EVALUATION OF LOW-FUSING CERAMIC SYSTEMS COMBINED WITH TITANIUM GRADES II AND V BY BENDING TEST AND SCANNING ELECTRON MICROSCOPY

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The bond strength by three point bending strength of two metal substrates (commercially pure titanium or grade II, and Ti-6Al-4V alloy or grade V) combined to three distinct low-fusing ceramic systems (LFC) and the nature of porcelain-metal fracture by scanning electron microscopy (SEM) were evaluated. The results were compared to a combination of palladium-silver (Pd-Ag) alloy and conventional porcelain (Duceram VMK68). Sixty metal strips measuring 25x3x0.5mm were made – 30 of titanium grade II and 30 of titanium grade V, with application of the following types of porcelain: Vita Titanerkarimik, Triceram or Duceratin (10 specimens for each porcelain). The porcelains were bonded to the strips with dimensions limited to 8x3x1mm. The control group consisted of ten specimens Pd-Ag alloy/Duceram VMK68 porcelain. Statistical analyses were made by one-way analysis of variance (ANOVA) and Tukey test at 5% significance level. Results showed that the bond strength in control group (48.0MPa + 4.0) was significantly higher than the Ti grade II (26.7MPa + 4.1) and Ti grade V (25.2MPa + 2.2) combinations. When Duceratin porcelain was applied in both substrates, Ti grade II and Ti grade V, the results were significantly lower than in Ti grade II/Vitatitankeramik. SEM analysis indicated a predominance of adhesive fractures for the groups Ti grade II and Ti grade V, and cohesive fracture for control group Pd-Ag/Duceram. Control group showed the best bond strength compared to the groups that employed LFC. Among LFC, the worst results were obtained when Duceratin porcelain was used in both substrates. SEM confirmed the results of three point bending strength.

UNITERMS: Titanium; Low fusion ceramic; Porcelain.
INTRODUCTION

The search for alloys to be employed in dental prosthesis, whether for better physical and mechanical properties or for economic factors, found attractive elements in titanium and its alloys. Among the various titanium alloys, the titanium-aluminum-vanadium (Ti-6Al-4V) system, or grade V, is the most used, because of its better physical and mechanical properties in comparison to commercially pure titanium Ti grade II\(^b\). Ti grade V shows greater bending strength, (890MPa, against 340MPa) and greater hardness (350VHN against 210VHN) than Ti grade II\(^b\). Ti grade II and Ti grade V have densities of 4.5g/cm\(^3\) and 4.43g/cm\(^3\) respectively, both of them lower than those of gold and palladium-silver alloys (18.3 and 10.7 g/cm\(^3\)) and of the systems Ni-Cr and Co-Cr (8.0 and 9.0 g/cm\(^3\)).

The development of technology and specific materials for casting allowed research to advance to themes such as marginal adaptation of titanium crowns\(^b,5,8,26\). The search for esthetic restorations has led to the development of ceramic systems that can be associated to titanium and its alloys\(^b,1,19\). From the technical point of view, firing of porcelain over titanium requires a special protocol\(^b,11,19,27\). Metal exposure to temperatures that exceed 800°C leads to the absorption of oxygen and nitrogen, providing the formation of a thick superficial layer of oxide that may attain a thickness up to 1mm and harms the bonding of ceramic to substrate\(^b,1,11,15\). In compliance with these criteria, low fusion ceramics were developed showing fusion temperatures close to 760°C (Togaya et al\(^b\)). It also displays color stability\(^b,5\), bending strength and chemical solubility\(^b\) similar to conventional porcelains and a thermal expansion coefficient close to or slightly lower than titanium, thus reducing the stresses at the interface and permitting satisfactory bonding of the elements\(^b,19\).

Research on the behavior of pure titanium substrates combined with low-fusing ceramics began in the last decade, but the subject is still hardly explored in literature. However, the use of the alloy Ti-6Al-4V as a substrate for ceramic combinations is still unavailable. The continual introduction of new low-fusing ceramic systems specifically for titanium instigates comparisons and new researches. The purposes of this study were:

1) To evaluate, by means of bending test, the bond strength between two titanium based metal substrates (Ti grade II pure and Ti grade V / alloy) combined to three commercially available low-fusing ceramic systems (Vita Titankeramik, Triceram and Duceramin);
2) Observe, through scanning electron microscopy, the bonding interface between metal and porcelain substrates after the bending test;
3) Compare the results to samples of the control group which were made by the combination of palladium-silver alloy (Pors-On 4) and Duceram ceramic.

MATERIALS AND METHODS

Strips were fabricated of acrylic resin (Duralay-Reliance Dental Mfg Co-Worth-USA) in the dimensions 25x3x1mm and invested in titanium investment material (Rematitan Plus - Dentaurum – Pforzheim – Germany). After set, the investment blocks were heated in an electric furnace following the firing cycle recommended by the manufacturer, and castings were performed in a vacuum casting machine (Rematitan – Dentaurum – Pforzheim – Germany). Sixty samples were made, being 30 of commercially pure titanium – Ti grade II (Tritan - Dentaurum - Pforzheim – Germany) and 30 of titanium-aluminum-vanadium alloy (Ti-6Al-4V) – Ti grade V (Broden Dahl A/S - Oslo – Norway). After casting, radiographs were obtained to verify eventual voids.

For control group, ten other strips were invested in phosphate-bonded investment (Deguvest-Impact – Degussa-Hüls, Hanau, Germany). The investment was allowed to heat-soak for 1 hour at 900°C. Pd-Ag alloy (Pors-On 4 - Degussa-Hüls Hanau – Germany) was melted in an electric heating furnace, and the investment patterns were cast with a non-vacuum centrifuge casting machine (Multicast, Degussa-Hüls, Hanau, Germany).

The samples were standardized in thickness\(^b,19\), 25x3x0,5mm by a plane horizontal grinding machine (Ferdimatik N-80 - Kristavorts - Brëmen – Germany) and width and length were confirmed with a digital caliper accurate to 0.01mm. After ultrasound cleaning (Thomton – Inpec Eletrônica Ltda – São Paulo – SP), they were submitted to a sandblasting process with 150-μm aluminum oxide at pressure of 2 bar in the central area of their surfaces according to the manufacturers’ recommendations, and then ceramic application was performed.

For titanium metals (Ti grade II and V), Vita Titankeramik (Vita Zahnfabrick-Sackinger Germany) porcelain was applied in 10 samples; in another 10 the porcelain Triceram (Dentaurum – Pforzheim – Germany) and in further 10 the porcelain Duceratin (Degussa-Hüls - Hanau – Germany). Standardization of the ceramic applications\(^b\) over the center of each metal strip was done by means of a die in the dimensions 8x3x1mm, complying by order, with the instructions of each manufacturer, being conducted in an electric furnace (Dekema – Degussa AG – Hanau – Germany). For the control group, the 10 samples were combined with the conventional porcelain Duceram (Degussa-Hüls – Hanau – Germany).

The samples were submitted to the 3-point bending test to evaluate ceramic/metal substrate bond strength. The test was carried out in a universal testing machine (Instron I.D. 4411 - Instron Corp., Canton - USA) with a 50kgf load cell. Porcelain-metal specimens were positioned on supports with 6.37-mm diameters and 20-mm span distances with the porcelain layer facing down. A compressive load was applied at the midline of the metal strip by a 6.37mm metal rod at a crosshead speed of 0.5mm/minute. The load was applied until disruption of the load-deflection curve occurred, which indicated bond failure. The load that resulted in bond failure was recorded in Newtons (N), and bending strength (in MPa)
was calculated according to the following formula

\[ \Sigma = \frac{3 \cdot P \cdot I}{2 \cdot b \cdot d^2} \]

where: 
- \( P \) is the maximum load at the point of fracture;
- \( I \), the distance between the supports (mm);
- \( b \), the width of the test specimen (mm);
- \( d \), the thickness of the test specimen (mm);
- \( S \), the bond strength (MPa).

Scanning Electronic Microscopy (SEM) (LEO 440 - Leica Zeiss - Köln - Germany) was carried out to characterize the type and morphology of the fracture in representative specimens selected from each combination in which there was complete separation between porcelain and metal after the bending test. The surfaces of the metal strips previously covered with porcelain were metallized with gold-palladium alloy under high vacuum (Balzers - SCD Sputter Coater - Fürstentum Liechtenstein - Germany) and photographed at 34, 48 and 500X magnification.

The data referring to the bond strength of the low-fusing ceramic systems applied to titanium grade II and V were analyzed by parametric means. Means and significant variables were obtained by the analysis of variance (ANOVA), considering the factors (commercially pure titanium, Ti-6Al-4V and Pd-Ag alloy control) and treatments (combination with the ceramics Vita Titankeramik, Triceram, Duceratin and Duceram, as control). Significant differences were analyzed by the Tukey test, at 5% significance level.

### RESULTS

#### Bending test

In TABLE 1 the means and the standard deviations of bond strength (in MPa) are observed for titanium grades II and V combined with different ceramics.

Statistically significant differences were found in relation to bond strength (in MPa) between the control group (48.0MPa ± 4.0) and the titanium combinations Ti grade II/ceramics (26.7MPa ± 4.1) and Ti grade V/ceramics (25.2MPa ± 2.2). Among the combinations involving titanium substrates (Ti grade II and V), the combination Ti grade II - Vita Titankeramik, was statistically different from Ti grade II – Duceratin and Ti grade V Duceratin.

#### Scanning Electronic Microscopy

For the combinations involving Ti grade II and for those where the Ti grade V alloy was present, few islands of residual porcelain adhering to the metal surface of the substrate were found, suggesting the occurrence of predominantly adhesive failures, corroborating the lower mechanical strength values obtained. Under greater magnifications, surface irregularities in the metal substrate could be seen, suggesting the treatment with aluminum oxide sandblasting.

Greater quantities of residual porcelain islands adhering to the metal surface of the substrate were differentiated in the control group, suggesting the occurrence cohesive type fractures in the ceramic body - observations that attest to a better mechanical performance of this combination.

The observation of the samples in the bending strength test between the combination Ti grade II–Vita Titankeramik, Ti grade II and V - Duceratin, under SEM, brought indications that would reinforce the numerical values.

<table>
<thead>
<tr>
<th>Substrates and Treatments</th>
<th>Bond Strength (MPa)</th>
<th>Mean</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti grade II Vita Titankeramik</td>
<td>30.8(^a)</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Ti grade II Triceram</td>
<td>26.6(^ab)</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Ti grade II Duceratin</td>
<td>22.7(^b)</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Ti grade V Vita Titankeramik</td>
<td>27.2(^ab)</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Ti grade V Triceram</td>
<td>25.53(^b)</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Ti grade V Duceratin</td>
<td>22.9(^b)</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Pd-Ag Duceram</td>
<td>48.0(^c)</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

Means followed by the same letters do not differ statistically by the Tukey test at 5% significance level.
DISCUSSION

For over 30 years, artificial metal ceramic crowns have been widely successful rehabilitating treatment options, because they combine esthetics and resistance. The searches for alternatives capable of satisfactorily replacing the traditionally used alloys made titanium become a target for researches in prosthetic dentistry. Bio-compatibility, resistance to corrosion, low specific weight, ductility and low heat conductivity of titanium are the attractive properties\textsuperscript{13.30}. The advent of specific low-fusing porcelains enabled the construction of metal ceramic crowns which, apart from their esthetics and strength characteristics\textsuperscript{6.7.20}, added the desirable properties to titanium\textsuperscript{11,15,18}.

In order to enable restorations to be clinically safely used, both the materials and the techniques employed should be exhaustively evaluated in laboratory tests, once even the atmosphere of porcelain firing can influence in titanium—ceramic bonding\textsuperscript{21}. The clinical performance of metal ceramic restorations is normally estimated by bond strength tests of the combinations between the metal substrates and the specific ceramics. The bending test, in comparison to other tests, has prevailed for friable materials like porcelains\textsuperscript{19} and is contained in the project proposed by the German Standard DIN 13.927. It is held as being preferable provided, because it simulates in the closest manner the stresses occurring in dental prostheses, like cantilever bridges, or multiple elements\textsuperscript{3}. Furthermore, to evaluate the combinations, standardization of the samples is fundamental to obtain reliable results\textsuperscript{4}.

The combinations involving porcelains and titanium substrates (Ti grade II and V) did not display similar resistance to the conventional combinations, as the former has shown to be
statistically inferior to the control group composed of the Pd-Ag substrate and conventional porcelain. The means of titanium substrates ranged from 22.7MPa to 30.8MPa, values intermediate to those of 26.0MPa found by White et al.\textsuperscript{29} In Pd-Ag alloy/conventional porcelain samples, the strength ranged from 41.8MPa to 52.7MPa (with a mean of 48.0MPa). These results corroborate the findings of Yilmaz & Dinçer\textsuperscript{30} for the combination Vita Titankeramik and substrate in Ti grade II by the three point bending test.

Studies using bending tests aimed at determining the bond strength between pure titanium and the LFCs have shown great variations in their results. Values ranging from 14.0MPa to 37.0MPa were found by Probster et al\textsuperscript{19} and Yilmaz & Dinçer\textsuperscript{30}. It should be emphasized that, in this study, the samples were standardized by means of rectifying the metal strips and using a die for applying the porcelain. Furthermore, before the porcelain was applied, all metal strips were radiographed in order to diagnose eventual internal defects that would interfere in the mechanical behavior of the samples under the bending test.

The results obtained by comparison of the substrates Ti grade II and V combined to Duceratin, Triceram and Vita Titankeramic porcelains showed that, in the groups where Ti grade II was used as substrate, the samples combined to Duceratin porcelain showed a significantly lower value than that combined to Vita Titankeramic. In the groups that used Ti grade V as substrate, no significant differences were detected among the samples, although the results pointed out that the combination Ti grade V/Duceratin showed significantly lower values than the combination Ti grade II/Vita Titankeramic. Similarly, Suansuwan, Swain\textsuperscript{22}, in a four point bending test, found that the combination Titanium/Titankeramic had the highest strain energy release rate among the groups, whilst
Titanium/Duceratin showed the lowest.

There may be various factors limiting a good clinically satisfactory bond between low-fusing porcelains and titanium substrates. The thickness of the oxide layer formed on the metal surface\(^1\) is one of them. The strength of the titanium-porcelain combination depends on the effects of oxidation that occurs at the interface. When working with temperatures between 700°C and 800°C, it is possible to obtain an unacceptable bond. Values that are close to or exceed 900°C promote the formation of a thick layer of oxide (TiO\(_2\)) between the porcelain and the metal, making the union unfeasible\(^1\). Whereas the explanation for the strength values or differences between the groups may be conjectured by hypotheses like diffusion of chemical elements during the firing of porcelain on the titanium,\(^{10,16,22,27,28}\) what could produce variations in the oxide formed on the surface and alteration in the bond strength, and differences in thermal expansion coefficients of the porcelains used in this study\(^9\). On the other hand, it is important to register that the firing cycles used for porcelain build-up may worsen the fit of titanium copings to values that suggest no inferences to the detriment of clinical applications\(^8\).

Residual stress and fractures are facts strictly related to the difference of thermal expansion between the metal substrate and the porcelain. In order for them to be compatible, the difference in the thermal expansion coefficient between the materials should be equal to or less than 1x10\(^{-6}\)/°C (Akagi, et al\(^7\)). Titanium has a thermal expansion coefficient of 9.41x10\(^{-6}\)/°C, in the interval of 25°C to 400°C (Togaya, et al\(^2\)). The thermal expansion coefficient of the porcelain Vita Titankeramik, according to its manufacturer, is 8.4–9.0x10\(^{-6}\)/°C. Triceram ceramic has 8.9x10\(^{-6}\)/°C (opaque) and 8.4 x10\(^{-6}\)/°C (dentin and enamel), and Duceratin, 8.7 x 10\(^{-6}\)/°C. However, Yilmaz & Dinçer\(^3\), did not find thermal compatibility between Ti-2 and Vitatitaneramik ceramic, detecting a thermal expansion coefficient of 7.9x10\(^{-6}\)/°C for opaque and 6.3x10\(^{-6}\)/°C for the porcelain body, values that exceed the difference between them by 2.9x10\(^{-6}\)/°C – a very different value from that disclosed by the manufacturers.

The combinations ruptured after the bending test and observed through SEM revealed a small amount of residual porcelain adhering to the Ti grade II and V substrates. These results are similar to those found by Adachi, et al\(^7\), Königsmüller & Kivilähti\(^2\), Pang, et al\(^18\), Yilmaz, Dincer\(^8\) and Sasaawan, Swain\(^23\). The observations made in the Ti grade II and V substrates covered by Duceratin porcelain showed a smaller quantity of porcelain adhering in comparison to the other substrates, ratifying the data obtained by mechanical testing. Predominance of fractures of the adhesive type was seen for all combinations involving Ti grade II and V substrates. The group composed of the Pd-Ag alloy, in turn, revealed the occurrence of predominantly cohesive fractures in the ceramic bulks.

Titanium as a biomaterial will probably continue to predominate in treatments involving osseointegrated implants. Although economically feasible, the processing technologies like casting, welding and bonding to ceramics are relatively new. In order for usual prosthetic constructions to become accessible and reliable, further clinical research and longitudinal studies are necessary. However, the bond of ceramic to titanium is a sensitive technique influenced by the effects provoked mainly by the layer of surface oxide. The factors involved in the formation and modification of this layer should be observed and respected. The surface treatment applied to the substrate, the size of the aluminum oxide particles used for sandblasting, as well as adequate waiting time between sandblasting and applying the ceramic, should be considered\(^16,24\). Furthermore, it is evident that the attempts to improve the bond strength of the set by applying chemical elements over the titanium are valid\(^16,28\).

**CONCLUSION**

- The bond strength of grade II and V titanium substrates combined to low-fusing ceramics were significantly weaker than control Pd-Ag / Duceratin;
- Among the combinations involving titanium substrates (grades II or V), the samples represented by Ti grade II /Vita Titankeramik (30.8MPa) had a significantly superior bond strength than those in Ti grade II / Duceratin (22.7MPa) and Ti grade V / Duceratin (22.9MPa).
- Under SEM observation, predominantly adhesive failures were found for the titanium substrate combinations, and cohesive failures in the ceramic bulks in the control combinations.

**RESUMO**

Foram avaliados dois substratos metálicos (titânio comercialmente puro ou grau 2 e a liga Ti-6Al-4V ou grau 5) combinados com a três sistemas ceráxicos de baixa fusão (PBF) sobre a resistência de união pelo teste de flexão de três pontos e a natureza da fraitura porcelana-metal através da microscopia eletrônica de varredura (MEV). Os resultados foram comparados a combinação da liga paládio-prata (Pd-Ag) com porcelana convencional (Duceram VMK68). Foram confeccionadas sessenta tiras de metal medindo 25x3x0.5mm, sendo 30 de titânio grau 2 e 30 de titânio grau 5 sobre os quais foram aplicadas as porcelanas: Vita Titankeramik, Triceram e Duceratin (10 espécies de cada porcelana) nas dimensões de 8x3x1mm. O grupo controle era composto de 10 espécies de Pd-Ag alloy/ com a porcelana Duceram VMK68. Na análise estatística utilizou-se análise de variância (ANOVA) e o teste de Tukey em nível de significância de 5%. Os resultados indicaram que a resistência de união do grupo controle (48.0 ± 4.0) foi estatisticamente significante maior que nos substratos Ti-2 (26.7 ± 4.1) e Ti-5 (25.2 ± 2.2). Os resultados dos substratos de Ti-2 e Ti-5 com a porcelana Duceratin foram estatisticamente significante menores quando comparados ao Ti-2 com a porcelana Vitatitaneramik. A análise pela MEV indicou fraturas predominantemente do tipo adesiva para as amostras de Ti-2 e Ti-5, e coesivas para o grupo controle Pd-Ag/Duceratin. O grupo controle apresentou menor resistência de união comparadas às amostras que empregaram as PBF. Entre as porcelanas de baixa fusão, os menores resultados foram obtidos com a porcelana Duceratin em ambos os substratos. A análise pela MEV confirmou os resultados do teste de flexão.

**UNITERMOS:** Titânio; Cerâmicos de baixa fusão; Porcelana.
REFERENCES


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