Tribocorrosion of Thermally Treated Ti-V Samples

Arman B. and Newton L.

Advisors

Professors Christos G. Takoudis, Cortino Sukotjo,

and Mathew T. Mathew

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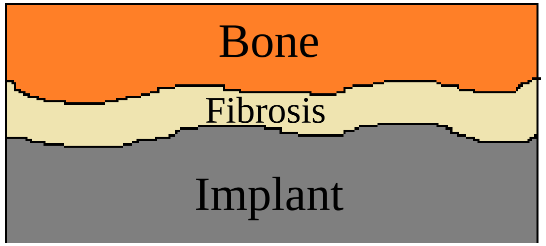
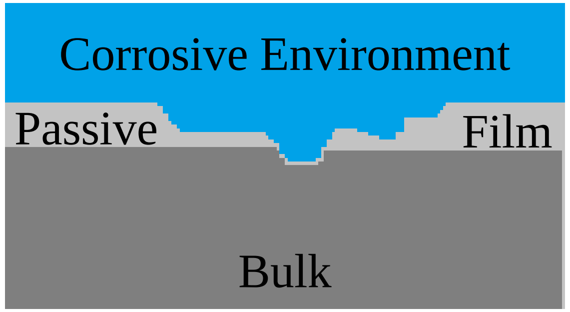
Background

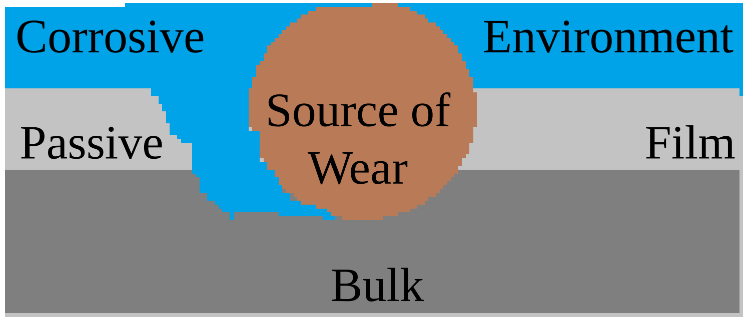
- Main reasons for revision
  - Aseptic loosening
    - wear and corrosion synergistically affect implant surface[1]
  - Instability and lack of osseointegration[2]
    - Implant surface does not readily promote cellular attachment
    - Poor bone quality and quantity
    - Over activity[3]



Localized cell death leads to fibrosis and inadequate osseointegration



Corrosive attack may lead to removal of passive film, exposing bulk to corrosive attack



Wear of passive film exposes bulk to corrosive attack

1. Yousef Abu-Amer *et al.* Arthritis Res Ther. 2007; 9(Suppl 1): S6.
2. Claudia Cristina Montes, *et al.* Implant Dentistry. Volume 16 (4). 401-408.
3. "Total Joint Replacement Patients Should Stick to Low-Impact Sports," BioMechanics 5(3):71-75, 1998.

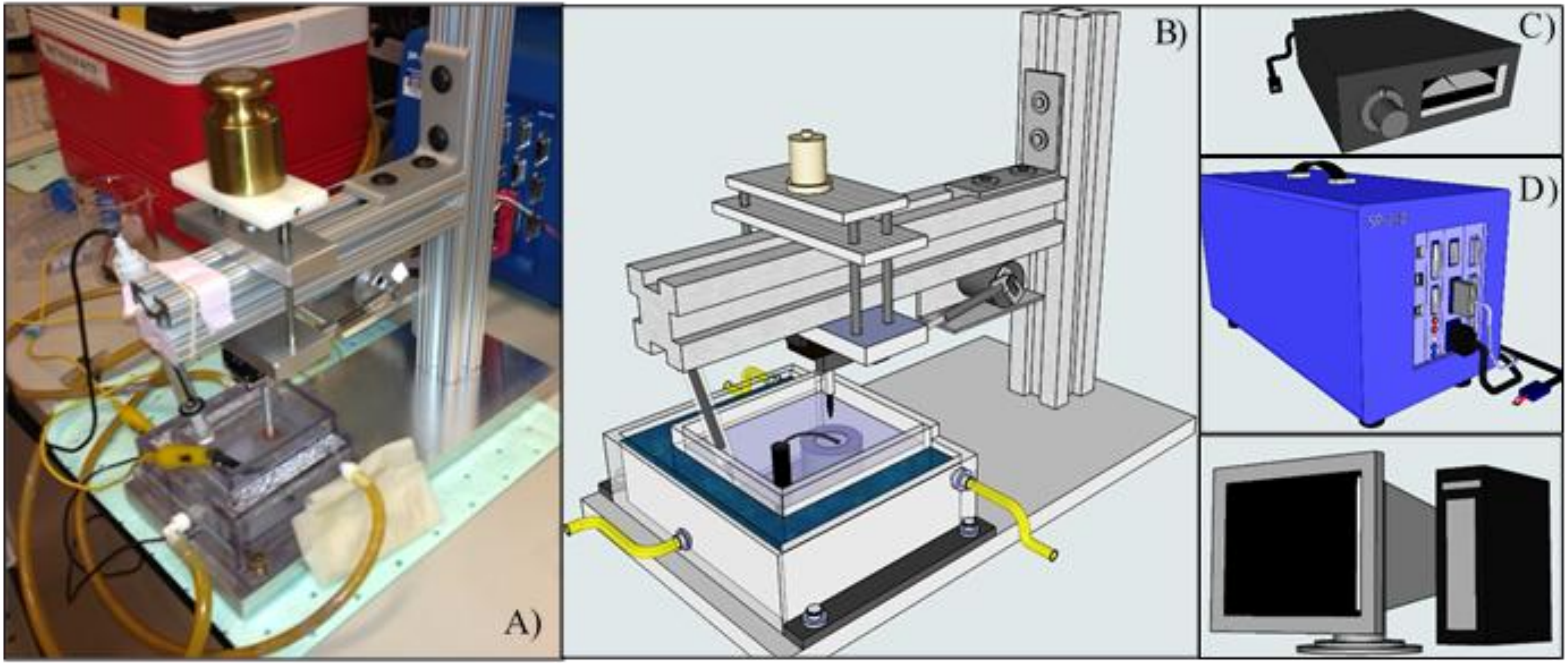
Tribocorrosion of Thermally Treated Ti-V Samples

- Thermally treat Ti-V surfaces at temperatures of 200, 400, and 700 °C at 1 and 6 hours
  - To test the effect of crystalline structure and oxide thickness on tribocorrosion and corrosion
  - Artificial Saliva (AS) at 37 °C
    - pH 6.5 ~ basic, normal conditions
    - pH 3.0 ~ infection
  - Validate custom designed and built tribocorrosion apparatus
- Hypothesis:
  - Crystalline and thicker oxide will protect bulk Ti-V from tribocorrosion and corrosion as compared to native TiO_2

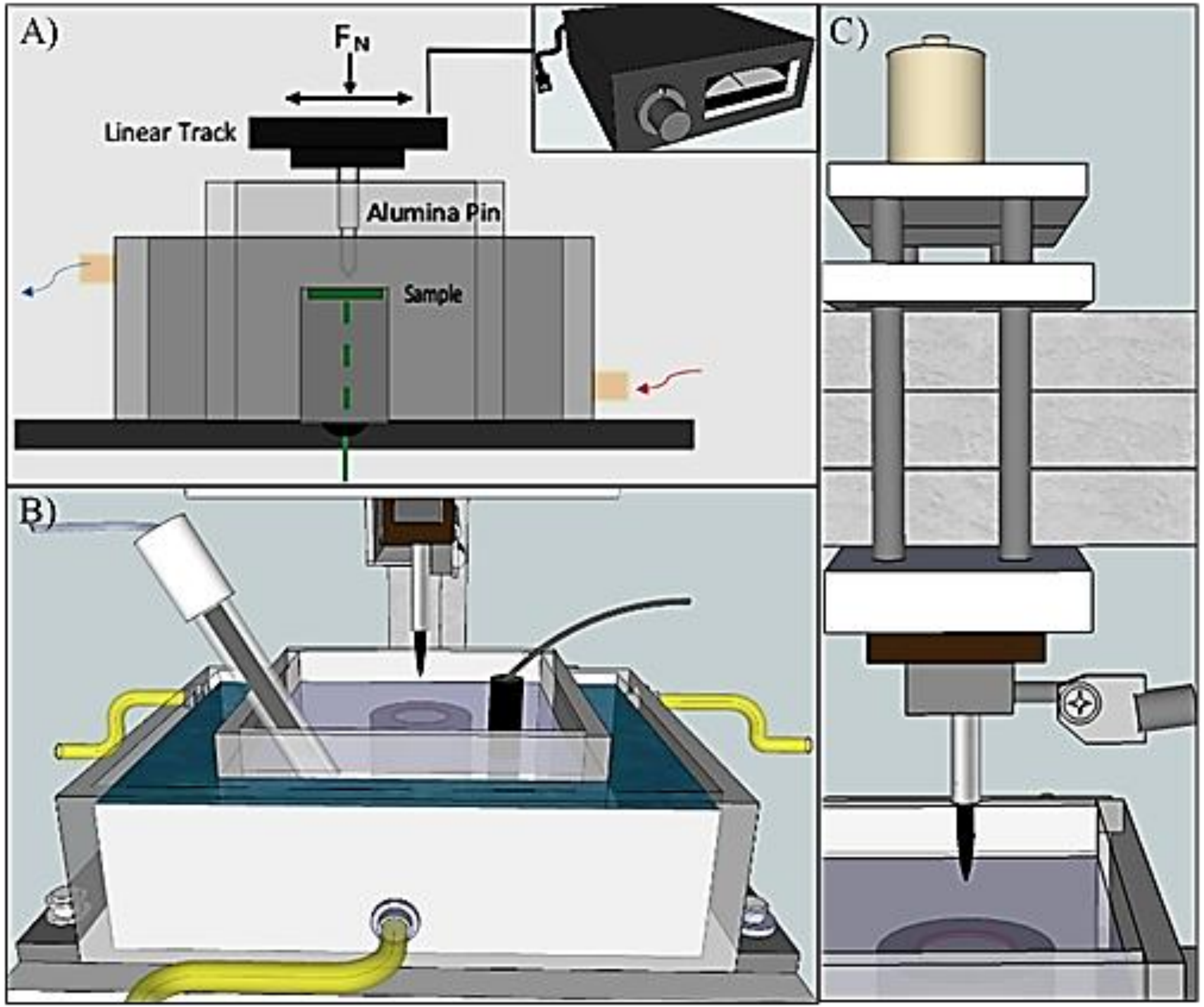
Source #	Citation	Working Electrode	Reference Electrode	Position of Ref. Electrode	Counter Electrode	Electrochemical Cell	Electrolyte and Volume	Pin	Movement	Comments
1	P. Jemmely, et. al., 1999.	AISI 430 Steel	Mercury Sulfate Electrode (MSE)	3 mm above and 10 mm away from sample	Coiled Platinum (Pt) Wire	Polyvinyl Chloride (PVC)	60 ml; 0.5 M H2SO4; 1 M NaOH	Alumina Pin w/ Flat Bottom	Pin Reciprocal Linear; 5, 10, and 20 Hz; Triangular Waveform Signal of Constant Amplitude; Track Length: 2.3-2.9 mm; Dead-time = 29 ms; 4-45 Mpa	Load Cell for Normal Force, Piezoelectric Force Transducer for Frictional Force, a LabView software with 32 kHz acquisition frequency
2	S. Mischler, et. al., 1999.	DIN 34CrNiMo6 Carbon Steel	MSE	3 mm above and 10 mm away from sample	Pt Wire	PVC	Borate Buffer Solution of pH 8.4 (H3BO3/Na2B4O7 0.3 M/.075 M)	Alumina Pin w/ Flat Bottom	Pin Reciprocal Linear; 5 Hz; Truncated Triangular Waveform Signal of Constant Amplitude; Track Length: 5.0 mm; 2, 5, 10 N	Load Cell for Normal Force, Piezoelectric Force Transducer for Frictional Force, a software with 10 kHz acquisition frequency
3	J. Takadoum, 1996.	Nickel and Iron of 99.95% Purity	Hg2SO4 Electrode (ESS)	_ _ _	2 cm2 Pt Sheet	Teflon	Aerated H2SO4 Solution; .01 - 1 M	Alumina Sphere (D= 5 mm)	Reciprocal Rotation of Ball; 0.2 Hz; Truncated Triangular Waveform Signal of Constant Amplitude; Track Length: 15.0 mm; 3.5 N	Strain Gauge for Frictional Force, a software with 10 kHz acquisition frequency
4	Sh. Hassani, et. al., 2009.	AISI 1045 Carbon Steel w/ Electrodeposited Ni-Co Coating	Standard Calomel Electrode (SCE)	_ _ _	Coiled Pt Wire	_ _ _	10 w/w % NaOH Solution at pH 13.2	Alumina Sphere (D= 4.75 mm)	Reciprocal Rotation of Ball; Classic Slider-Crank Mechanism; 1 Hz; Track Length: 5.0 mm; 4.5 N	Load Cells for Normal and Frictional Force
5	A. Berradja, et. al., 2006.	Stainless Steel AISI 304L	Hg/Hg2SO4/Saturated K2SO4	_ _ _	Circular Pt Gauze	_ _ _	0.5 M H2SO4; Ringer's Solution w/ 8.402g/L NaCl, 0.302 g/L KCl and 0.298 g/L CaCl2 6.6 pH	Corundum Cylinder (D= 7 mm) with Spherical End (D= 200 mm)	Continious and Intermittend Unidirectional Circular Motion r= 8 mm; 6, 60, and 120 rpm; 5 and 20 N (96 and 207 MPa	_ _ _
6	S. Mischler, et. al., 1993.	Armco Iron Plate	_ _ _	_ _ _	_ _ _	PVC	60 ml; H2SO4: 2, 6, 8, 10, 14, 18 M; Double-distilled Water	Alumina Pin (D= 4 mm) w/ Truncated Cones (D= .5 mm, 120* Included Angle)	Pin Reciprocal Linear; 5 Hz; Triangular Waveform Signal of Constant Amplitude; Track Length: 5 mm; Rest-time = 29 ms; 5 N = 25 MPa	Load Cell for Normal Force, Piezoelectric Force Transducer for Frictional Force, a LabView software
7	A. Berradja, et. al., 2006.	AISI 304L and SS 3M Stainless Steel	Ag/AgCl (3 M KCl)	_ _ _	Pt Microelectrod	_ _ _	Ringer's Solution: 8.402g/L NaCl, 0.302 g/L KCl and	Corundum Sphere (D= 10 mm)	Reciprocal Rotation of Ball (Fretting); 1, 10 Hz; Truncated Triangular Waveform Signal of Constant Amplitude; Track Length: 200 um; 1, 2, and 5 N = 493,	_ _ _
					Graphite		Body Wear: SiC P1200 and Al2O3	mm)		
9	M. S. Jellesen, et. al., 2007.	Stainless Steel AISI 316L	SCE	1 cm away from sample	Titanium Net	Polypropylene	0.5 M H2SO4	Alumina Ring	Reciprocal Rotation of Ball; Sinus-wave Frequency, 15-20 N, 100 rpm	Strain Gauges for Normal and Frictional Force
10	S. Mischer, et. al., 1998.	Stainless Steel 316L; Ti6Al4V; 99.2% Pure Chromium; Low Carbon-Pure Nickel	MSE	3 mm above and 5 mm away from sample	Pt Wire	PVC	0.5 M H2SO4; 0.5 M Na2SO4	Alumina Pin (D= 4 mm) w/ Truncated Cones (D= .5 mm, 120* Included Angle)	Pin Reciprocal Linear; 5 Hz; Triangular Waveform Signal of Constant Amplitude; Track Length: 5 mm; Rest-time = 20 ms; 5 N = 25 MPa	Load Cell for Normal Force, Piezoelectric Force Transducer for Frictional Force, a LabView software
11	M. Azzi and J.A. Szpunar, 2007.	ASTM F67 Pure Ti	SCE	_ _ _	Pt Coil	_ _ _	Ringer's Solution: 9.0 g/L NaCl, 0.4 g/L KCl and 0.17 g/L CaCl2, 2.1 g/L NaHCO3	Alumina Sphere (D= 3/16")	Reciprocal Rotation of Ball; Classic Slider-Crank Mechanism; 1 Hz; Track Length: 5.0 mm; 4.5 N	Load Cells for Normal and Frictional Force
12	S. Barril, et. al., 2001.	TiN Coating on X20Cr13 Steel	Ag/AgCl	_ _ _	Pt Wire	PVC	Borate Solution, pH 8.4	Alumina Sphere (D= 6 mm)	Reciprocal Linear Motion of Ball; Truncated Triangular Waveform Signal; 2.0 Hz; Dead-time = 69 ms; Track Length: 5.0 mm; 5 N = 767 MPa	Piezoelectric Force Transducer for Normal and Frictional Force, a LabView Software
13	Y. Yan, et.al., 2006.	High and Low Carbon CoCrMo, Stainless Steel 316L	Ag/AgCl	5 mm away from sample	Pt Wire	_ _ _	50 % Calf Bovine Serum w/ 0.1 % Sodium Azide; Dulbecco's Modified Eagle's Medium (DMEM); 0.36 % NaCl Solution	Silicon Nitride Sphere (D= 12 mm)	Reciprocating Working Electrode; 1 Hz; 80 N	Load Transducer for Frictional Force,
14	S. C. Ferreira, et. al., 2006.	ZrxONy Thin Films on AISI M2 High-Speed Steel	SCE	_ _ _	Pt Wire	Arcylic	20 ml; Artificial Sweat Solution: 7.5 g/L NaCl, 1.2 g/L KCl, 1 g/L CH4N2O, 1 g/L C3H6O3	Alumina Pin	Reciprocating Linear Motion; 1 Hz; Track Length = 6 mm; 5 N	_ _ _
15	L. Benea, et. al., 2009.	20 nm Ni-SiC Coatings on Stainless Steel	Hg/Hg2SO4/Saturated K2SO4	_ _ _	Circular Pt Gauze	_ _ _	0.5 M K2SO4	Alumina Pin (D= 7 mm) w/ Spherical End (D= 200 mm)	Intermittent Unidirectional Circular Motion r= 8 mm; 30-120 rpm; 5 - 20 N; Dead-time = .5 -20 s	_ _ _
16	F. Bratu, et. al., 2007.	50 um Ni-SiC Coatings on AISI 304L Stainless Steel	Ag/AgCl (3 M KCl)	_ _ _	Pt Microelectrode	_ _ _	0.5 M Na2SO4, pH 6.5	Corundum Sphere (D= 10 mm)	Reciprocal Rotation of Ball (Fretting); 10 Hz; Truncated Triangular Waveform Signal of Constant Amplitude; Track Length: 200 um; 1, 2, and 5 N = 493, 621, 842 Mpa; Dead-time = 6.6 s	_ _ _

Working Electrode Reference Electrode Counter Electrode Cell Material Electrolyte Pin (Counter Body) Pin Movement

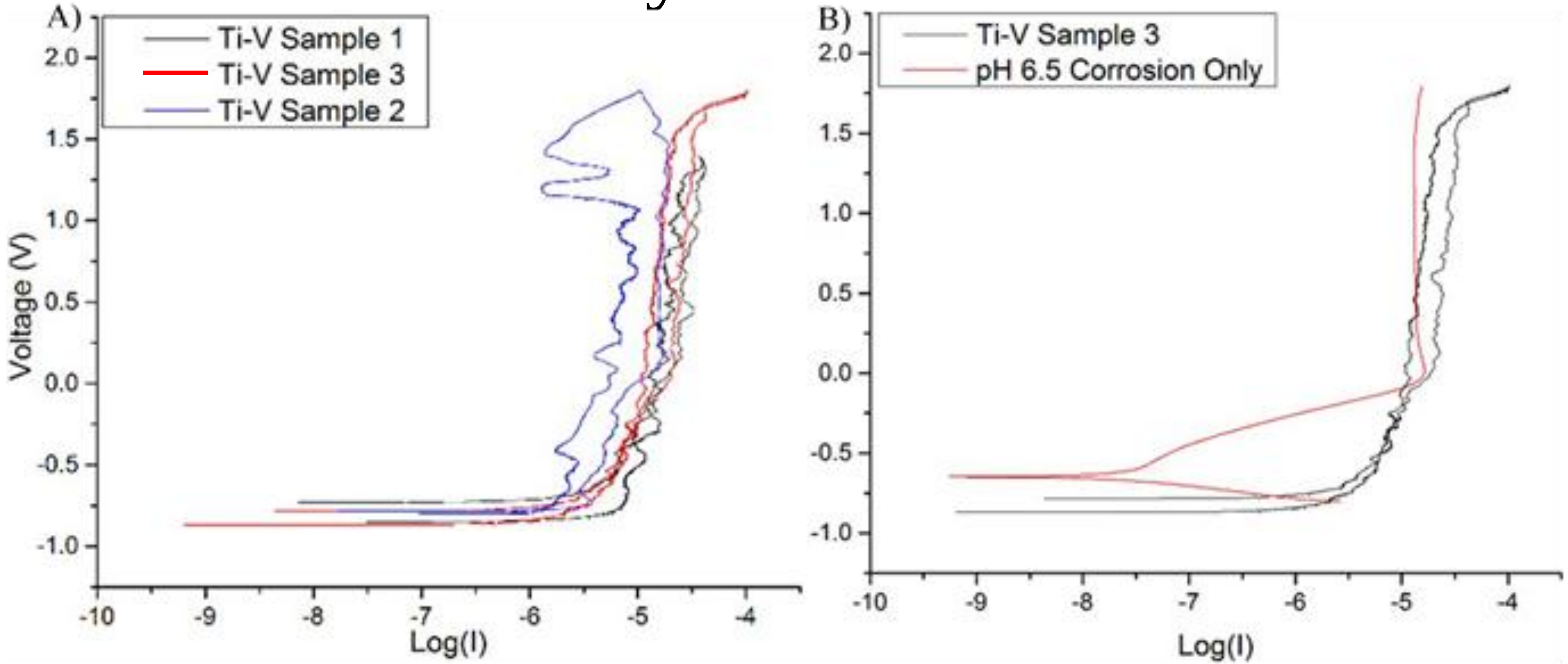
Tribocorrosion Apparatus



Tribocorrosion Apparatus



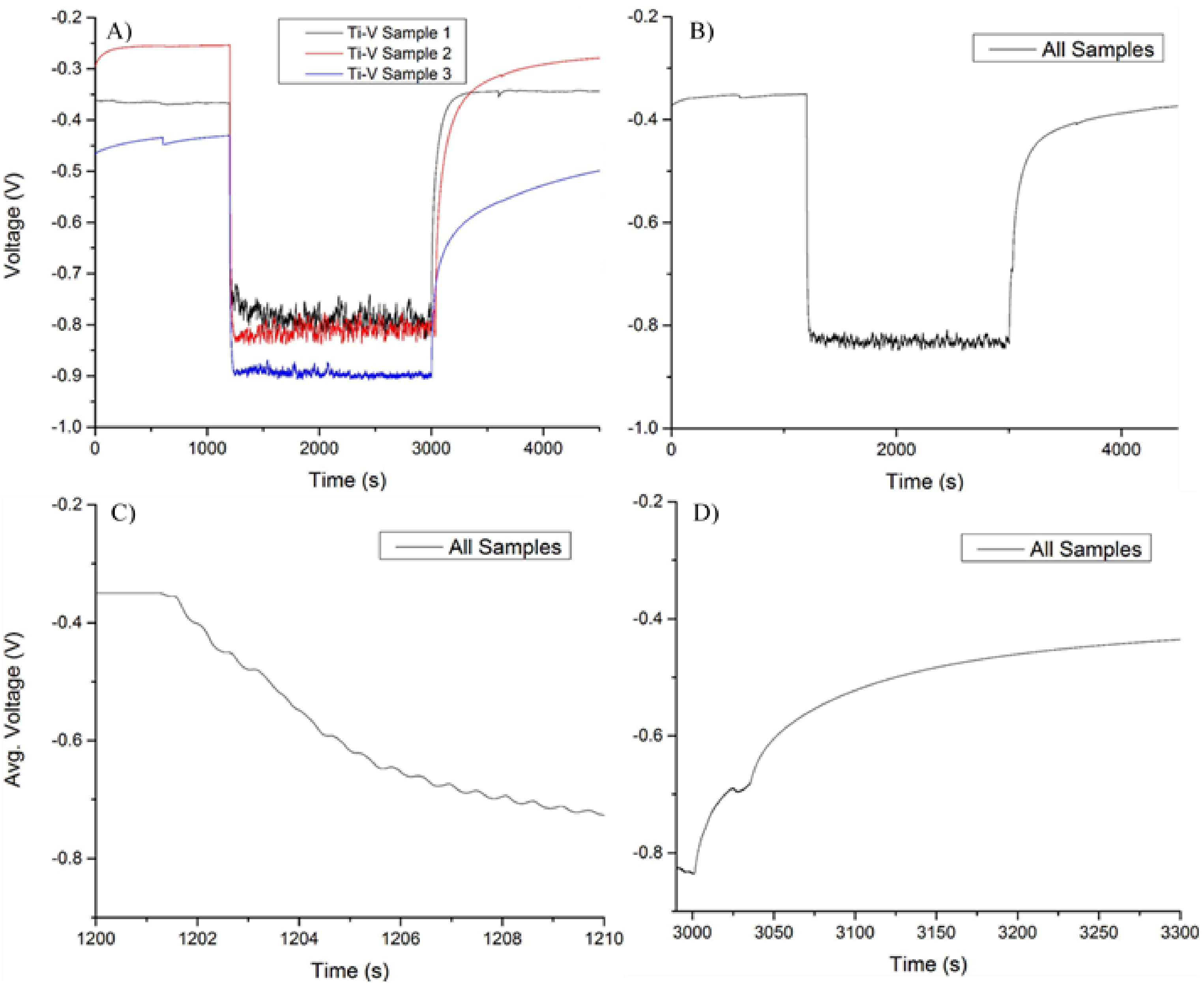
Validation: Potentiodynamic



A) Initiation of sliding = cathodic shift → current range of 1 and 100 μ A = the passive layer is formed and destroyed during sliding. The passivation current (I_{PASS}) is similar to those reported in literature.[1-4] The sloped I_{PASS} region indicates increasing surface damage due to corrosion and wear. B) E_{corr} values are notably higher for tribocorrosion.

1. Hwa J, Olivares-navarrete R, Baier RE, et al. *Acta Biomater*. 2012;8(5):1966–75.
2. Liu C, Chu PK, Lin G, Yang D. *Corros. Sci*. 2007;49(10):3783–3796.
3. Mathew MT, Uth T, Hallab NJ, Pourzal R, Fischer a., Wimmer M a. *Wear*. 2011;271(9-10):2651–2659.
4. Mathew MT, Abbey S, Hallab NJ, Hall DJ, Sukotjo C, Wimmer MA. *J. Biomed. Mater. Res. B. Appl. Biomater*. 2012;100(6):1662–71.

Validation: Free Potential



Literature Values[1-5]

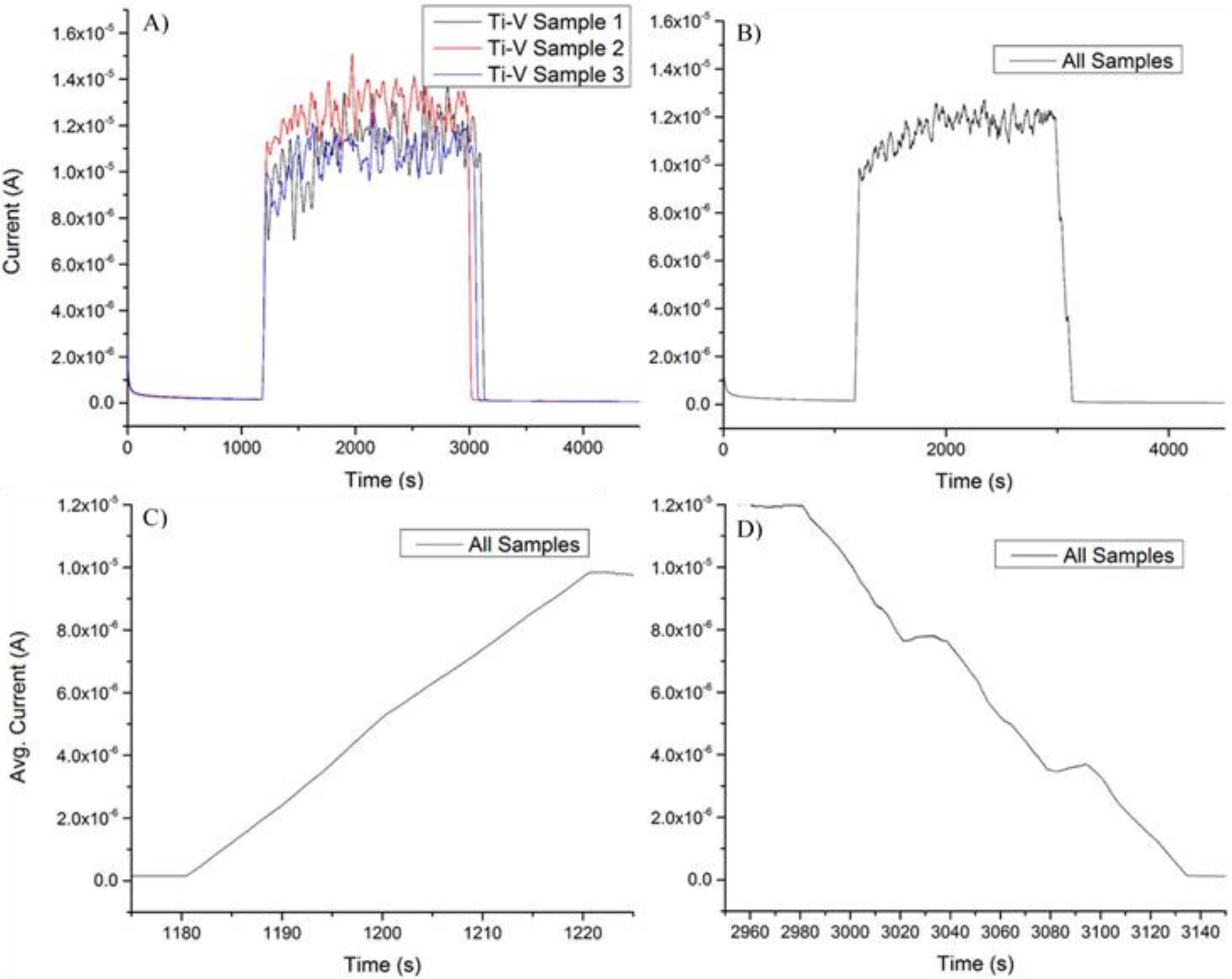
	Before Sliding	During Sliding
1)	-0.2 to -0.3 V	-0.7 V
2)	-0.2 to -0.3 V	-0.6 V
3)	-0.3 V	-1.1 V
4)	0.0 V	-0.6 V
5)	0.0 to -0.2 V	-1.10 V

A-B) Potential increased from OCP in the cathodic direction to a range of -0.7 and -0.9 V. Such a trend is observed in several studies.[1,6,7]

C-D) Initiation and cessation of sliding results in gradual depassivation and repassivation, respectively.

1. M. P. Licausi *et al.* J. Phys. D: Appl. Phys. **46** (2013) 404003.
2. J. Chen *et al.* Materials and Corrosion, **64** (5) 2013.
3. Iwabuchi *et al.* Wear. 263 (2007) 492-500.
4. F Galliano *et al.* 145 (1–3), 2001, Pages 121–131
5. A C Alves *et al* 2013 *J. Phys. D: Appl. Phys.* **46** 404001
6. Sivakumar B, Kumar S, Sankara Narayanan TSN. *Wear*. 2011;270(3-4):317–324.
7. Mathew MT, *et al Wear*. 2011;271(9-10):2651–2659.

Validation: Potentiostatic

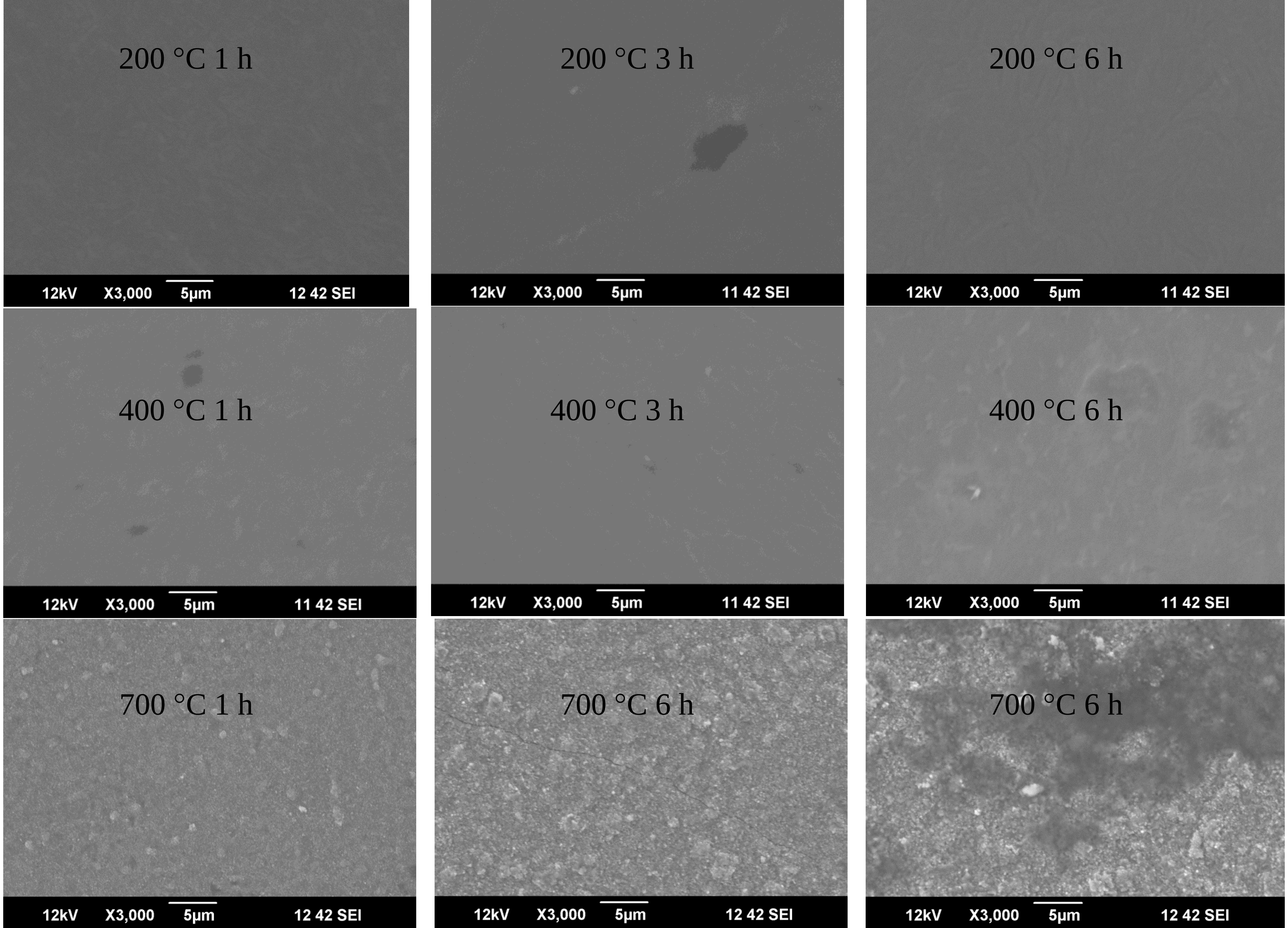


A-B) In similar studies involving neutral pH, the current values increased dramatically for tribocorrosion PS scans.[1-3] In the present study, the current values fluctuated between 8.0 and 14.0 µA during sliding.
C-D) Initiation and cessation of sliding results in gradual depassivation and repassivation, respectively. Notice the step-wise decrease in current values after cessation of sliding.

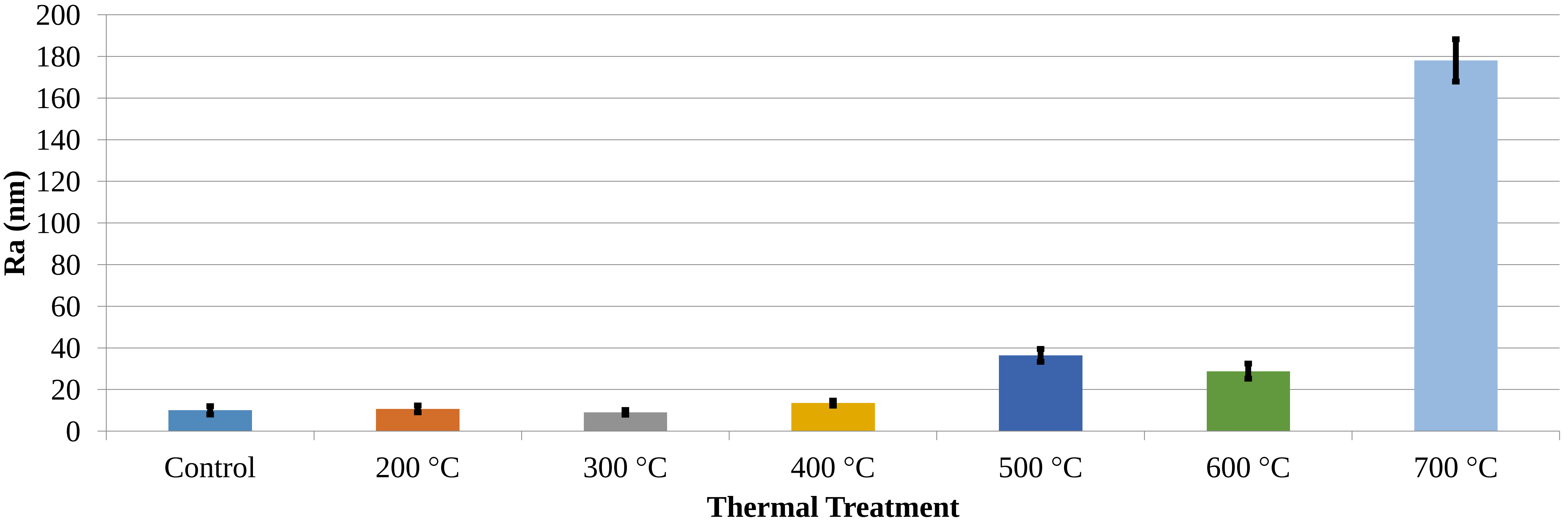
1. M. P. Licausi *et al.* J. Phys. D: Appl. Phys. **46** (2013) 404003.
2. Barril S, Mischler S, Landolt D. *Wear*. 2004;256(9-10):963–972.
3. Mathew MT, Abbey S, Hallab NJ, Hall DJ, Sukotjo C, Wimmer MA. *J. Biomed. Mater. Res. B. Appl. Biomater*. 2012;100(6):1662–71.

Results

- The tribocorrosion data of control Ti-V sample validate the apparatus
- Now lets look at results of thermally treated samples
  - Temperatures of 200, 400, and 700 °C are chosen for their amorphous, mixed anatase-rutile, and rutile crystalline structures, respectively
  - In addition, 1 h and 6 h duration of treatment provided variation in thickness of thermally formed oxides

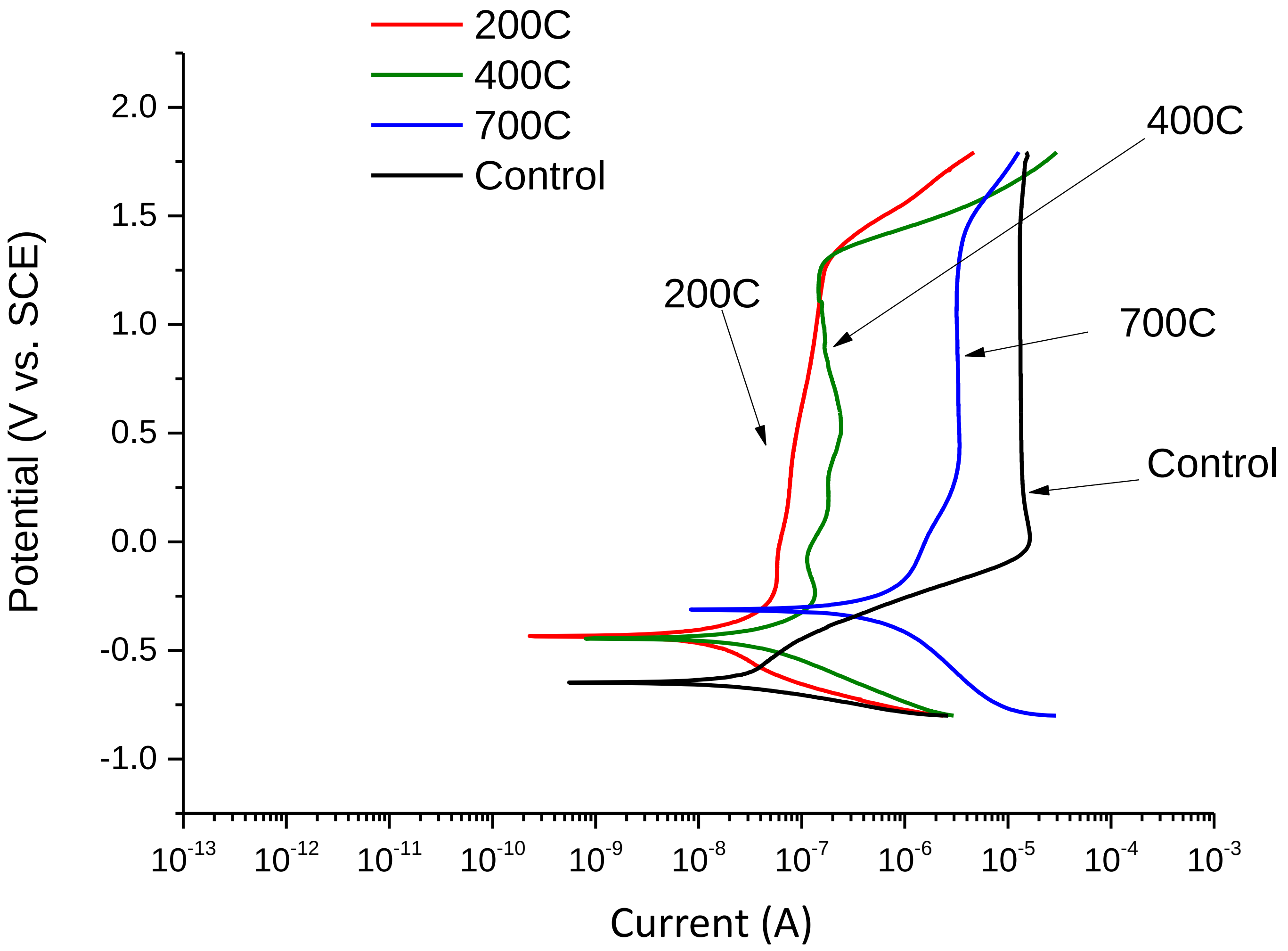

200 °C 1 h
12kV X3,000 5μm 12 42 SEI
200 °C 3 h
12kV X3,000 5μm 11 42 SEI
200 °C 6 h
12kV X3,000 5μm 11 42 SEI
400 °C 1 h
12kV X3,000 5μm 11 42 SEI
400 °C 3 h
12kV X3,000 5μm 11 42 SEI
400 °C 6 h
12kV X3,000 5μm 11 42 SEI
700 °C 1 h
12kV X3,000 5μm 12 42 SEI
700 °C 6 h
12kV X3,000 5μm 12 42 SEI
700 °C 6 h
12kV X3,000 5μm 12 42 SEI

White Light Interferometry
Average Roughness

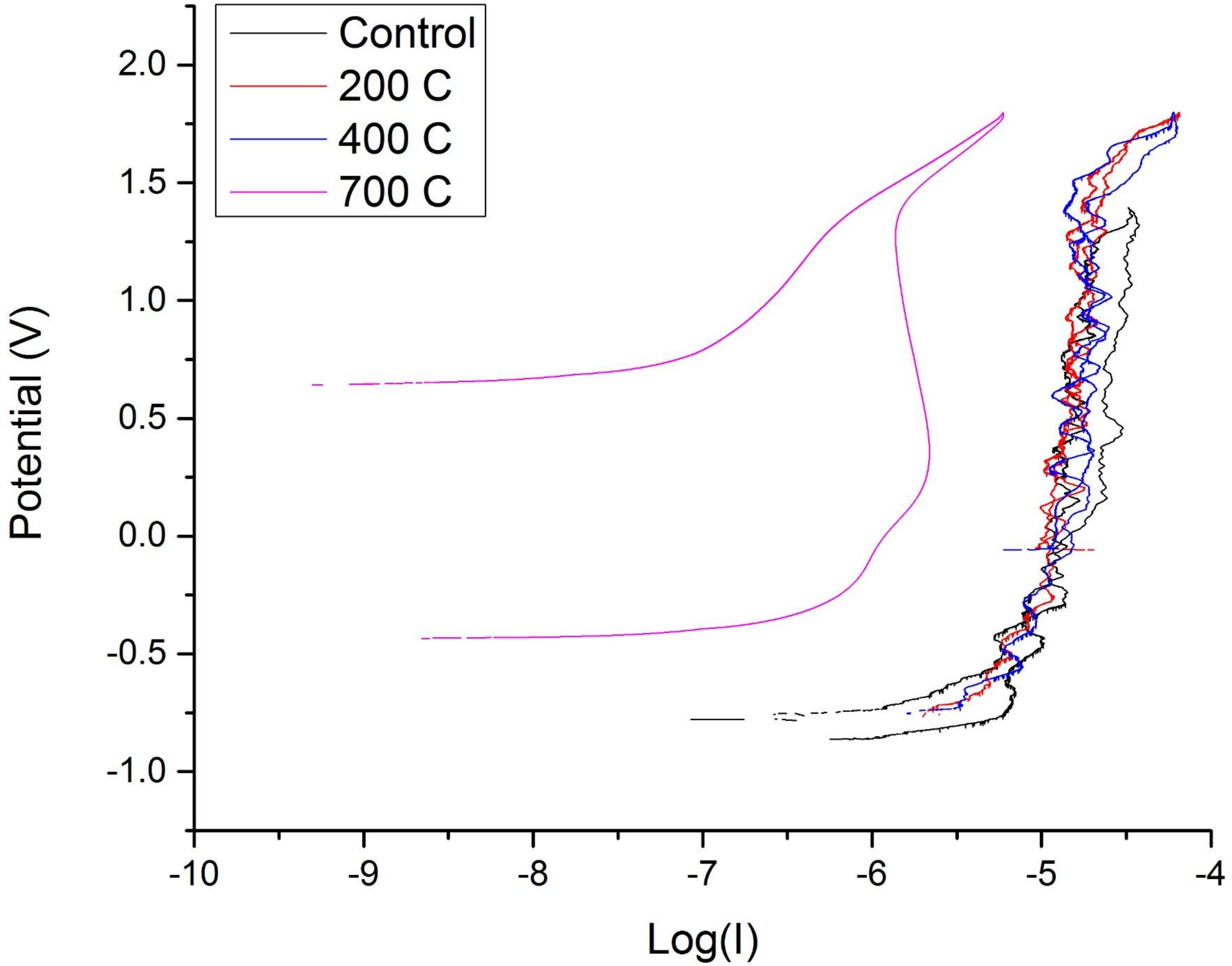


Control, 200, 300, and 400 °C TO-treated samples have similar surface roughness while 500, 600 and 700 °C TO-treated sample shows an increase in surface roughness.

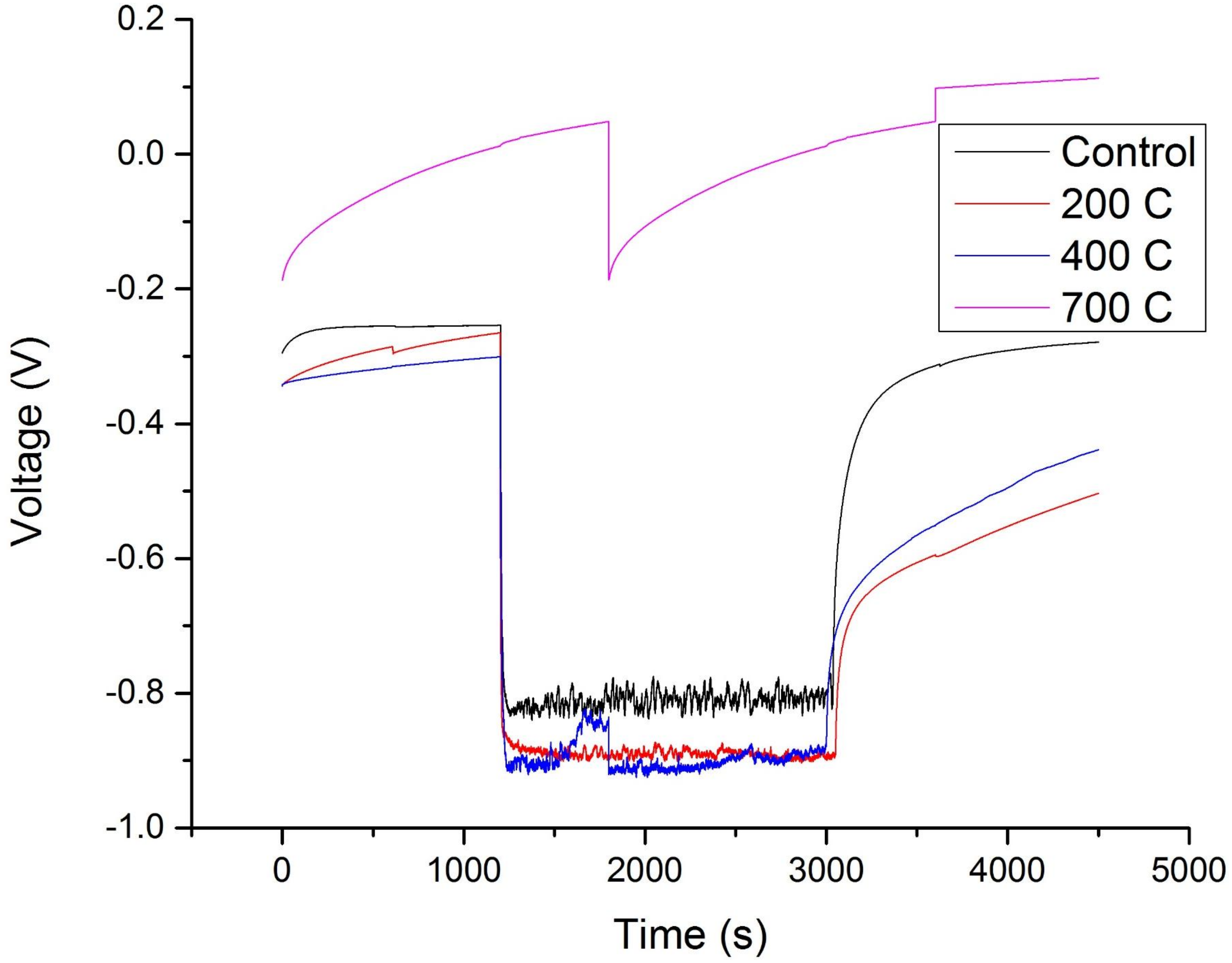
Potentiodynamic pH 6.5



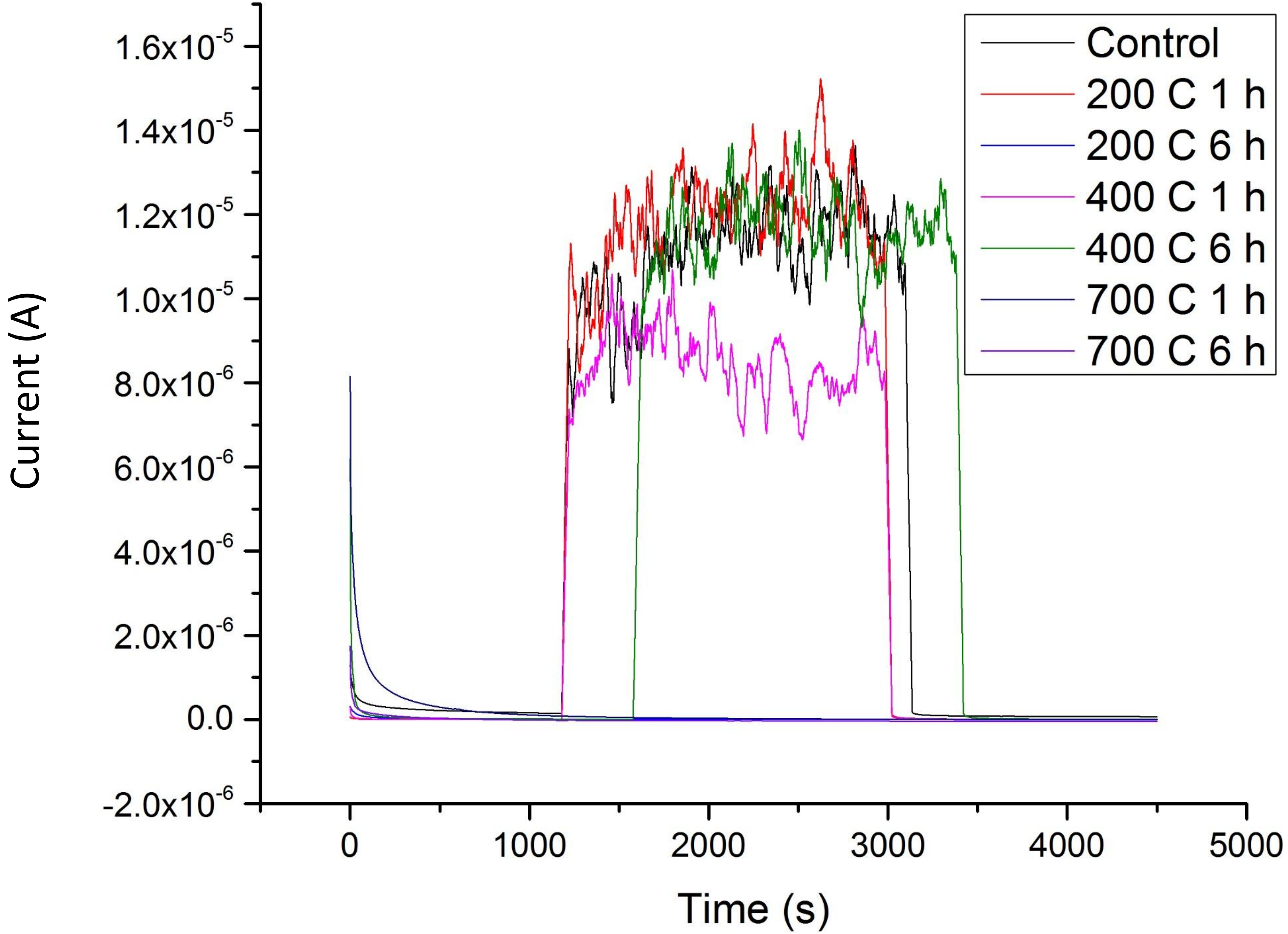
Potentiodynamic



Free Potential



Potentiostatic



Wear Scar Depth

Free Potential

- Control = ≤ 14 µm (12.4 ± 1.5 µg)
- 200 C 6 h = ≤ 12 µm
- 400 C 6 h = ≤ 14 µm
- 700 C 6 h = ≤ 3 µm

Potentiostatic

- Control = ≤ 19 µm (12.0 ± 0.9 µg)
- 200 C 1 h = ≤ 19 µm
- 200 C 6 h = ≤ 16 µm
- 400 C 1 h = ≤ 19 µm
- 400 C 6 h = ≤ 15 µm
- 700 C 1 h = ≤ 3 µm
- 700 C 6 h = ≤ 3 µm

Results

- Based on PS scans, 1 h vs. 6 h thermal treatment does not seem to affect the results
- 700 °C of thermal treatment seems to have preferable results
- Samples thermally treated at 200 °C (thin oxide, amorphous)
  - Displaying better corrosion results
  - Deeper wear scars
- Samples thermally treated at 700 °C (thick oxide, rutile)
  - Displayed better tribocorrosion results
  - Shallower wear scars

Discussion

- Hypothesis:
  - Crystalline and thicker oxide will protect bulk Ti-V from tribocorrosion and corrosion as compared to native TiO_2
- Brittle/crystalline TiO_2 created at higher temperatures
  - Better wear resistance
- Amorphous TiO_2 created at lower temperatures
  - Improved corrosion resistance, but poor wear resistance
- Need to have combination of thick but amorphous oxide
  - Sub-oxides created underneath the TiO_2 is amorphous
- Future Direction:
  - Complete tribocorrosion project for AS pH 3.0
  - Thermally treat Ti-V samples followed by polishing/sanding to remove the brittle/crystalline TiO_2
  - Stay below 650 °C (melting point of aluminum)
  - AS is for dental applications, expand to orthopaedic applications: synovial fluid