ACP AMERICAN COLLEGE OF PROSTHODONTISTS
Your smile. Our specialty.

Evaluation of Anodic Behavior of Commercially Pure Titanium in Tungsten Inert Gas and Laser Welds

Iara Augusta Orsi, DDS, MS, PhD,[1] Larica B. Raimundo, DDS, MS,[1] Osvaldo Luiz Bezzon, DDS, PhD,[1] Mauro Antonio de Arruda Nóbilo, DDS, MS, PhD,[2] Sebastião E. Kuri, PhD,[3] Carlos Alberto D. Rovere, PhD,[3] & Valeria Oliveira Pagnano, DDS, MSc, PhD[1]

[1]Department of Dental Materials and Prosthodontics, School of Dentistry of Ribeirão Preto, Brazil
[2]Department of Prosthodontics and Periodontics, School of Dentistry of Piracicaba, Brazil
[3]Department of Materials Engineering, Federal University of São Carlos, Brazil

Keywords
Laser welding; tungsten inert gas welding; corrosion resistance; titanium; dental alloys.

Correspondence
Larica B. Raimundo, Avenida do Café s/n, Ribeirão Preto 14040–904,Brazil. E-mail: larica.raimundo@hotmail.com

This investigation was supported by Research Grants Nos. 06/55784–2 and 06/58428–2 from the State of Sao Paulo Research Foundation (FAPESP).

Accepted January 24, 2011

doi: 10.1111/j.1532-849X.2011.00771.x

Abstract

Purpose: This study evaluated the resistance to corrosion in welds made with Tungsten Inert Gas (TIG) in specimens made of commercially pure titanium (cp Ti) in comparison with laser welds.
Materials and Methods: A total of 15 circular specimens (10-mm diameter, 2-mm thick) were fabricated and divided into two groups: control group—cp Ti specimens (n = 5); experimental group—cp Ti specimens welded with TIG (n = 5) and with laser (n = 5). They were polished mechanically, washed with isopropyl alcohol, and dried with a drier. In the anodic potentiodynamic polarization assay, measurements were taken using a potentiostat/galvanostat in addition to CorrWare software for data acquisition and CorrView for data visualization and treatment. Three curves were made for each working electrode. Corrosion potential values were statistically analyzed by the Student's *t*-test.
Results: Statistical analysis showed that corrosion potentials and passive current densities of specimens welded with TIG are similar to those of the control group, and had lower values than laser welding. TIG welding provided higher resistance to corrosion than laser welding.
Conclusion: Control specimens welded with TIG were more resistant to local corrosion initiation and propagation than those with laser welding, indicating a higher rate of formation and growth of passive film thickness on the surfaces of these alloys than on specimens welded with laser, making it more difficult for corrosion to occur.

The most important factors considered in the choice of dental metals and alloys are biocompatibility, mechanical properties, manipulation, and resistance to tarnish and corrosion.[1] Titanium has many desirable properties for dental use, such as low density, excellent biocompatibility, corrosion resistance, high strength-to-weight ratio,[2,3] and relatively low thermal conductivity.[2,4] Notwithstanding, Ti presents some difficulties with melting and welding because of its high melting point and great affinity for gases, such as oxygen, hydrogen, and nitrogen[5] and high reactivity at elevated temperatures.[6] The high reactivity of Ti with gases will cause Ti materials to become brittle because of oxygen diffusion through interstitial spaces interlaced throughout the Ti during the melting/solidification process. This change in the microstructure has effects on the mechanical properties of Ti and its alloys.[2]

To weld cast Ti and its alloys, laser welding is commonly used. This is an adequate method because of its higher proportions of laser beam absorption and lower thermal conductivity than those of other dental casting alloys; however, because of the strong reactivity of molten Ti with ambient air oxygen, the incorporation of oxygen during laser welding may affect the union resistance.[5] When exposed to the atmosphere soon after casting, Ti oxidizes extremely quickly because of its high affinity with oxygen. This adherent oxide is around 10 μm thicker and determines the chemical properties and corrosion resistance of the metal.[7] Due to this thick and adherent oxide, Ti presents a passive state determined by the protective passivating oxide film layers that form in moist media.[8]

The corrosion behavior depends on the passive film properties influenced by the microstructure and chemical composition

of Ti alloys, although other factors, such as surface finish quality, residuum quantity, microstructure homogeneity level, and defects, may affect resistance to corrosion.[8]

The strong chemical reactivity of Ti and its fast level of reaction and diffusion at elevated temperatures result in problems with welding, melting, and brazing processes.[2] Conventional welding techniques do not work well in commercially pure (cp) Ti because of Ti's high reactivity, which promotes a thicker oxide layer. The welding process may have a significant influence on the physical properties of the Ti restoration.[9] Therefore, these methods are not recommended for uniting Ti prostheses.[2,3]

Procedures used to weld Ti are Metal Inert Gas, Tungsten Inert Gas (TIG),[2] plasma, laser,[2,10] hearth brazing, and infrared brazing[10]—all performed with a protective atmosphere.[2] Researchers have concluded that the laser welding method is effective, but results can vary greatly because of the different radiation intensities used.[2]

Because of the difficulties evolved in the welding process and the high cost of laser welding equipment, a preliminary study by Wang and Welsh[2] showed it is possible to perform welding by applying the TIG method, requiring less expensive equipment. This process is extensively used in Ti industrial production; its corrosion resistance is one of the important properties of this welding system.

As the oral environment is favorable to metal biodegradation, due to its ionic, thermal, microbiological, and enzymatic conditions, one assumes that the patient should be exposed to a large amount of products from the corrosion process. Dental alloy biocompatibility is mainly linked to corrosion behavior. The higher corrosion of an alloy is more related to the amount of elements that will be released, and the risk of unexpected reaction by the oral tissues may be increased.[11] According to Kobayashi et al,[12] corrosion resistance is one of the most important characteristics of biomedical materials, because it concerns not only the service life of devices made from them, but also their harmfulness to the living body. So, it is necessary to search for adequate materials where corrosion resistance relies on the presence of a passive film on its surface.[13]

The goal of this study was to analyze the in vitro anodic behavior of Ti specimens welded by laser and by TIG processes in an artificial saliva environment, using the electrochemical potentiodynamic polarization technique. The research hypothesis was that there was a difference between the corrosion potentials (E_{corr}) of different groups.

Materials and methods

This in vitro study evaluated the anodic behavior of specimens made from cp Ti without weld, welded with laser, and TIG processes. Specimens were made in a circular Teflon matrix (DuPont, Wilmington, DE) (10-mm diameter, 2-mm thick). The matrix was isolated with petroleum jelly and wax (Kerr Corporation, Romulus, MI), then was melted and put into the matrix. After solidification, excesses were removed with a spatula and the wax pattern was removed from the matrix. Specimens ($n = 15$) were divided into three groups: control group—specimens melted with cp Ti ($n = 5$) and experimental groups—specimens melted with cp Ti welded with TIG ($n = 5$) and with laser ($n = 5$). A metal matrix was used to standardize placement of brass stems and make central cuts of experimental wax patterns with a microtome blade.

Brass stems (2-mm diameter) were cut, and at one of the extremities, the retention was made with a flexible diamond disc (K.G. Sorensen Ind. e Com. Ltd., Barueri, Brazil) to facilitate union with the wax pattern. Afterward, the wax patterns were put into the metal matrix. Stems were positioned and fixed in the wax patterns. In the experimental patterns, stems were used as feed channels as well as to position the device for welding. Patterns were positioned in the metal matrix and cut through the middle with a surgical blade, so that in each semicircle, marks were made on the stems to identify the parts of the same specimen.

Wax patterns—control group and experimental groups (identified semicircles)—were adapted to the ring base and invested with Rematitan Plus (Dentaurum, Pforzheim, Germany—Batch Number 060645) in a proportion of 56 mL/350 g, then manipulated under vacuum and put into the silicone ring. The casting rings were placed in a furnace (Model Edgcon 5P, EDG, Sao Carlos, Brazil) to burn out patterns and thermally expand the molds. After removal from the furnace, the rings were positioned in a Discovery Plasma Ar-arc vacuum-pressure casting machine (Rematitan, Dentaurum), where casting of the cp Ti specimens, Titan—grade 1 (Ti min 99.5%, additional elements Fe, O, H, N, and C) (Dentaurum—Batch Number 0100) was melted with a voltaic arc. This casting machine produces electric arc melting in vacuum and an argon-inert atmosphere, with vacuum-pressure injection of the alloy into the mold. After the rings cooled, the castings were manually divested and airborne-particle abraded (Model Microjet III, EDG) with 100-μm aluminum oxide particle abrasive under 2-bar pressure for 5 seconds to remove residual investment, and then put into isopropyl alcohol. Ultrasound was used to remove any aluminum oxide residuum.

Specimens were positioned in the device by the lateral stems for the TIG and laser welds to be performed. The device/specimen set was put inside the laser machine (Desktop Laser, Dentaurum, Ispringen, Baden-Württemberg, Germany) and welded with 380 V and pulse length of 8 ms. For the TIG welding, the device/specimen set was placed on a work surface, and the welding was done with an Esab machine (Esab S/A, Contagem, Brazil) with electric current of 36 A and 12 seconds of argon post flow. After welding, the rods were removed with a carborundum disk 223 (Dentorium Products Co. Inc., New York, NY) mounted on a high-speed device (Nevoni, Sao Paulo, Brazil).

Specimens were placed in a wood device, and the set placed on a flat polisher (Model DPU-10, Struers, Denmark, SC) mounted with carborundum abrasive papers and a stream of water. The two faces of specimens were finished with abrasive paper numbers 80, 360, 400, 600, and 1200 (Norton Ind. e Com. Ltda., Sao Paulo, Brazil) and polished with felt (Fortel Ind. e Com. Ltda., Sao Paulo, Brazil) and an aluminum suspension (AP-A Suspension aluminum agglomerated, Struers). Specimens with mirror-like finish were washed with isopropyl alcohol and dried with a drier.

Specimens with any porosity were discarded to avoid interferences in the assay results. The control group was obtained

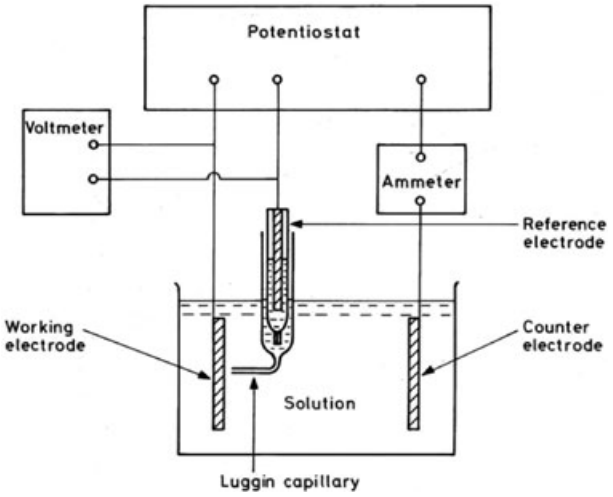

Figure 1 Apparatus for the determination of polarization curves of a metal in a solution using a potentiostat.

by placing the wax patterns into the metal matrix and only one stem, which worked as a sprue for welding, was put in.

For electrochemical potentiodynamic polarization technique, a conventional electrochemical cell, constituting a reference electrode (saturated calomel electrode—SCE), a platinum counter electrode, and the working electrode (specimens of cp Ti) was used (Fig 1). The typical anodic polarization curve generally consists of regions showing active, passive, and transpassive states. In the active state, current density increases quickly with an increase in the applied potential, resulting in the formation of an oxidized layer on the surface. In the passive state, increase in current density is reduced and fixed at a specific level due to the protective effect of the previously formed film. As potential is increased, the passive film begins to disrupt, and current density increases vertiginously.

Measurements were taken using a potentiostat/galvanostat (Model SI 1287 A, Solartron, Farnborough, Hamphsire, UK) in addition to CorrWare software (Scribner Associates Inc., Southern Pines, NC) for data acquisition and CorrView (Scribner Associates Inc.) for data visualization and treatment. The potentiodynamic polarization was performed in an artificial saliva solution (Table 1), with pH 6.9 naturally aerated, in an ambient temperature of 25°C, with scanning rate of 2 mV/s, starting from a cathodic overpotential equal to 100 mV until a 1000 mV (SCE) anodic potential. After 1 hour in open-circuit conditions, specimen potentials did not range over ± 2 mV for 180 seconds. This potential value was considered as the E_{corr}.

To assure reproducibility in the polarization results, three similar curves were made for each working electrode. Corrosion potential values were statistically analyzed by the Student's *t*-test.

Results

Figure 2 shows the potentiodynamic polarization curves representative of the studied specimens in artificial saliva environment. From Figure 2 the electrochemical parameter, i_{pass}, was measured and included in Table 2 with the E_{corr} values.

Figure 2 indicates that the control specimen and TIG specimen have a similar anodic behavior, different than the laser specimen. Similarly, the control specimen and TIG specimen have a more active potential than the laser specimen.

The mean potential corrosion values were established (Table 3) using Student's *t*-test as shown in Table 4. The values are in accordance with the experimental results indicated in Table 2 and Figure 2.

Table 1 Artificial saliva composition

Substances	Concentration (1L)
Potassium diacid phosphate	0.326 g
Potassium dibasic phosphate	0.803 g
Potassium chloride	0.62 g
Sodium chloride	0.865 g
Magnesium chloride ($6H_2O$)	0.125 g
Calcium chloride (H_2O)	0.072 g
Sodium fluoride	4.25 mg
Sorbitol 70%	42.7 g
Flavoring and colorant	Minimal quantity for pleasant odor and taste
Preservative (Nipagin/Nipasol)	10 mL
Thickening	5.0 g
Qsp water	1.0 L

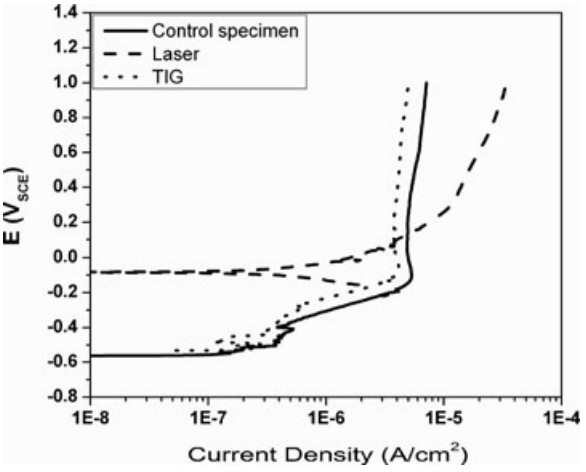

Figure 2 Potentiodynamic polarization curves representative of experimental and control groups. (Electrolyte: mimetizing saliva solution, v = 2mV/s, T = 25°C.)

Table 2 Corrosion potentials (E_{corr}) and values of passive current (i_{pass}) densities obtained from the representative anodic polarization curves

Specimen	E_{corr} (V)	I_{pass} (A/cm^2)
Control	−0.47	5.69×10^{-6}
Laser	−0.06	1.65×10^{-5}
TIG	−0.43	4.19×10^{-6}

Table 3 Medium values of corrosion potentials (E_{corr}) obtained from the representative anodic polarization curves

Specimen	E_{corr} (V)
Control	−0.49
Laser	−0.16
TIG	−0.45

Table 4 Results of Student's *t*-test—distribution of corrosion potential values

Control × TIG	Control × Laser	TIG × Laser
Nonsignificant ($p > 0.05$)	Significant ($p < 0.01$)	Significant ($p < 0.05$)

Discussion

The control and the TIG specimens had a similar anodic behavior with clear passive regions and well-defined passive current densities (i_{pass}) around 5×10^{-6} A/cm^2 (Fig 2). On the other hand, the laser specimen does not show a specific passive region, because the current densities increase slowly with the applied potential. Despite the improvement of current density with potential, the level of current is still very low around 3×10^{-5}A/cm^2 at 1000 mV × SCE. As a consequence, it is possible to observe a very low anodic current in all specimens as a typical characteristic of titanium. Even though the artificial saliva environment has a significant amount of chlorides, the polarization curves do not show a characteristic pitting potential, indicating that superficial film remains intact because film disruption does not occur in any case. Laser and TIG processes have a typical heat input during the welding processes and, as a consequence, the Ti microstructures are different in both cases, promoting a different anodic behavior. For Ni-Ti alloys, intermetallic phases may promote places of passive film disruption and decrease resistance to corrosion at the points of union of laser welding.[13]

The hypothesis was accepted, because the analysis of E_{corr} indicates a remarkable difference in specimen E_{corr}, showing that control and TIG specimens have a similar E_{corr} (around −0.46 V), which corresponds to 400 mV more active than the E_{corr} of the laser specimen (around −0.06 V). This fact indicates that laser specimens are less susceptible to corrosion than the other two specimens. On the other hand, it is more difficult to reach the passive condition with laser specimens than with control and TIG specimens. These results indicate that the laser and TIG welding processes have distinct roles in corrosion resistance of cp Ti due to different heat input occurring during the welding processes. Each process promotes specific Ti microstructures with different anodic behavior.

Conclusions

Within the limitations of this study, the following conclusions can be drawn:

1. Specimens welded by laser processes are less susceptible to corrosion.
2. Specimens welded by TIG are easier to passivate.

Although in vitro electrochemical polarization techniques are valuable aids in the comparison of metal electrochemical behaviors, data obtained from these studies are useful for comparative purposes only, and direct extrapolation to the clinical situation should be made with caution and supported with long-term clinical studies.

References

1. Kedici SP, Aksüt AA, Kílíçarslan MA, et al: Corrosion behaviour of dental metals and alloys in different media. J Oral Rehabil 1998;25:800-808
2. Wang RR, Welsh GE: Joining titanium materials with tungsten inert gas welding, laser welding and infrared brazing. J Prosthet Dent 1995;74:521-530
3. Uysal H, Kurtoglu C, Gurbuz R, et al: Structure and mechanical properties of Cresco-Ti laser-welded joints and stress analyses using finite element models of fixed distal extension and fixed partial prosthetic designs. J Prosthet Dent 2005;93: 235-244
4. Aoki T, Okafor ICI, Watanabe I, et al: Mechanical properties of cast Ti-6Al-4V-XCu alloys. J Oral Rehabil 2004;31:1109-1114
5. Watanabe I, Topham DS: Laser welding of cast titanium and dental alloys using argon shielding. J Prosthodont 2006;15: 102-107
6. Kikuchi M, Takada Y, Kiyosue S, et al: Mechanical properties and microstructures of cast Ti-Cu alloys. Dent Mater 2003;19: 174-181
7. Taher NM, Al Jabab AS: Galvanic corrosion behavior of implant suprastructure dental alloys. Dent Mater 2003;19:54-59
8. Bayramoglu G, Alemdaroglu T, Kedici S, et al: The effect of pH on the corrosion on dental metal alloys. J Oral Rehabil 2000;27: 563-575
9. Chai T, Chou CK: Mechanical properties of laser-welded cast titanium joints under different conditions. J Prosthet Dent 1998;79:477-483
10. Liu J, Watanabe I, Yoshida K, et al: Joint strength of laser-welded titanium. Dent Mater 2002;18:143-148
11. Fathi MH, Salehi M, Saatchi A, et al: In vitro corrosion behavior of bioceramic, metallic, and bioceramic-metallic coated stainless steel dental implants. Dent Mater 2003;19:188-199
12. Kobayashi E, Wang TJ, Doi H, et al: Mechanical properties and corrosion resistance of Ti-6AI-7Nb alloy dental castings. J Mater Sci Mater Med 1998;9:567-574
13. Yan XJ, Yang DZ: Corrosion resistance of a laser spot-welded joint of NiTi wire in simulated human body fluids. J Biomed Mater Res 2006;77A:97-102