Effect of Storage Temperature on Ti-6Al-4V Surface Wettability

Advanced Materials Research Laboratory

Caio Peixoto

Federal University of Rio Grande do Norte, caiopsousa@gmail.com, +55 84 99089171

Arman Butt

University of Illinois at Chicago, butt2@uic.edu, (773) 807-9328

Christos Takoudis

University of Illinois at Chicago, takoudis@uic.edu, (312) 355-0859

Abstract

The relationship between storage conditions and wettability of annealed micro-rough samples was investigated in this study. Micro-roughness (2.45 ± 0.43 µm) was obtained through sandblasting and acid-etching in sulphuric acid and hydrogen peroxide. Non-annealed samples (control) and samples annealed at 400ºC and 600ºC were used. In order to investigate the influence of storage conditions on the surfaces wettability, Ti-6Al-4V disks were 1) wrapped in Kimwipe inside a plastic bag, 2) stored in petri-dishes containing 20 mL deionized water (DI-water) at room temperature, and 3) stored in petri-dishes containing 20 mL cold DI-water (8±2 ºC). Surface characterization was conducted using water contact angle measurements, Zygo, and FTIR. Disks immersed in DI-water maintained higher wettability when compared to Kimwipe groups over the course of 34 days regardless of the storage temperature. In addition, samples annealed at 600 ºC showed superior wettability due to the rutile nature of the oxide film.

1. Introduction

Titanium based materials are extensively used for biomedical applications such as dentistry, orthopedics and cardiovascular surgery. In 1969, Branemark observed that titanium had good adhesion when in contact with rabbit bone and was highly biocompatible.[1] Since then, numerous studies have been conducted confirming titanium and its alloys as suitable choices for such applications. As reported in 2010, 1000 tons of titanium are used for biomedical purposes worldwide every year on average.[2]

Biomaterials, materials used in biomedical applications, have to exhibit a superior combination of several characteristics: adequate mechanical properties, high corrosion and wear resistance, high osseointegration and, most importantly, high biocompatibility.[3]

Inadequate mechanical properties such as low fracture toughness or low fatigue strength can cause implants to fail. Properties such as elasticity modulus can induce mechanical failure through stress shielding effect.[3] The stress cannot be fully transferred trough the biomaterial and is reflected, causing implant loosening. Titanium and its alloys are found to present better combination of such properties when compared to other biomaterials such as Co-Cr and Stainless Steel.

Corrosion and wear can accelerate the process of mechanical failure. In addition, metal ions released due to corrosion and wear from Co-Cr implants were found to induce the formation of cancerous tumors.[2] Titanium is known to be inert in all body fluids, therefore corrosion resistant.[2] However, wear and fretting can damage the passive film and lead to transient corrosion. All the oxidative reactions occur during the repassivation time, gap between the damage and the reformation of the film. Compared to stainless steel 316L, Co-28Cr-6Mo and Zr-2.5Nb, Ti-6Al-4V had the fastest repassivation time.[2]

Poor osseointegration, the connection between the implant and the living bone, can result in implant loosening and failure.[3] Better cell attachment, proliferation and differentiation result in superior osseointegration.[3] Hydrophilicity is an indicator of cell attachment, since the more hydrophilic a surface is the more proteins attach over the water molecules which will lead to more cell adhesion on the implant.

One way to improve the hydrophilicity of a surface has been demonstrated by Park et al. and Watanabe et al. They observed significant changes in the water contact angle related to sterilization methods such as Oxygen Plasma, Ultraviolet and Gamma Irradiation.[4,5] Furthermore, they mentioned that the surface wettability decreases over time due to poor storage methods[4]. In this respect, improvement in storage methods could prevent potentially good biomaterials to be classified erroneously as bad by further cell culture tests.

The gap of time between samples preparation and cell culture tests may be a factor that is characterizing some biomaterials as not suitable. At least one company stores their

implants in liquid solutions to keep them hydrophilic for an extended shelf life.[6] Preliminary water contact angle measurements conducted in our lab suggested that storing Ti-6Al-4V samples in water, rather than in air, might keep the hydrophilicity obtained by surface modification treatments longer when compared to those stored in air. However, a decrease of wettability over time was still observed. As reported by Linsebigler et al., increase in temperature correlates with water desorption and loss of hydroxyl groups at ultra high vacuum condition.[7] The presence of these hydroxyl groups is found to be responsible for the increase in wettability of the TiO_2 passive layer.[8] Based on this, this study evaluates the effect of storage temperature on Ti-6Al-4V samples surface wettability.

2. Experimental Description

2.1 Sample Preparation and Storage

Ti-6Al-4V discs (15 mm in diameter and 1 mm-thick) were obtained from McMaster-Carr. To obtain micro-rough surfaces, the Ti-6Al-4V discs were blasted with 50μm alumina grit particles (Alumina (Al_2O_3) powder, Trinity Tool Company, Fraser MI) at a pressure of 517 kPa and acid-etched in a solution of 1:1 ratio sulfuric acid to 30% hydrogen peroxide for 2 hours, washed with DI-water of 17.7 MΩ-cm resistivity (Barnstead NANOPure, Infinity Ultrapure Water System®).Micro-rough surface samples were temporarily stored submerged in DI-water in a glass dish.

As detailed in Table 1, the disks were divided in 9 groups, which were non-annealed and annealed at 400 ºC and 600 ºC in a furnace (Lindberg furnace, S# 54032)for three hours in open air and stored in petri-dishes (Advantec®, MFS, Inc.) submerged in 20mL of room temperature or cold DI-water. Samples in cold water were stored in a refrigerator (Haiser) with average temperature of 8 ± 2 ºC. Before annealing disks were cleaned with sonication for 1 hour in 99.8% methanol (Sigma Aldrich)using an Ultrasonic Wafer Cleaning System (Branson) and washed for 30 seconds with DI-water. Samples that were not annealed underwent the same cleaning procedure before being stored.

	Annealing	Storage Conditions
Group 1		Kimwipe
Group 2	Not Annealed	DI-Water
Group 3		Cold DI-Water
Group 4		Kimwipe
Group 5	400 ºC	DI-Water
Group 6		Cold DI-Water
Group 7		Kimwipe
Group 8	600 ºC	DI-Water
Group 9		Cold DI-Water

Table 1 – Groups Division Detail. Ti-6Al-4V groups include non-annealed, annealed at 400 ºC and 600 ºC in air. After annealing, the samples were stored wrapped in Kimwipe and in petri-dishes with DI-water either at room temperature or cold (8 ± 2 ºC).

2.2 Surface Characterization

2.2.1 Roughness
Scanning white light interferometric microscope (NewView 6300, Zygo Corporation, Middlefield, Connecticut, USA) was used to measure surface roughness and generate 3D profile of the surface. This is an optical microscope which gathers light from the test area of the sample. The objective lens divides light into 2 paths, one that shines

onto the surface of the test material, and another into an internal reference surface. Surface irregularities on the test material cause the measurement wave-front to travel different distances than the reference wave-front, which cause interference bands when they are recombined. This interference is read by a photo-detector, which translates the interference wave-front into a 3D image, representing the surface topography.

2.2.2   Chemistry

Surface composition was studied using absorbance Fourier Transform Infrared spectroscopy (FTIR, Nicolet, S#ADU9700221). A non-annealed sample was used as a control/background. Prior to conducting FTIR analysis, each sample was left inside the FTIR chamber to purge for one hour in order to optimize signal to noise ratio. FTIR spectrum was obtained with the resolution of 1 cm^{-1} and 512 scans over the range of 4000-400 cm^{-1}.

2.2.3   Wettability

Prior to water contact angle (WCA) measurement, fifteen seconds of nitrogen gas (Zero Grade, Airgas) spray was used to remove any residue deposited on the surfaces of samples stored in Kimwipe and to dry samples stored in DI-water. Using a micro-syringe (Hamilton), a drop of 5 µL of DI-water was gently placed on the center of the sample. The WCA was then measured using a Rame'-Hart NRL CA Goniometer (M#100-0, S#2067) on both sides of the drop. The value computed for each disk is the average of these two.

Preliminary work in the lab showed drastic change in WCA over the course of one day after heat treatment. To observe short term and long term changes, WCA measurements were conducted after 0, 3, 6 and 12 hours and 1, 2, 6, 9, 13, 6 and 20 days. Samples stored in cold DI-water were warmed up to room temperature on Day 20 and subsequent measurements were performed after 3, 6, 12 and 24 hours and 3 and 7 days. After these sets of measurements, on day 27, all samples were immersed in DI-water and warmed up to 37 ºC, average body temperature, using a heating plate (Corning Glass Works) wrapped in a flexible heating tape (OMEGAFLUX). Temperature was monitored using a digital thermometer with a TYPE K thermocouple (Omega Engineering Inc., HH-25KC, S# T-116666).

After a WCA measurement was taken, each disk was dried for fifteen seconds with nitrogen gas and restored to respective storage condition. For WCA measurements of sample groups stored in cold water, samples were transferred to another petri-dish with 20 mL of DI-water for 10 minutes to warm up to room temperature. They were not cold while the measurement was performed.

Arithmetic average of the five measurements in each group is used to represent the group tendency. And population standard deviation was used as the error. The

distribution of the data was assumed to be normal. Two disks (24 and 63) were identified as outliers using Chauvenet's Criterion and removed from data shown hereafter.

3. Results and Discussion

3.1 Zygo

As shown in Table 2, micro-roughness was achieved by sandblasting and acid-etching. Different annealing temperatures did not change significantly the average roughness.

Roughness (µm)			
	Not Annealed	**400 ºC**	**600 ºC**
RMS	2.27 ± 0.27	2.57 ± 0.47	2.51 ± 0.56
RA	1.76 ± 0.16	2.02 ± 0.41	1.97 ± 0.48

Table 2 – Average surface roughness of samples after annealing: non-annealed, and annealed at 400 ºC and 600 ºC in air.

3.2 FTIR

Figure 1 shows the FTIR spectrum of a non-annealed sample. Due to the FTIR apparatus' requirement of a background sample for comparison, the spectrum is flat. This implies the control sample is similar to the background sample, as expected. Peaks are present on the spectra of annealed samples at 400 ºC and 600 ºC (Fig. 2-4). Peak deconvolution points the presence of Ti-O bonds and anatase on the samples annealed at 400 ºC. However, signatures related to vanadium and aluminum oxides and rutile are shown by the peak deconvolution for spectrum of the samples annealed at 600 ºC.

This suggests that annealing promotes the formation of crystalline TiO_2 structures and higher annealing temperatures result in reactions between oxygen and other alloy elements in addition to titanium. Further studies need to be carried to confirm the formation of vanadium and aluminum oxides for higher annealing temperatures and to better establish their ratio compared to titanium oxide as well as compare the amount of anatase and rutile titanium oxides formed on the surface.
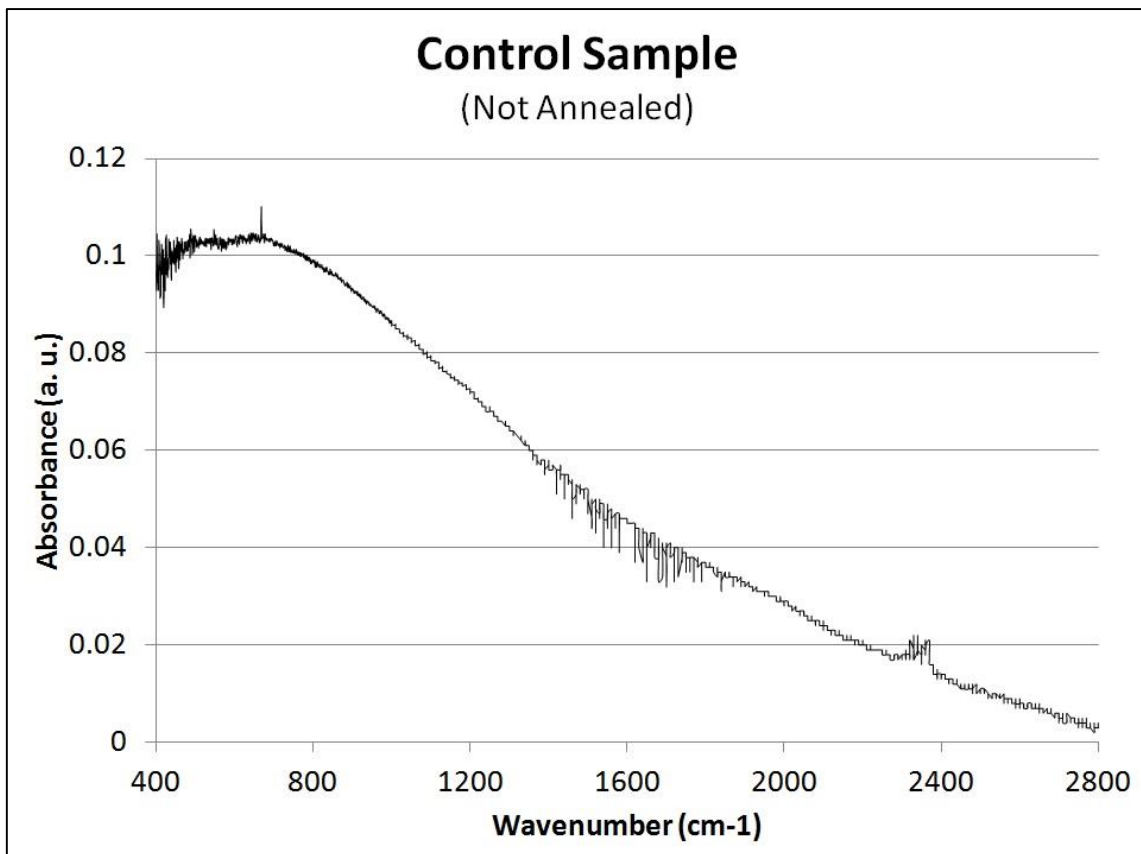
Figure 1 – Control Sample (Not Annealed) FTIR Spectrum. Background noise from carbon dioxide (667 cm^{-1} and 2300-2400 cm^{-1}) and water (1200-2000 cm^{-1}) in the air and on the sample surface is seen.
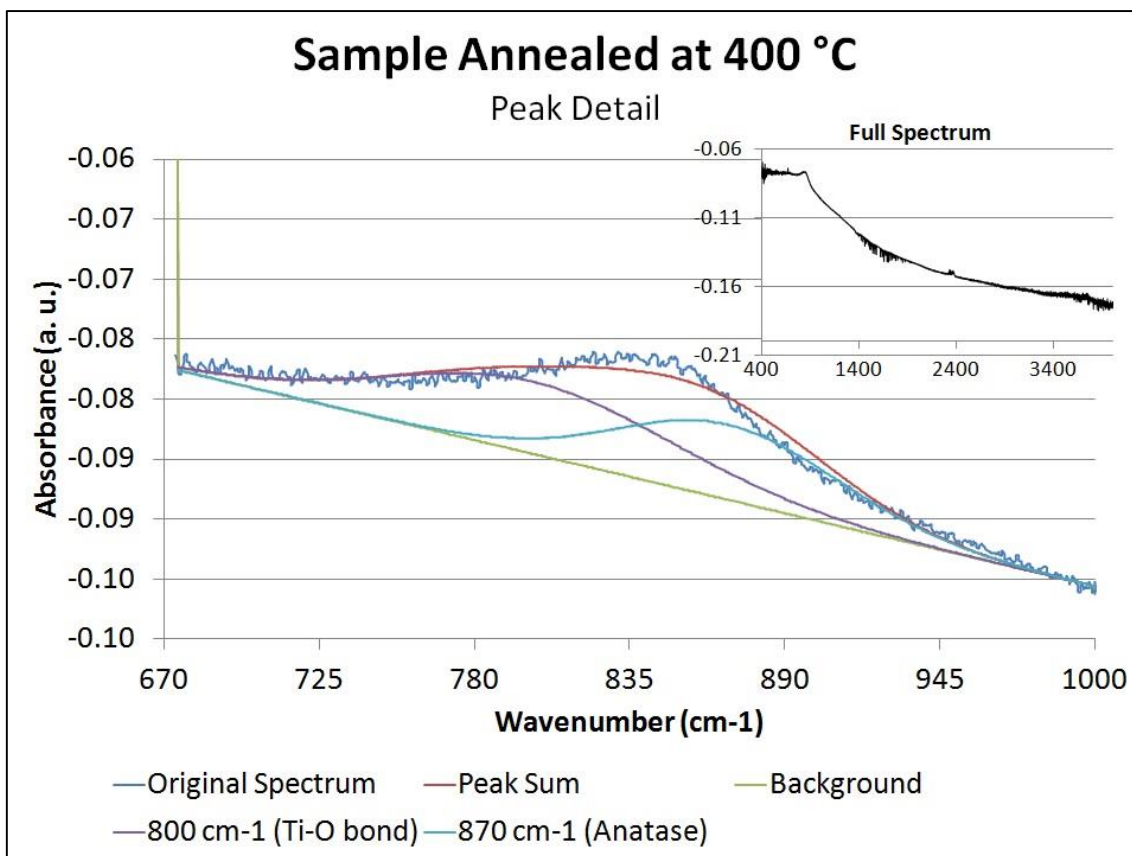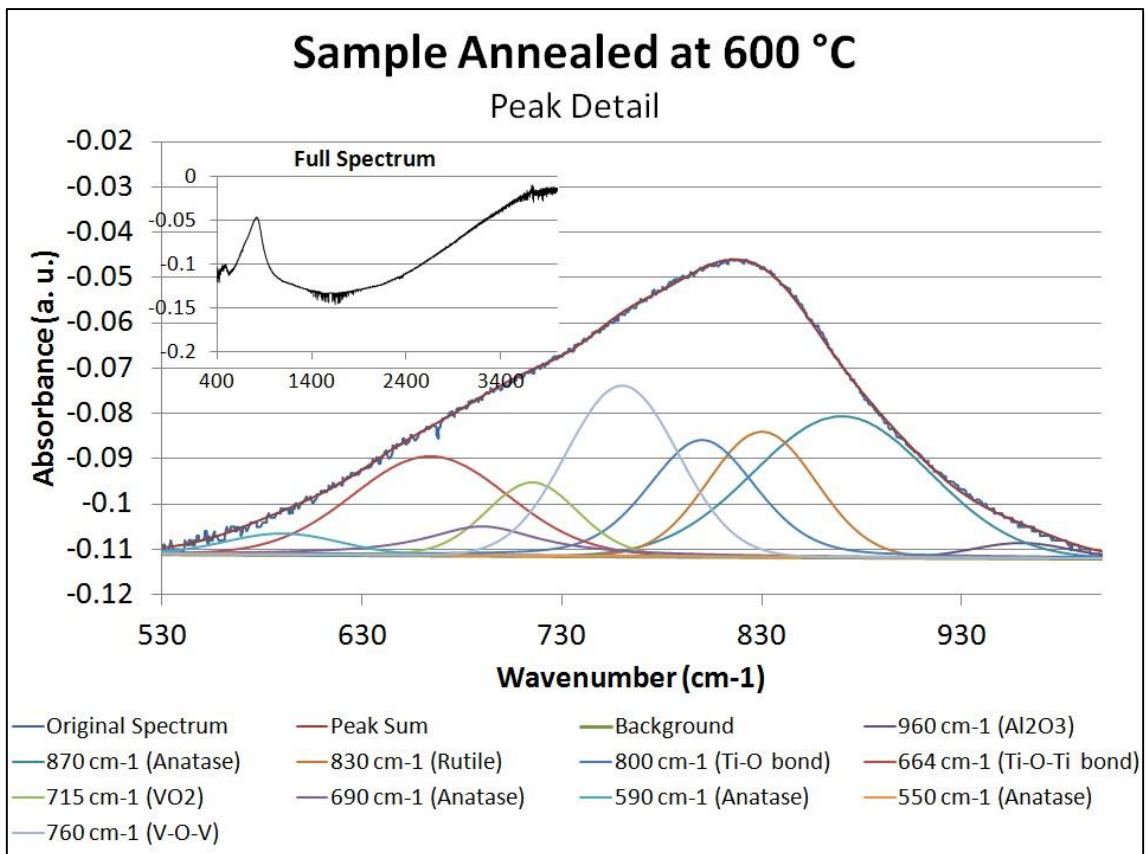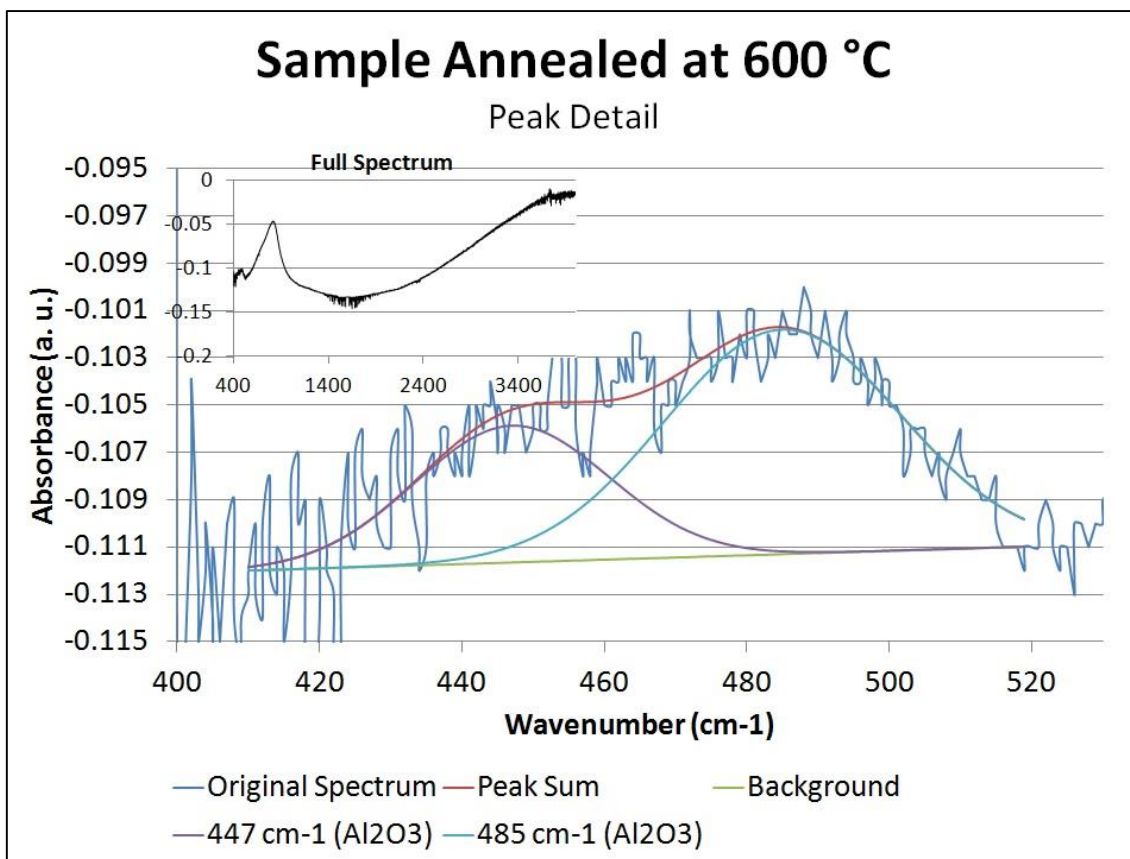
Figure 2 – Sample Annealed at 400 ºC FTIR Spectrum and Peak Detail. Background noise from carbon dioxide (667 cm^{-1} and 2300-2400 cm^{-1}) and water (1200-2000 cm^{-1}, 3000-3800 cm^{-1}) in the air and on the sample surface is seen. Peak deconvolution using XPSpeak shows growth of anatase on the surface (870 cm^{-1}).

Figure 3 – Sample Annealed at 600 ºC FTIR Spectrum and Peak Detail. Background noise from carbon dioxide (667 cm^{-1} and 2300-2400 cm^{-1}) and water (1200-2000 cm^{-1}, 3000-3800 cm^{-1}) in the air and on the sample surface is seen. Peak deconvolution using XPSpeak shows growth of anatase (550 cm^{-1}, 590 cm^{-1}, 690 cm^{-1} and 870 cm^{-1}) and rutile (830 cm^{-1}). Also, signatures of vanadium oxide (760 cm^{-1} and 715 cm^{-1}) and aluminum oxide (960 cm^{-1}) are seen.

Figure 4 – Sample Annealed at 600 ºC FTIR Spectrum and Peak Detail. Background noise from carbon dioxide (667 cm^{-1} and 2300-2400 cm^{-1}) and water (1200-2000 cm^{-1}, 3000-3800 cm^{-1}) in the air and on the sample surface is seen. Peak deconvolution using XPSpeak shows aluminum oxide signatures (447 cm^{-1} and 485 cm^{-1}).

3.3 Water Contac Angle

As seen in figures 5-7, samples wrapped in Kimwipe for all annealing conditions become very hydrophobic in less than a day, WCA reaching as high as 120º. Comparatively, all the samples stored in DI-water kept low water contact angles throughout the entire study regardless of the storage temperature. Furthermore, an increase in wettability was observed on the samples wrapped in Kimwipe after they were immersed in DI-water on day 27.

Water molecules are known to dissociate in contact with TiO_2 due to reaction with oxygen vacancies of both anatase and rutile. Hydroxyl groups are then formed at the vacancy and by protonation of a neighbor oxygen atom and diffused through the surface.[9] As mentioned before, the presence of hydroxyls on the surface correlates with high levels of wettability.[8] Therefore, storing samples in DI-water is a better storage method than the methods currently used.

In addition, samples annealed at 600 ºC and wrapped in Kimwipe (group 7) took more time to reach the level of hidrophobicity observed in groups 1 and 4, stored in the same condition but annealed at 400 C and non-annealed. Samples in group 7 water contact angle only passed 100º on day 6, whereas group 1 reached this level on day 1 and group 4 on day 2. Also, the increase in wettability in group 7 was larger than in groups 1 and 4 when immersed in water on day 27. On day 34, group 7 water contact angles were below 40º while groups 1 and 4 still have water contact angles above 50º.

This difference may be due to the difference in surface chemistry. As discussed earlier, samples annealed at 600 ºC show absorbance signatures related to vanadium and aluminum oxides and rutile titanium oxide. Further studies to understand what exactly causes increase in wettability related to increase in annealing temperature can be carried out.
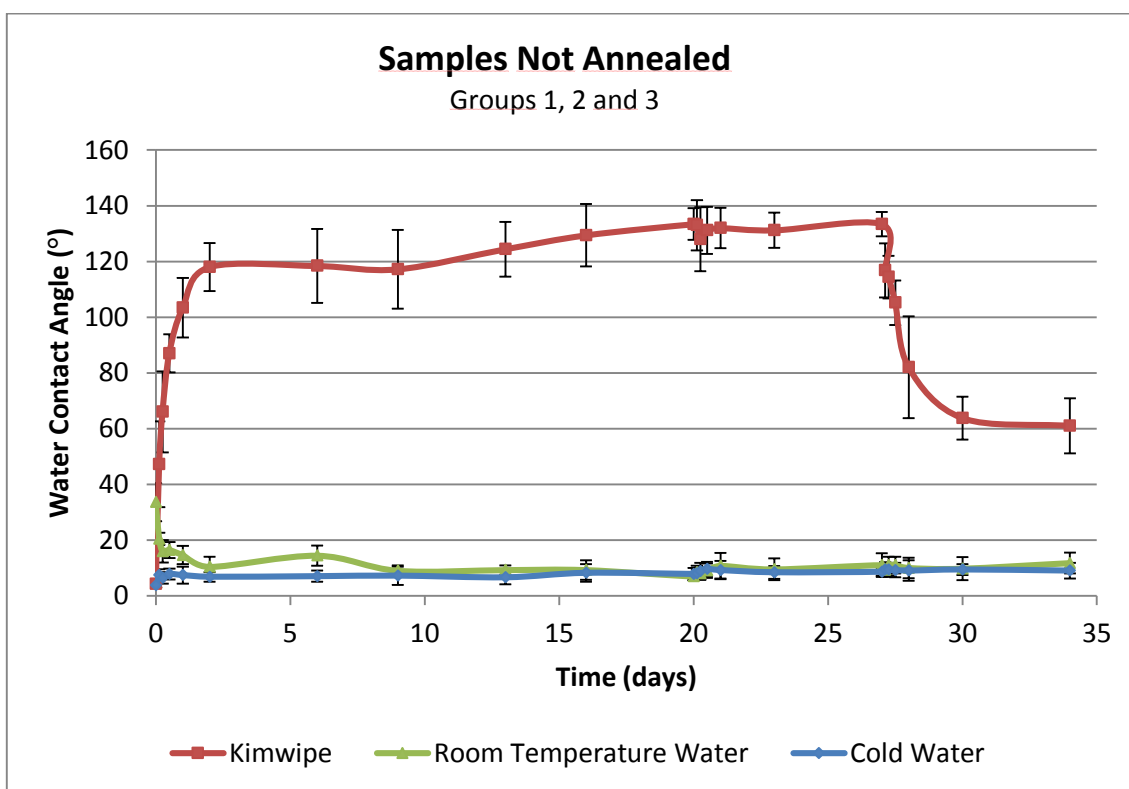
Figure 5 – Water Contact Angle Evolution of Non-annealed Samples. Water contact angle increases drastically for samples wrapped in Kimwipe (group 1). In the same group, increase in wettability is observed once the samples are immersed in warm DI-water. Groups 2 and 3 maintained low water contact angle.
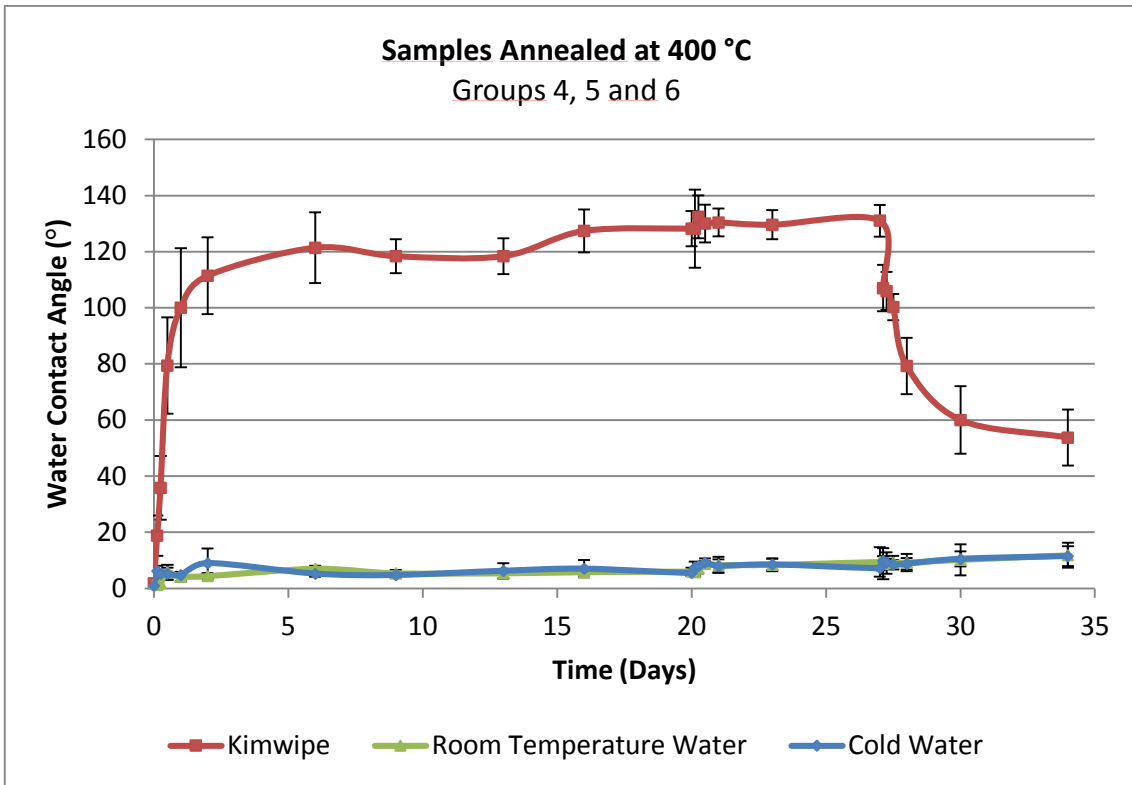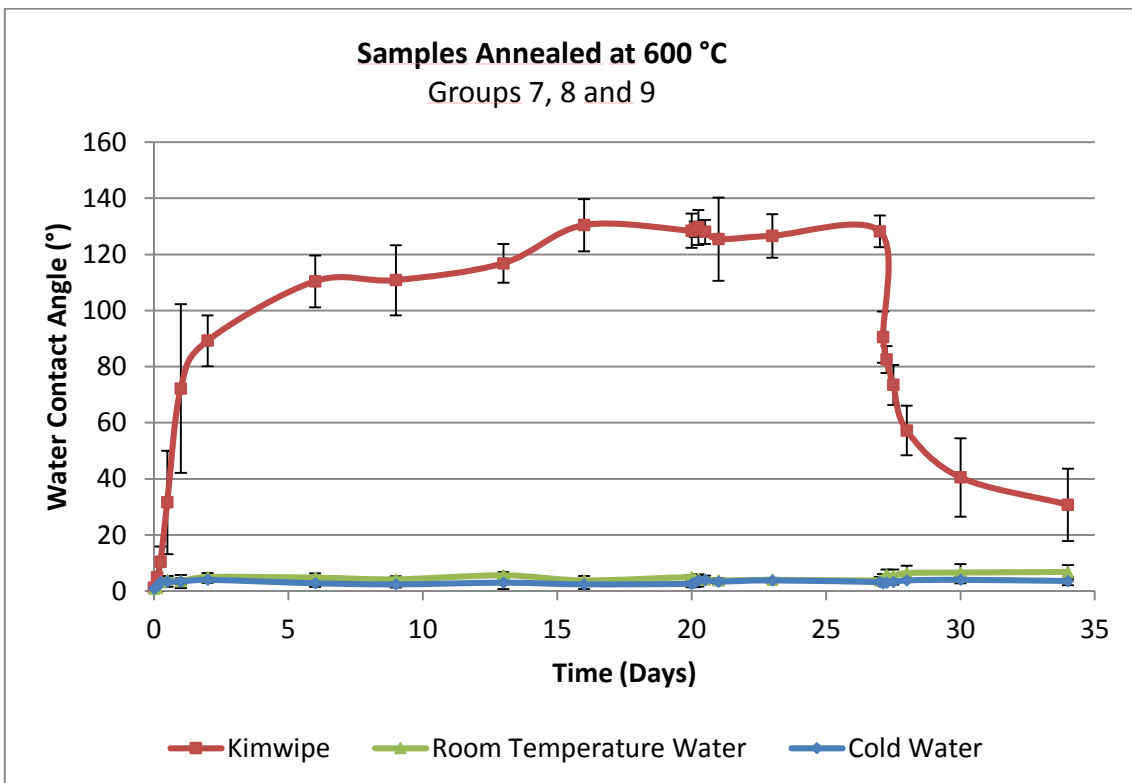
Figure 6 – Water Contact Angle Evolution of Samples Annealed at 400 ºC. Water contact angle increases drastically for samples wrapped in Kimwipe (group 4). In the same group, increase in wettability is observed once the samples are immersed in warm DI-water. Groups 5 and 6 maintained low water contact angle.

Figure 7 – Water Contact Angle Evolution of Samples Annealed at 600 ºC. Water contact angle increases drastically for samples wrapped in Kimwipe (group 7). In the same group, increase in wettability is observed once the samples are immersed in warm DI-water. Groups 8 and 9 maintained low water contact angle.

4. Summary

Micro-roughness (2.45 ± 0.43 μm) was achieved by sequential sandblasting and acid-etching. Samples were annealed at 400 ℃ and 600 ℃. FTIR confirmed presence of anatase and rutile titanium oxides for 400 ℃ and 600 ℃, respectively. Interestingly, FTIR peak deconvolution showed signatures of vanadium and aluminum oxides on samples annealed at 600 ℃. Storing samples in DI-water was found to maintain high wettability regardless of storage temperature. In addition, annealing samples at 600 ℃ showed to be better for wettability than at 400 ℃ and non-annealed samples due to the rutile nature of the oxide film, which is known to dissociate water at a higher rate than anatase.

5. Acknowledgements

References

1. **Antoni P. Tomsia, Maximilien E. Launey, Janice S. Lee, Mahesh H. Mankani, Ulrike G.K. Wegst, Eduardo Saiz**. Nanotechnology Approaches for Better Dental Implants. Int J Oral Maxillofac Implants. 2011, pp. 25-49.

2. **Geetha Manivasagam, Durgalakshmi Dhinasekaran, Asokamani Rajamanickam.** Biomedical Implants: Corrosion and its Prevention - A Review. *Recent Patents on Corrosion Science.* 2010, pp. 40-54.

3. **M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia.** Ti based biomaterials, the ultimate choice for orthopaedic implants - A review. *Pregress in Materials Science.* 2009, pp. 397-425.

4. **Jung Hwa Park, Rene Olivares-Navarrete, Robert E. Baier, Anne E. Meyer, Rina Tannenbaum, Barbara D. Boyan, Zvi Schwartz.** Effect of cleaning and sterilization on titanium implant surface properties and cellular response. *Acta Biomaterialia.* December 6, 2011, p. 10.

5. **T. Watanabea, A. Nakajimaa, R. Wanga, M. Minabea, S. Koizumia.**Photocatalytic activity and photoinduced hydrophilicity of titanium dioxide coated glass. *Thin Solid Films.* 1999, Vol. 351.

6. *SLActive - Scientific Overview*. **Straumann.** 2005.

7. *Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results.* **Amy L. Linsebigler, Guangquan Lu, John T. Yates, Jr.** 1995, Chemical Reviews, pp. 735-758.

8. **G. S. Herman, Z. Dohnalek, N. Ruzycki and U. Diebold.** Experimental Investigation of the Interaction of Water and Methanol with Anatase - TiO2(101). *J. Phys. Chem. B.* 2003.

9. **Z. Zhang, O. Bondarchuk, Bruce D. Kay, J. M. White, and Z. Dohnalek.** Imaging Water Dissociation on TiO_2 (110): Evidence for Inequivalent Geminate OH Groups. *J. Phys. Chem. B 2006, 110, 21840 - 21845*