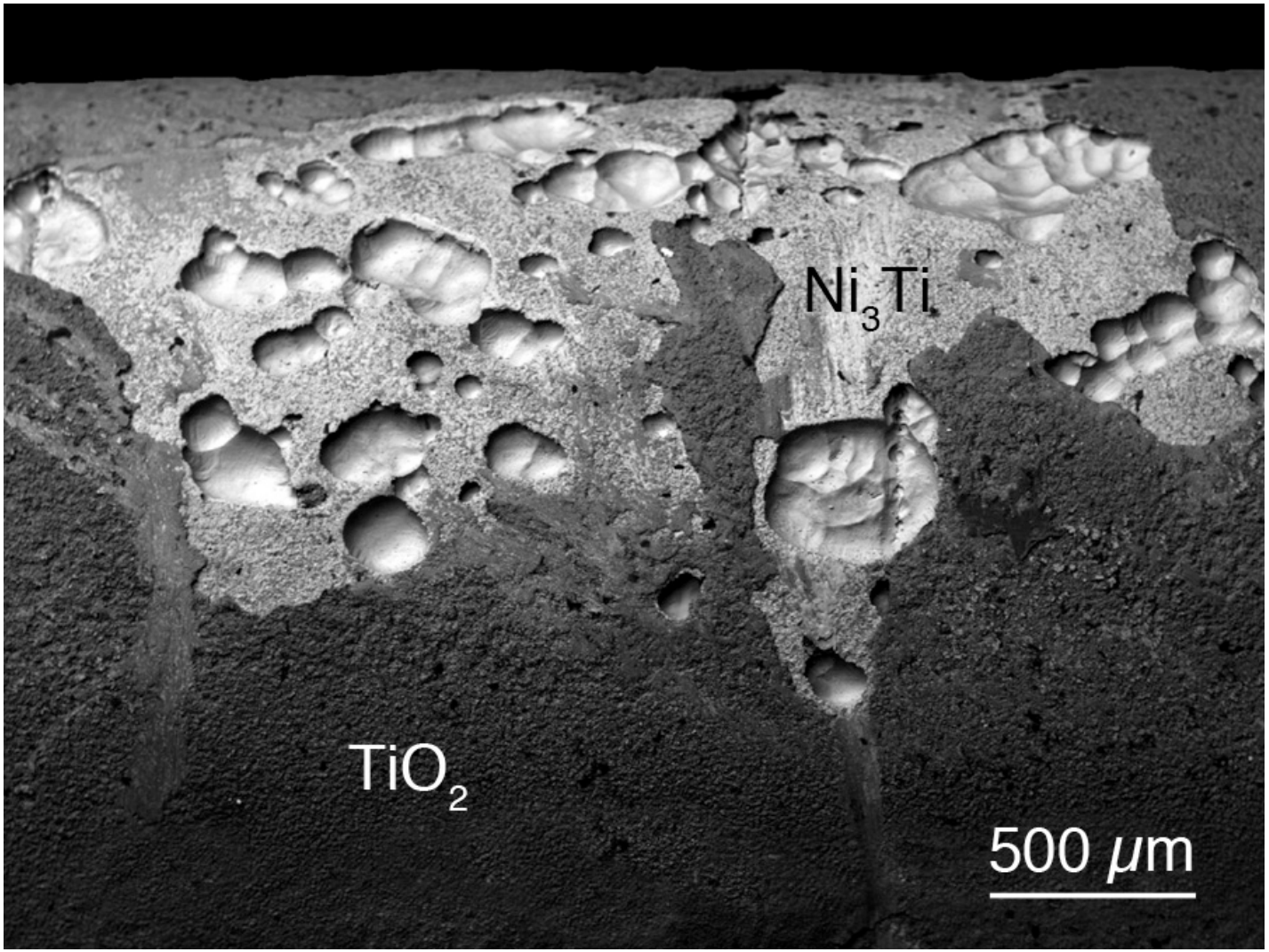


NiTi stent post-fatigue & corrosion

Breakdown Potential



Localized Corrosion



Uniform Corrosion Resistance

Biological evaluation of medical devices—Part 15: Identification and quantification of degradation products from metals and alloys

1 Scope

This part of ISO 10993 provides guidance on general requirements for the design of tests for identifying and quantifying degradation products from finished metallic medical devices or corresponding material samples finished as ready for clinical use. It is applicable only to those degradation products generated by chemical alteration of the finished metallic device in an *in vitro* accelerated degradation test. Because of the accelerated nature of these tests, the test results may not reflect the implant or material behavior in the body. The described chemical methodologies are a means to generate degradation products for further assessments.

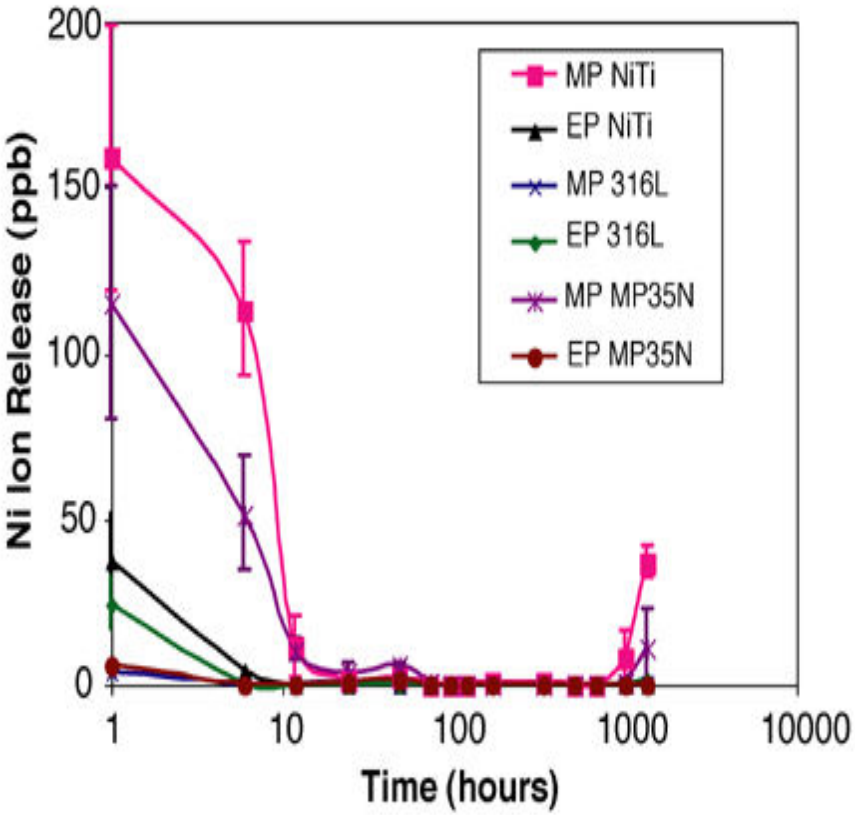
This part of ISO 10993 is not applicable to degradation products induced by applied mechanical stress.

NOTE—Mechanically induced degradation, such as wear, may be covered in the appropriate product-specific standard. Where product-group standards provide applicable product-specific methodologies for the identification and quantification of degradation products, those standards should be considered.

Because of the wide range of metallic materials used in medical devices, no specific analytical techniques are identified for quantifying the degradation products. The identification of trace elements ($< 10^{-6}$) contained in the

Effect of Surface Treatment on Uniform Corrosion

2 Months Immersion Study
37°C Hank's Solution, pH=7.4



Trepanier, et al., SFB 2000

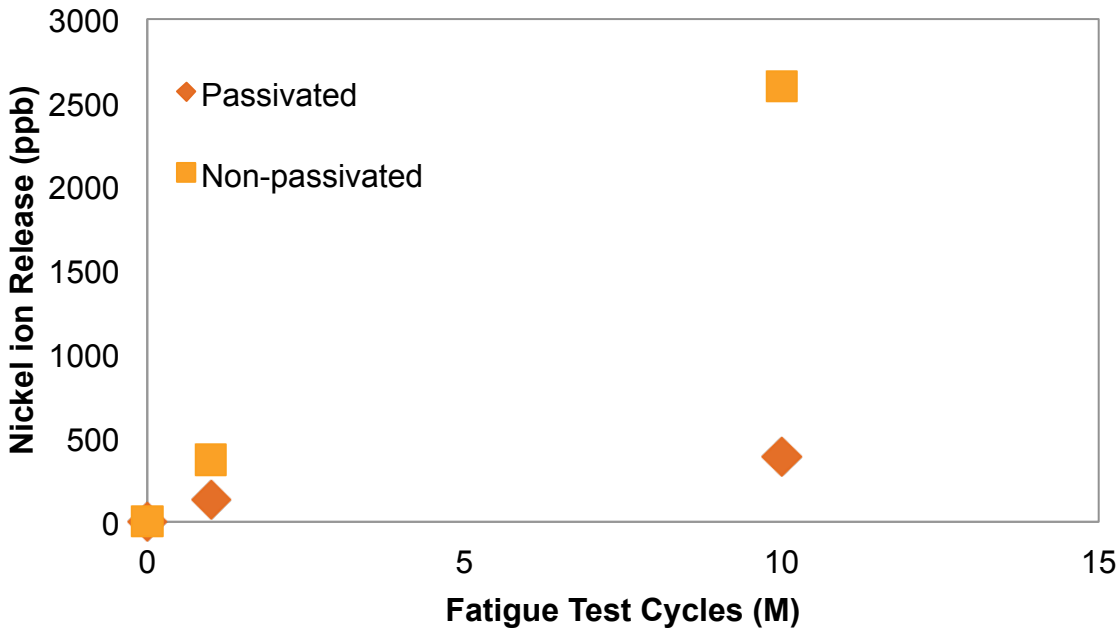
Acceptance Criteria – Nickel Leaching

- Predicate device
- Literature reference
  - US Pharmacopeia (USP) Permissible Daily Exposure (PDE) of 0.5 μg/kg/day. ~ 35μg/day (70kg person)

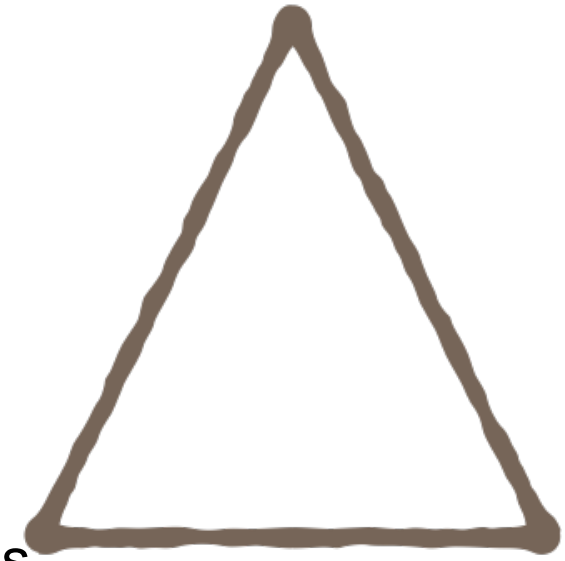
- Assumes daily excretion of Ni
- What about Localized effects?
- Effects of exposure route and type of nickel compound?

Effect of Fretting on Ion Release

- Nickel Ion Release
- Passivated and Non-Passivated Braided Nitinol device
- 1M and 10M cycles Fatigue Test



Biocompatibility



Surface properties

Corrosion resistance

Effect of Nitinol Oxide Layer Composition on Corrosion Resistance and Biocompatibility

Stacey J. Sullivan, Maureen L. Dreher, Jiwen Zheng, Lynn Chen and Srinidhi Nagaraja[1]

Daniel Madamba, Katie Miyashiro, Christine Trépanier[2]

[1]Food and Drug Administration, Center for Devices and Radiological Health, Office of Science and Engineering Laboratories, Silver Spring, Maryland USA

[2]Nitinol Devices & Components, Fremont, CA, USA

Goals & Materials

- Assess impact of oxide layer composition on:
  - Localized corrosion resistance
  - Uniform corrosion resistance
  - Biocompatibility

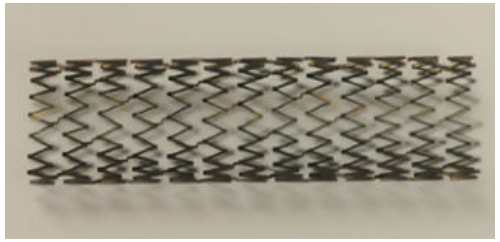
Group	Target $E_{b\ (vs\ SCE)}$	Comments
1	>600 mV	Complex Thermal oxide
2	>600 mV	Passivated oxide
3	300-600 mV	Mechanical polish
4	<300 mV	Positive E_b
5	<300 mV	Negative E_b

Method

- ☑ Identify processes to achieve target E_b
- ☑ Characterize Surface Properties via AES
- ☑ Quantify Localized Corrosion Resistance ASTM F2129
- ☑ Quantify Uniform Corrosion Resistance, Nickel leaching
  - 60 day study (1,2,3,5,7,14,21,30,45,60 days)
- ☐ Animal study – in progress
  - Minipig implantation: left and right iliac arteries (24 animals implanted)
  - Single and overlapped stent conditions (n=6/group)
  - 6 month implantation period
  - Periodic serum & urine nickel analysis
  - Explanted stent (SEM) and artery (histopathology) analysis

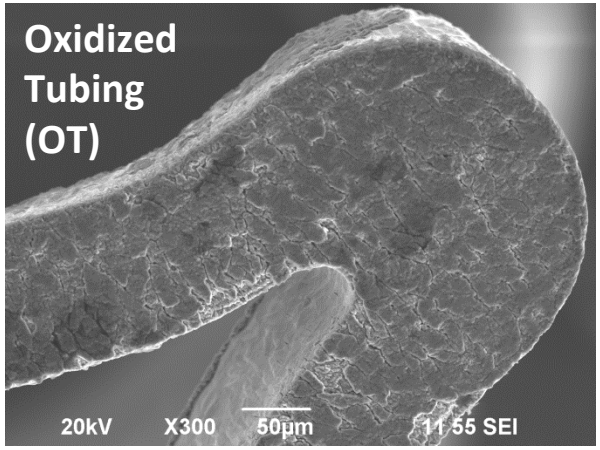
Stent Processing

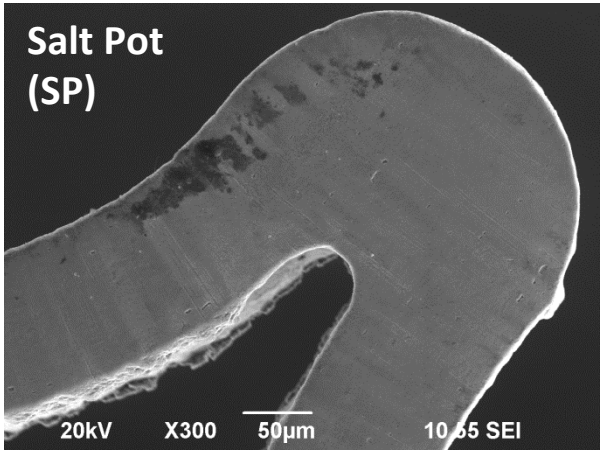
- Materials: Laser cut generic stents (ground and oxidized tubing)

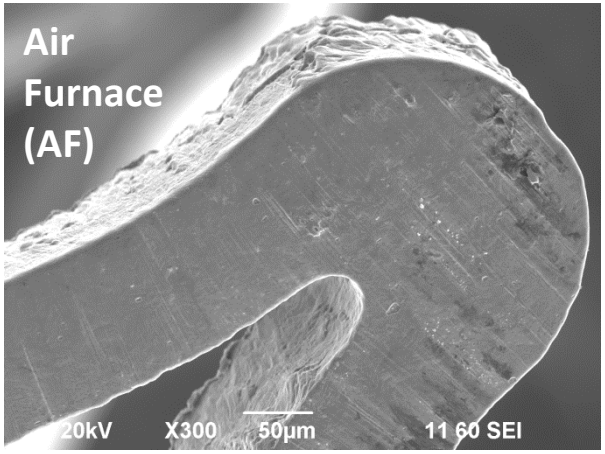


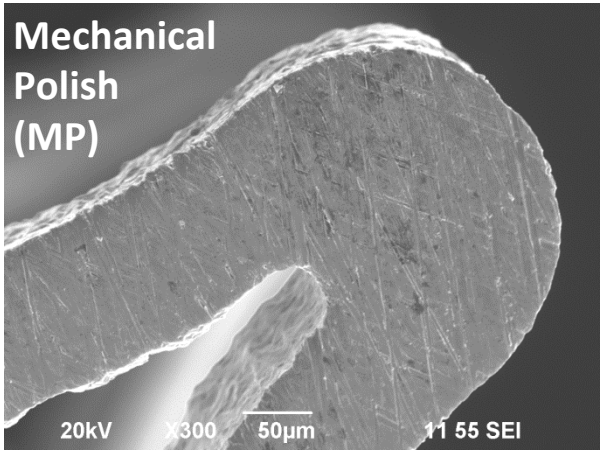
Group	OT	AF	SP	MP	EP
Tubing	Oxidized	Ground			
Removal of HAZ	N/A	Chemical Polishing			
Stress Relief	505°C	540°C	505°C	505°C	505°C
Expansion	505°C	505°C	505°C	505°C	505°C
A_f Tuning	505°C	550°C	505°C	505°C	505°C
Finishing	Ultrasonic clean	Ultrasonic clean	Ultrasonic clean	Etch Burnish	Etch EP

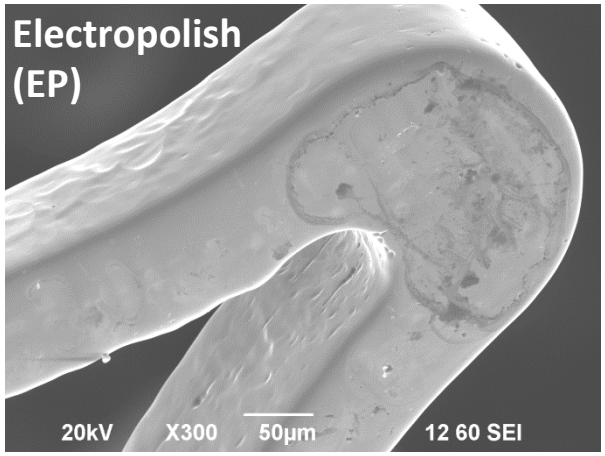
Surface Topography



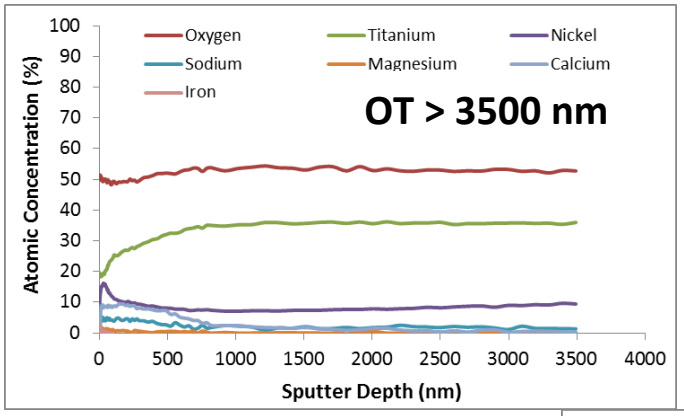


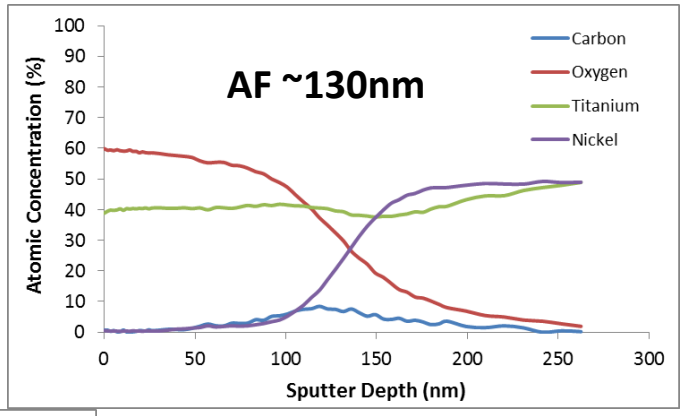


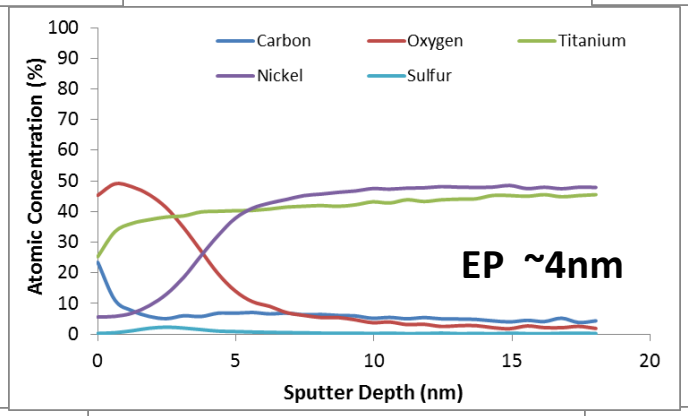


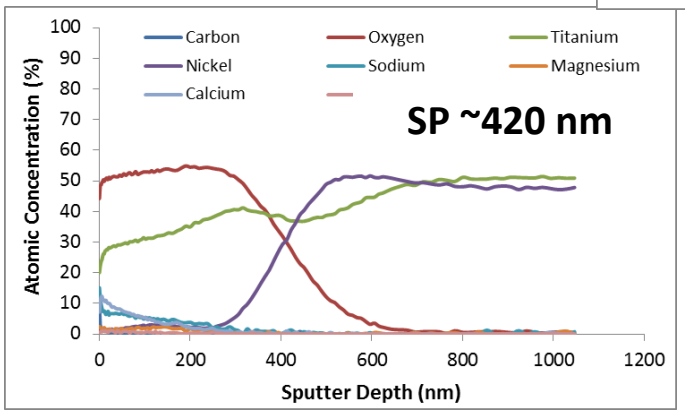


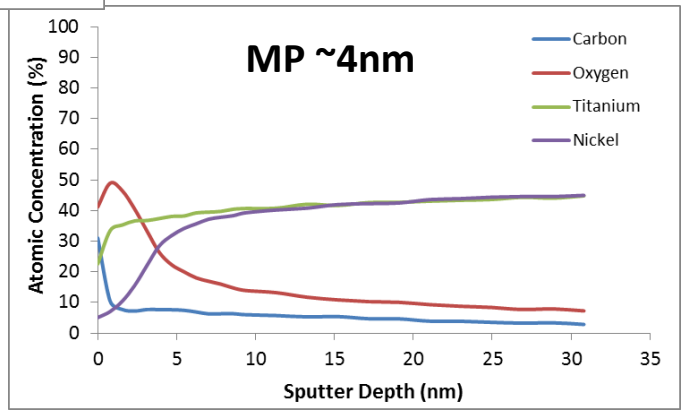
Oxide Layer Composition







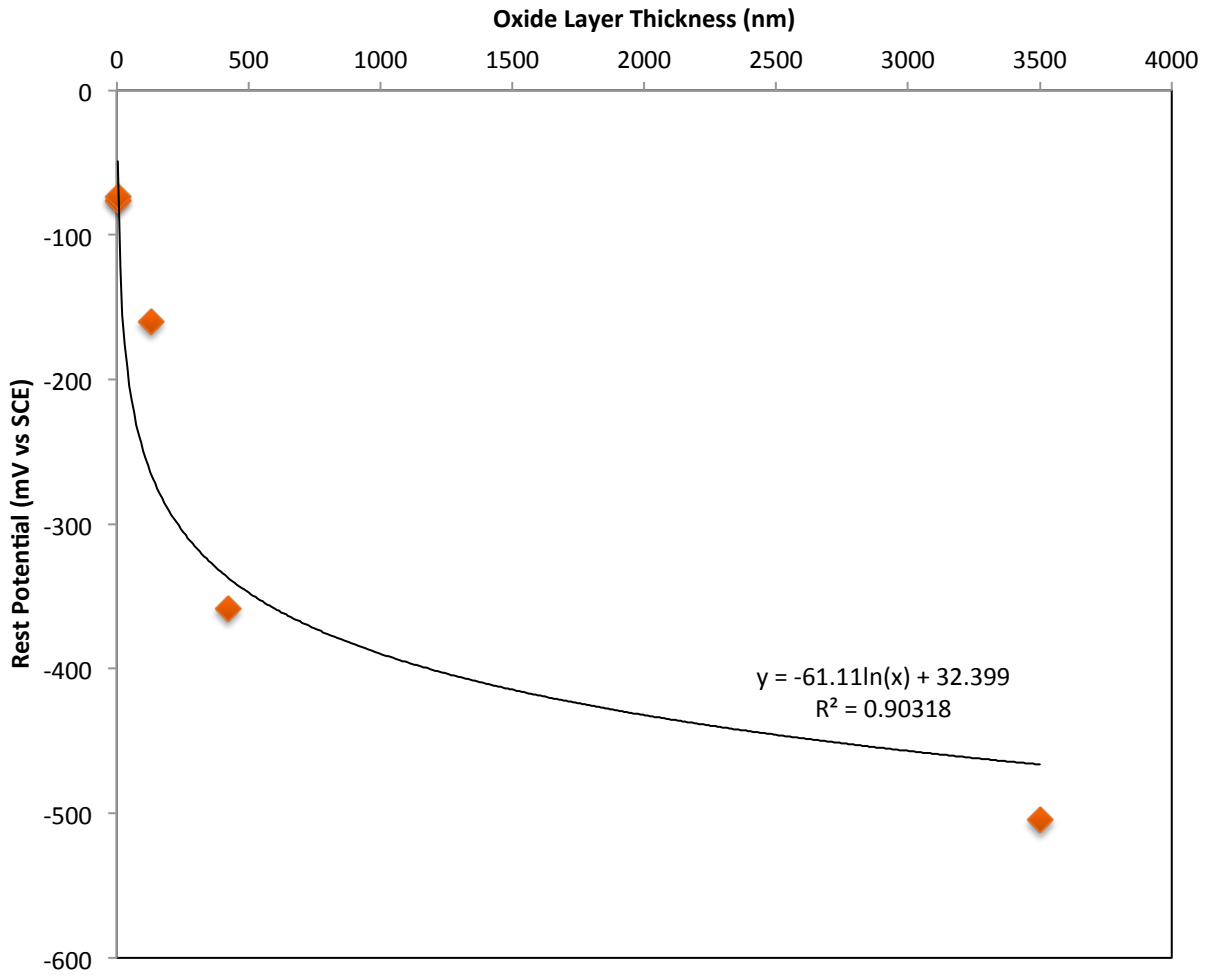




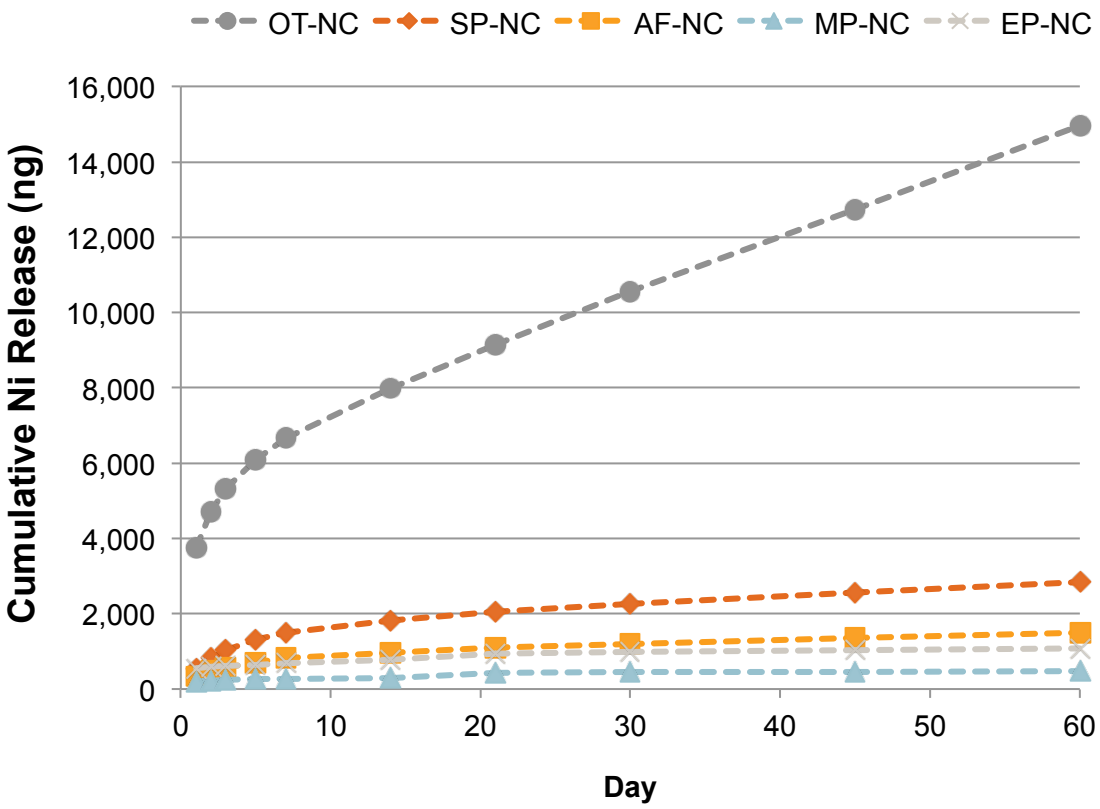
Localized Corrosion Resistance

Group	OT	AF	SP	MP	EP
E_r (mV vs SCE)	-505 +/- 6	-160 +/- 43	-359 +/- 196	-74 +/- 29	-76 +/- 62
E_b (mV vs SCE)	-117 +/- 15	144 +/- 73	NB	832 +/- 256	NB

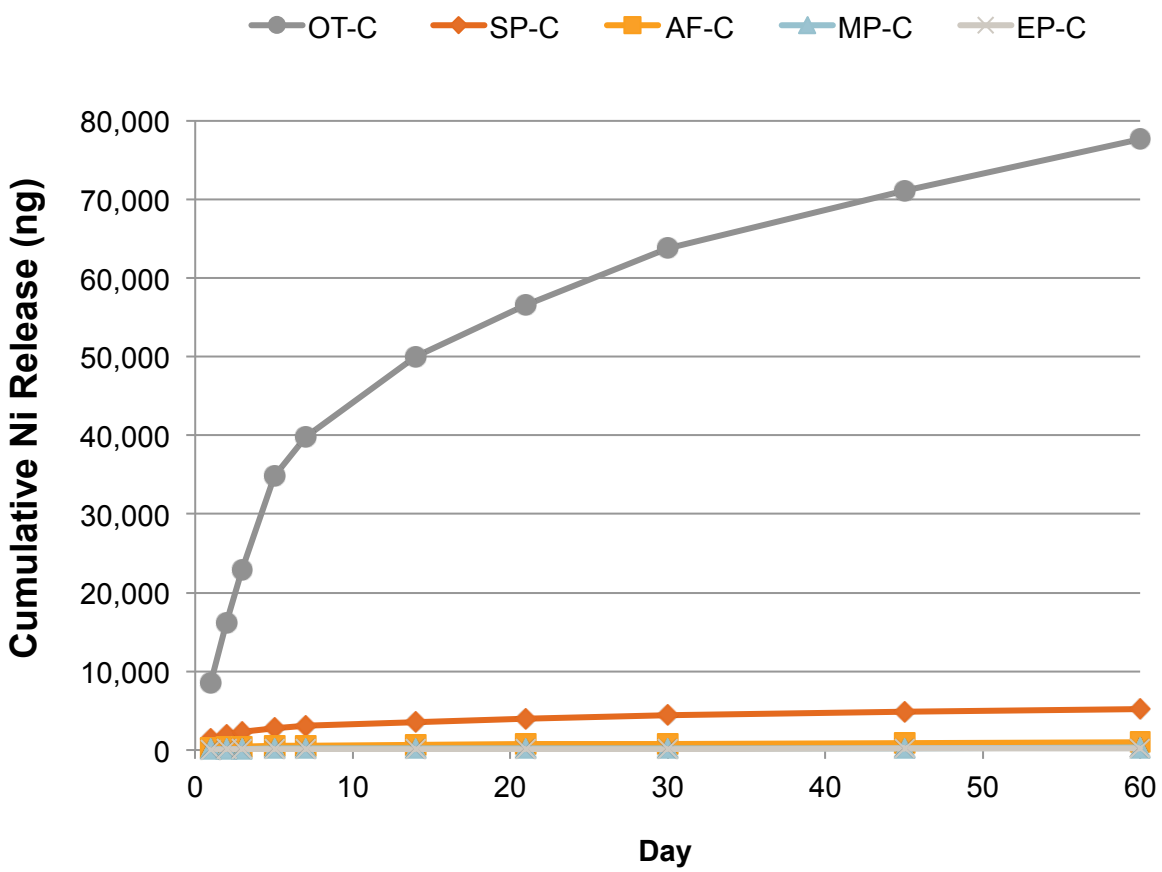
Correlation between Oxide Layer Thickness and Er



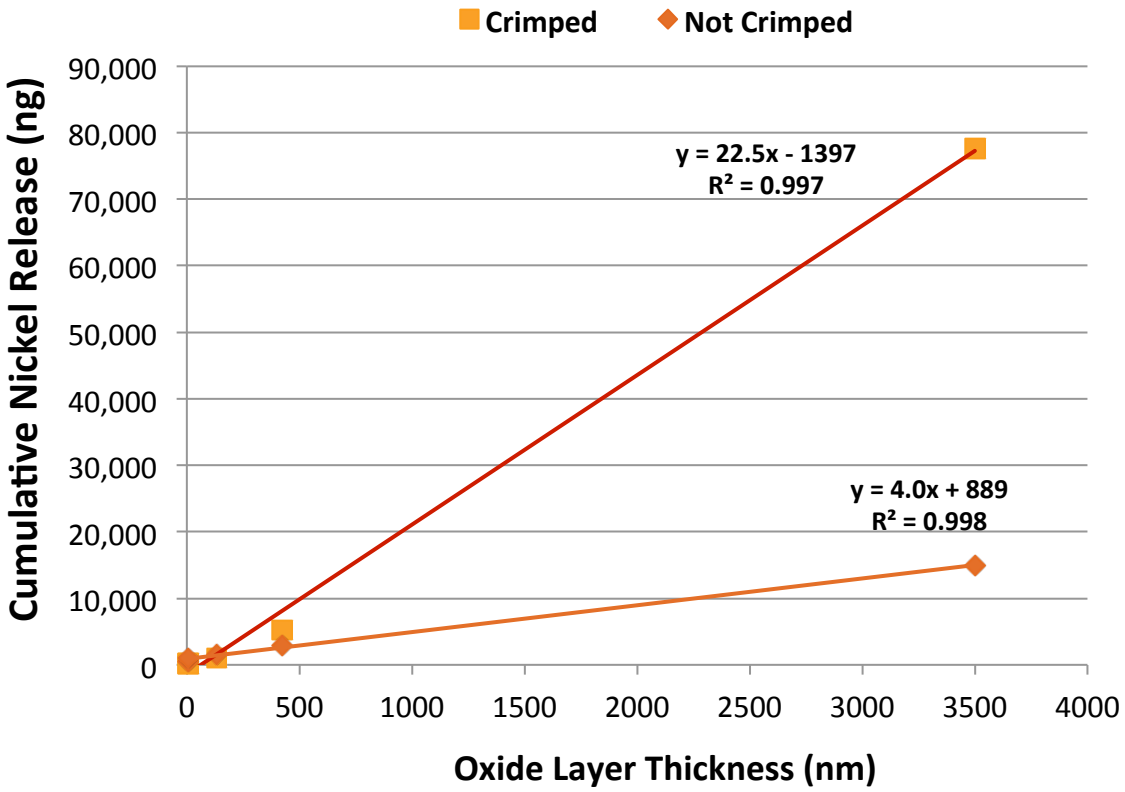
Nickel Release – As manufactured



Nickel Release – Post-Crimp



Correlation Oxide Layer Thickness and Nickel Release



Summary

- Surface Properties
  - Formation of complex oxide layer during HT
  - Ti oxide and Nickel-rich phases
- Localized & Uniform Corrosion Resistance
  - Effect of outer surface layer
  - Impact of deformation and fretting on corrosion resistance
  - Acceptance criteria?
- Biocompatibility