# The Influence of Commercially Pure Titanium and Titanium-Aluminum-Vanadium Alloy on the Final Shade of Low-fusing Porcelain

Khalid A. Al Wazzan, BDS, MS; Ibrahim S. Al Hussaini, BDS, MSc

## Abstract

**Aims:** The aims of this study were to investigate the influence of commercially pure titanium (PTi) and titanium-aluminum-vanadium (Ti-6Al-4V) alloys (TiA) on the final shade of low-fusing porcelain bonded to them and to compare the shade changes with those of three conventional metal-ceramic systems.

**Methods and Materials:** A titanium casting unit was used to cast PTi and Ti-6Al-4V alloy specimens followed by A3 shade low-fusing porcelain (Noritake) being bonded to them. Gold-based (AuA), palladium-based (PdA), and nickel-chromium (Ni-Cr) alloys were cast with an automatic centrifugal casting machine, then A3 shade conventional porcelain material (Vita, VMK 95) was applied to them. Ten specimens of each metal were then fabricated. The CIE L* a* b* color coordinates of the specimens were measured with a spectrophotometer.

**Results:** All alloys had significant color changes when compared with A3 shade tabs. The color differences from the shade tabs were 5.79 for the Ti-6Al-4V group, 6.46 for PdA alloy, 8.12 for AuA alloy, 8.15 for Ni-Cr alloy, and 12.58 for PTi. The specimens differed from the shade tabs primarily because of the differences in a* and b* coordinate values.

**Conclusions:** Predictable shade reproduction of metal-ceramic restorations (MCRs) may be impaired by the underlying metal. The PTi had the greatest color differences among all the tested metal when compared with the shade tabs, whereas the Ti-6Al-4V alloy had the lowest. PTi is more likely to affect the final shade of low-fusing porcelain than Ti-6Al-4V alloy.

**Keywords:** Commercially pure titanium, PTi, metal-ceramic restoration, shade, CIE L* a* b* coordinates, colorimetry

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## Introduction

Advancements in dental porcelain technology in the 1960s along with a significant increase in the price of gold in the 1970s prompted the development of alternative metal restorative materials such as palladium and base metal alloys. Recently, there have been increasing efforts to develop titanium technologies for use in dentistry due to its superior biocompatibility, relatively low cost, and desirable physical and mechanical properties.[1-3] It appears titanium is considered a good substitute for expensive gold and palladium-based (PdA) alloys and for the less biocompatible base metal alloys. Therefore, it has been used in tooth supported, or implant supported metal-ceramic restorations (MCRs).[4-6]

Titanium reacts strongly with gaseous elements such as oxygen at a high temperature (>800°C) that yields an excessive thick layer of titanium dioxide ($TiO_2$). Therefore, porcelain firing should take place below 800°C in order to prevent excess oxide formation.[7,8] Manufacturers have introduced low-fusing porcelains designed for titanium application, some of them with a special bonding agent that controls the oxide layer thickness and improves titanium-ceramic bonding.[9,10]

Shade matching is another source of complexity in the MCR. The accurate shade selection and correct tooth preparation are all necessary elements of MCR but are of little value if the final restoration does not closely match the surrounding natural dentition. Several investigators studied numerous factors that may influence the shade duplication process of dental porcelain.[11-24] To overcome the color differences caused by these factors, use of a 1 mm thickness of body porcelain seems to be a good guideline for success.[25]

The type of substructure metal can affect the shade of the ceramics in the MCR. Several studies have evaluated various metal-porcelain combinations to determine the effect of underlying metal on the color of the ceramic material.[15-24,26] Barghi and Richardson[26] found the final porcelain color was not influenced by various high-gold alloy substrates. Brewer et al.[15] used spectrophotometric analysis to quantify color differences of three alloys combined with a single porcelain. They reported significant differences between the color of porcelain applied on palladium-silver alloy and those of high-gold and nickel-chromium alloys (Ni-Cr), which were very similar. Jacobs et al.[16] found the spectrophotometric assessment indicated for porcelain shade A3 in the Ni-Cr and high-palladium alloy groups showed different hue values compared to the gold-platinum-palladium alloy. When shades B1 and C4 were evaluated, the Ni-Cr alloy group was significantly different than both the high-palladium and the gold-platinum-palladium alloy groups. Crispin's et al.[20] colorimetric analysis indicated the color production of porcelain on high-noble metal alloys showed the best performance, whereas the palladium-silver and Ni-Cr alloys resulted in significantly greater color changes of porcelain relative to the high-gold alloy. Brewer et al.[21] also reported perceptible color differences between high-gold/conventional porcelain and palladium-silver/non-greening porcelain. Using a colorimeter, Stavridakis et al.[24] evaluated the effect of eight high-palladium alloys on the resulting color of opaque porcelain with the gold-palladium alloy serving as the control. They found only three palladium alloys, that contained copper, showed significantly greater color changes than the control group.

Photometric and colorimetric instruments offer great potential as a tool for evaluating color in dentistry.[27-29] They offer an objective and quantitative evaluation of color differences. The color of an object measured by these instruments will be expressed in terms of three color coordinates values "L* a* b*." These coordinates should provide a numerical description of the color location in the CIE-LAB (Commission Internationale de l'Eclairage) three-dimensional color space.[30] The L* color coordinate value represents the lightness of the object, the a* represents greenness on the positive axis and redness on the negative, and the b* represents yellowness (positive b*) and blueness (negative b*). The total color difference value (ΔE*) between two objects can be determined by comparing the differences between respective coordinate values of the two objects using the following formula:

$$\Delta E^* = [\, (L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2 \,]^{1/2}$$

Where 1 stands for the values for object number 1 and 2 stands for object number 2.[30]

The ΔE values are used to describe whether the differences in the overall color were perceivable to the observer. A magnitude of color differences greater than 1 ΔE unit are visually detectable by 50% of trained observers under ideal viewing conditions.[28] However, in the oral environment such small differences in color might be undetectable since average color differences up to 3.7 ΔE units have been described as an acceptable shade match.[31]

The metallic color of titanium and titanium alloys can be factors that may affect the color of dental porcelain. Therefore, the purposes of this study were to investigate the influence of the cast commercially pure titanium (PTi) and titanium-aluminum-vanadium (Ti-6Al-4V) titanium alloys on the final shade of the low-fusing porcelain bonded to them, and to compare the shade changes with those of three conventional metal-ceramic systems.

### Materials and Methods
The five metals tested in this investigation were PTi Ti-6Al-4V alloy (TiA); gold-based alloy (AuA), which served as the control; PdA; and Ni-Cr. The tested metals and their compositions are listed in Table 1.

Ten specimens of each of the five metals were fabricated (50 total). A Rematitan titanium casting unit (Dentaurum Inc, Pforzheim, Germany) was used to cast the PTi and TiA specimens. Wax patterns were invested in silica- and phosphate-free, alumina, and magnesia-based investment (Rematitan Plus, Dentaurum Inc. Pforzheim, Germany). The investment and casting procedures were completed according to the manufacturer's instructions. For the AuA, PdA, and Ni-Cr groups, the wax patterns were invested with FastFire 15, a phosphate-bonded investment material (Whip Mix Corporation, Louisville, KY, USA) and cast according to the manufacturer's recommendations. The alloys were melted and cast with a Fornax 35EM automatic centrifugal casting machine (Bego, Bremen, Germany).

The specimens were sequentially wet ground with Polo250/3 silicon 500, 600, and 1000 grit abrasive papers (JeanWirtz, Düsseldorf, West Germany) to achieve the final dimensions for the specimens of $25 \times 3.0 \times 0.5$ mm. All specimens were sandblasted using a Microblaster, Sandstorm (Vaniman Inc, Fallbrook, CA, USA) with 250 $\mu m$ aluminum oxides and 2-3 bars (29 - 44 PSI) of air pressure. Specimens were then subjected to ultrasonic cleaning using distilled water for ten minutes and rinsed in distilled water.

Low fusing porcelain (Noritake Super Porcelain, Nagoya, Japan), supplied with a special bonding agent, was applied on the PTi and TiA specimens. For the AuA, PdA, and Ni-Cr specimens,

**Table 1. Alloys studied.**

| Alloy Type | Product Name | Manufacturer | Composition* | Code |
|---|---|---|---|---|
| Pure titanium | Rematitan M | Dentaurum Inc, Pforzheim, Germany | > 99.5% Ti, 0.003% N, 0.1% C, 0.015% H, 0.02% Fe, 0.18% O | PTi |
| Titanium alloy | Ti-6Al-4V | VSMPO, Verkhnaya Salda, Russia | > 89% Ti, 6.5% Al, 4.2% V, 0.01 C, 0.17% Fe, <0.0005% Y, 0.178% O2, 0.008% N2, 0.0003% H2 | TiA |
| Gold-base | Heraloy G | Heraeus Kulzer, Hanau, Germany | 51.5% Au, 37.9 % Pd, 8.5 % In, 2.0 % Ga, < 0.1 % Ir, <0.1% Ru | AuA |
| Palladium-base | Pors-on 4 | DeguDent, Hanau, Germany | 57.8% Pd, 30.0% Ag, 0.2% Ru, 6.0% Sn, 2.0% Zn, 4.0% In | PdA |
| Base metal | Remanium CS | Dentaurum Inc, Pforzheim, Germany | 61.0% Ni, 26.0% Cr, 11.0% Mo, 1.5% Si, < 1.0% Fe, Ce, Al, Co | Ni-Cr |

* provided by the manufacturers.

conventional porcelain material Vita VMK 95 (Vita, Bad Sackingen, Germany) was used.

For the PTi and TiA specimens, a thin layer of the porcelain-bonding agent was painted on the porcelain bearing area of the respective specimens. Bonding porcelain powder and liquid were mixed according to the manufacturer's instructions, painted with a short bristle brush on the specimens, and fired as recommended by the manufacturer.

The A3 shade of the designated porcelain was applied to the respective specimens in the central portion of each metal substrate so the porcelain was 8 mm in length, 3 mm in width, and 1 mm in thickness. This was accomplished by applying two uniform coats of opaque porcelain prepared according to the manufacturer's instructions. The opaque porcelain was then applied with a brush on the porcelain bearing area and fired as recommended by the manufacturer. The body porcelain was subsequently applied with the help of an aluminum matrix then fired according to the manufacturer's instructions. Compensation for firing shrinkage was accomplished with a second application of body porcelain and yielded a final thickness of 1 mm. The thickness of each specimen was measured with a Mitutoyo digital micrometer (Mitutoyo Corporation, Tokyo, Japan) to verify the proper thickness of the ceramic. The glazed layer was applied and fired according to the manufacturer's instructions. The specimens were fabricated by one investigator.

The CIE L* a* b* color coordinates of the specimens were measured with a Color-Eye 7000A spectrophotometer (CretagMacbeth, New Windsor, NY, USA). Before every measuring session, the spectrophotometer was calibrated according to the manufacturer's instructions using a supplied white ceramic calibration tile. The color data of each specimen were transferred to a personal computer and processed with color-formulation software (ProPalette 3.1, GretagMacbeth). The spectrophotometer viewing area of $8 \times 3$ mm was selected, and color coordinate values were recorded based on an average D65 daylight light source. Five independent measurements were carried out for each specimen and the average was calculated.

Since A3 shade porcelain was used throughout, the mean L* a* b* coordinates of the A3 shade tab were used for determination of color differences (ΔE) for all specimens. Two new disc-shaped A3 body porcelain shade tabs (VMK 95, Vita) were obtained for colorimetric evaluation. Five independent measurements were carried out for each shade tab and the average was calculated. The ΔE*1 (mean color difference) value of each specimen was calculated between the shade tab and each specimen's L* a* b* coordinates values using the following formula:

$$\Delta E^* = [\, (L_1{}^* - L_2{}^*)^2 + (a_1{}^* - a_2{}^*)^2 + (b_1{}^* - b_2{}^*)^2 \,]^{1/2}$$
Where 1 represents the values for the shade tab and 2 represents the experimental spacemen.

Likewise, the ΔE*2 value of each specimen was calculated between the L* a* b* coordinates of the AuA group and the specimens of the remaining groups.

The L* a* b* and ΔE* data were analyzed with one-way analysis of variance (ANOVA) and Tukey's multiple range tests to determine the statistical significance of the mean differences between groups ($\alpha$=.05).

## Results

The means of the color coordinates (L* a* b*) values for the A3 shade tabs were 69.68, 0.91, and, 12.41, respectively. All alloys had significant color changes in comparison with the shade tabs. The means of the color coordinates and the color differences (ΔE*) are shown in Table 2. The ΔE*1 between the A3 shade tabs and the other groups was in the range of 5.79 to 12.58 units. The ΔE*1 from the smallest to the highest were 5.79 for the TiA group, 6.46 for PdA, 8.12 for AuA, 8.15 for Ni-Cr, and 12.58 for PTi. Specimens differed from the shade tabs primarily because of the differences in a* and b* coordinate values. Differences in L* coordinate values contributed little to overall color differences.

The ΔE*2 between the control group (AuA) and the rest of the groups was in the range of 1.49 to 4.66 units. The ΔE*2 from the smallest to the highest were 1.49 for the Ni-Cr group, 2.15 for PdA, 3.81 for TiA, and 4.66 for PTi.

**Table 2. Color coordinates and color differences of the metal-ceramic systems.**

| Specimen | L* | a* | b* | ΔE*1 | ΔE*2 |
|----------|------|------|------|------|------|
| PTi | 77.61 (±1.25) | 3.33b (±0.30) | 21.38 (±0.87) | 12.58 (±1.47) | 4.66g (±1.45) |
| TiA | 70.63 (±0.97) | 2.55 (±0.10) | 19.33c (±0.31) | 5.79e (±0.84) | 3.81g (±0.86) |
| AuA | 74.14a (±1.41) | 3.50b (±0.23) | 18.32d (±0.81) | 8.12f (±1.60) | 0.0 |
| PdA | 72.29 (±1.22) | 3.50b (±0.18) | 18.39d (±0.69) | 6.46e, f (±1.36) | 2.15h (±0.82) |
| Ni-Cr | 73.98a (±1.55) | 3.32b (±0.27) | 18.74c,d (±0.82) | 8.15f (±1.73) | 1.49h (±0.98) |

ΔE*1 Differences from shade tab.
ΔE*2 Differences from control group.
Values with similar superscript letters in each column were not significantly different.

The one-way ANOVA showed significant differences between values of both ΔE*1 and ΔE*2 of the tested metals (P<0.001) (Table 3). The Tukey's multiple range test showed PTi had significantly greater (P<0.001) ΔE*1 values than the control group (AuA), while TiA had significantly smaller (P=0.006) values. For the ΔE*2, both titanium groups showed significantly greater (P<0.01) values than the conventional groups.

Furthermore, the one-way ANOVA for the color coordinates showed significant differences for the L* a* b* values of the different metals (P<0.001) (Table 3). The Tukey's multiple range tests showed significant differences between L* and b* values of the AuA group and both the PTi and TiA groups (P<0.05). However, for the a* values, there was no significant difference between the AuA and PTi groups (P=0.467), but a significant difference was found between the AuA and TiA groups (P<0.001).

## Discussion

The use of commercial shade guide tabs is the predominant method for associating the color of a tooth with a given shade of porcelain. Color differences (ΔE*1) in this study were calculated between the metal-ceramic specimens and the disc-shaped A3 body porcelain shade tabs. The ΔE values used to describe whether the differences in the overall color were perceivable to the observer. A magnitude of color differences greater than 1 ΔE unit can be visually detectable under ideal viewing conditions.[28] However, in the oral environment, color differences up to 3.7 ΔE units can be described as an acceptable shade match.[31] The results of the present study showed all tested alloys had significant color changes in comparison with the shade tabs. These color differences could be visually detected, as they were greater than 3.7 ΔE unit. This is consistent with previous investigations[15-22,24] reporting the effect of underlying metal on the shade of the ceramic. One of the possible explanations for the observed color differences is some elements from the alloys may have reacted with the adjacent opaque porcelain along the interface. Tuccillo[32] proposed three possible mechanisms of such reactions. Bulk transfer involves the migration of an element or its oxides from the alloy into the porcelain. Surface diffusion takes place when atoms of an element diffuse to the exposed metal surface and subsequently into the porcelain. The third mechanism is vapor deposition, where an element from an alloy vaporizes and consequently is deposited onto the porcelain surface.

Assessment of the direction of the color differences in the L* a* b* axis revealed the specimens differed from the shade tabs primarily because of the differences in values of a* and b* coordinates. This indicated the specimens were more red (+Δa*) and more yellow (+Δb*) than the shade tabs. This may be explained

**Table 3. One-way ANOVA of the color coordinates and color differences.**

| | | Sum of Squares | df | Mean Square | F | P |
|---|---|---|---|---|---|---|
| **L\*** | Between Groups | 269.248 | 4 | 67.312 | 40.122 | <0.001 |
| | Within Groups | 75.496 | 45 | 1.678 | | |
| | Total | 344.744 | 49 | | | |
| **a\*** | Between Groups | 6.213 | 4 | 1.553 | 30.417 | <0.001 |
| | Within Groups | 2.298 | 45 | 0.051 | | |
| | Total | 8.511 | 49 | | | |
| **b\*** | Between Groups | 64.258 | 4 | 16.065 | 30.254 | <0.001 |
| | Within Groups | 23.895 | 45 | 0.531 | | |
| | Total | 88.153 | 49 | | | |
| **ΔE\*1** | Between Groups | 280.428 | 4 | 70.107 | 34.199 | <0.001 |
| | Within Groups | 92.249 | 45 | 2.050 | | |
| | Total | 372.677 | 49 | | | |
| **ΔE\*2** | Between Groups | 64.313 | 3 | 21.438 | 19.158 | <0.001 |
| | Within Groups | 40.284 | 36 | 1.119 | | |
| | Total | 104.597 | 39 | | | |

by the presence of the metal background of the metal-ceramic specimens which may absorb the light. The comparison of porcelain specimens on discolored substrates with specimens on a white background showed the resulting color is largely affected by the background color.[33]

Nevertheless, differences in L\* coordinate contributed little to the overall color differences. However, the minimal increase of L\* coordinate values revealed the specimens were slightly lighter (+ΔL\*) than the shade tabs. The body porcelain shade tab's thickness was twice the thickness of the metal-ceramic specimens. It has been reported as body porcelain thickness increases more light is scattered and absorbed[25], thereby, allowing less light to be reflected back.

The color production of porcelain on high-gold alloys was found to show the best performance.[20,26] In addition, to the gold alloys used by several authors as a reference for the other alloys.[15,16,21,24] In this study, color differences (ΔE\*2) were also calculated between the specimens of PTi, TiA, PdA, and Ni-Cr groups and the AuA group. The color differences for

the PTi group could be visually detected, as they were greater than 3.7 ΔE units, whereas the values of the TiA lie just above this limit and the two conventional groups lie below it. Assessment of the color shift in the L\* a\* b\* axis revealed the PTi specimens were darker (+ΔL\*) and more yellow (+Δb\*) than the AuA specimens. On the other hand, the TiA specimens were lighter (-ΔL\*) and greener (-Δa\*) than the AuA specimens. However, these findings should be considered with caution as two different porcelain brands were compared. Several studies showed different porcelain brands on the same metal may have a different effect on the final porcelain color.[11,12,19,21]

The PTi had the greatest ΔE\*1 values among all the tested metal, while the Ti-6Al-4V had the lowest. In addition, Ti-6Al-4V showed better performance than PTi with respect to ΔE\*2 values. Titanium is alloyed with various elements primarily to improve mechanical properties.[34] It appears alloying elements such as Al and V may also improve the color behavior of the PTi subsequent to porcelain application.

The results of this study showed underlying PTi can be a factor that may affect the final shade of low-fusing porcelain. It appears a 1 mm thickness of body porcelain does not completely mask the influence of underlying titanium. It is likely a greater porcelain thickness would be able to mask the observed color differences. Studies showed the shade of metal-ceramic systems was influenced by porcelain thickness[14,16,25], and the color of metal-ceramic systems was more dependent on porcelain thickness than were the semi-translucent all-ceramic systems.[25] Further research in this area is required to determine the necessary porcelain thickness for PTi and Ti-6Al-4V alloy.

The findings of the present study suggested PTi is more likely to affect the final shade of low-fusing porcelain than Ti-6Al-4V alloy. However, the final judgment in any color assessment in the clinical environment is a visual one, and this study did not include the factor of human judgment. Also, measurements of color differences on clinical crowns simulating complex geometries instead of experimental specimens of simple geometry may generate more practical color information.

## Conclusions

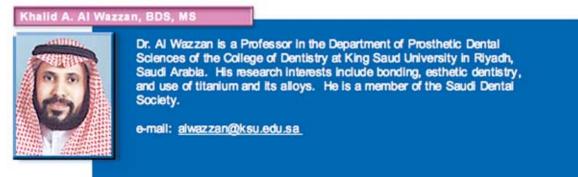Within the limitations of this study, the following conclusions can be made:

1. Predictable shade reproduction of MCR may be impaired by the underlying metal.
2. PTi had the greatest color differences among the tested metal when compared with the shade tabs, whereas the Ti-6Al-4V alloy had the lowest.
3. PTi had the highest color differences when compared with the AuA alloy.
4. PTi is more likely to affect the final shade of low-fusing porcelain than Ti-6Al-4V alloy.
5. A 1.0 mm-thick layer of low-fusing body porcelain applied to PTi was not reliable in reproducing the color of porcelain.

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## About the Authors

**Khalid A. Al Wazzan, BDS, MS**

Dr. Al Wazzan is a Professor in the Department of Prosthetic Dental Sciences of the College of Dentistry at King Saud University in Riyadh, Saudi Arabia. His research interests include bonding, esthetic dentistry, and use of titanium and its alloys. He is a member of the Saudi Dental Society.

e-mail: alwazzan@ksu.edu.sa

**Ibrahim S. Al Hussaini, BDS, MSc**

Contact Info:

Ibrahim S. Al Hussaini
Specialist, Security Forces
P.O. Box 32299, Riyadh 11428.
Saudi Arabia

E-mail: ialhussaini@hotmail.com