Effect of Cathodic Arc Plasma Deposition on Shear Bond Strength between Palladium Cobalt Chromium Coated with Titanium Nitride and Titanium Aluminium Nitride with Ceramic

Abstract

Background: The success of esthetic ceramo-metal restoration is strongly influenced by its bond strength. The success of ceramo-metal restoration is subjective to its bond strength. **Aim and Objectives:** The aim of this study is to evaluate the shear bond strength between palladium-based cobalt chromium (Co-Cr) alloy coated with titanium nitride (TiNi) and titanium aluminum nitride with feldspathic ceramics. **Materials and Methods:** According to the International Organization for standardization 9693; technical report 1,140,640 samples were prepared using Palladium-based Co-Cr alloy with ×4 vertical projection resting on 5 mm diameter base. The samples were divided into Group: A (control), Group: B (Sandblasted), Group: C (TiNi coated), and Group: D (titanium aluminum nitride coated by cathodic arc plasma deposition, following which feldspathic ceramic application was performed. Shear bond test was performed using universal testing machine and surface analysis was performed using scanning electron microscope. **Results:** The mean shear bond strength for Group A was 172.994 ± 3.739 N, Group B 209.485 ± 5.913 N, Group C 176.536 ± 4.780 N, and Group D 260.576 ± 16.351 N. Comparison within the groups was made using one-way ANOVA, and multiple group comparisons were made using Tukey's honestly significant difference *Post hoc* test where the $P < 0.001$ was considered statistically significant. **Conclusion:** Palladium based Co-Cr alloy coated with titanium aluminum nitride by cathodic plasma arc deposition showed maximum shear bond strength with feldspathic ceramic compared to noncoated, sandblasted, and TiNi coated alloy.

Keywords: *Palladium-based cobalt-chromium, shear bond strength, titanium nitride*

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Introduction

Esthetic means the science that deals with the nature of beauty, art, taste, and the creation and appreciation of beauty.[1] Esthetic demand of today's patients has been achieved by veneering the metal base to materials such as resin and porcelain. Metal ceramic restoration is defined as an artificial crown or fixed complete or partial denture that uses a metal substructure and porcelain veneer.[2] The terms porcelain fused to gold or metal or porcelain baked on gold or metal, as well as ceramo-metallic terminology, have been used nowadays. These restorations present first-class durability, commendable clinical performance, low cost, simple cementation technique, and natural facsimile of the lost dentition.[3]

The metal-ceramic bond takes place invariably by three possible mechanisms, i.e., mechanical bonds, chemical bonds or by van der Waal's forces.[4-6] The bond strength between the two metals depends on surface roughness, dovetails, projections, and anchor points.[5] The chemical bond is dictated by the oxide layer on the metallic substrate, which forms ionic, covalent, or metallic bonds with oxides in the ceramic opaque. The van der Waal's forces suggested the bonding due to electrical dipoles or dispersion effect without any chemical interaction.[7]

Cobalt chromium (Co-Cr) alloys present difficult handling characteristics with critical melting technique and high melting temperatures, also its oxidation heat treatment has a poor influence on porcelain bonding. Palladium cobalt alloys have limited use as they form a dark oxide layer compromising esthetics, and liquid palladium absorbs excessive gas released during casting, leading

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to microporosities and dark oxide formation which compromises esthetics.[8-11]

Application of microlayered coatings such as chromium, silver, gold silicon nitride, and titanium nitride (TiNi) on metal surface to improve the bond strength has been analyzed.[12] The deposition of the intermediate layer on the underlying metal substrate before application of dental porcelain acts as a barrier to diffusion of components without micro gaps, improves surface corrosion resistance, thermal stability, bacterial resistance, and improve suitability for patients with certain metal allergy.[13,14]

TiNi deposition had been used previously to enhance bond strength.[13] The TiNi has poor pyrochemical properties at high temperatures, during porcelain firing TiO_2 formation adversely affects the metal-ceramic bond strength.[15] The bond strength is dependent on its oxide layer that is formed during porcelain firing. If the oxide layer is very thick or thin or removed during porcelain firing, ceramic adhesion is weakened.[12] The addition of TiO_2 layer to Co-Cr alloy has been found to improve the wettability but did not improve the bond strength. Therefore, more stable TiAlNi was used in this study to improve bond strength.[15,16] However, these inadequacies can be overcome by the advancement in material with the newer Pd-based Co-Cr alloys. Hence, this study was performed to evaluate and compare the shear bond strength between palladium-based Co-Cr alloy surface treated with airborne particle abrasion, coated with TiNi and (Ti, Al) Ni deposition using cathodic arc plasma deposition process. A hypothesis was formulated that the shear bond strength between Palladium-based Co-Cr alloy and ceramic will be similar after various surface treatment.

Materials and Methods

According to the International Organization for standardization 9693; technical report 11,406, samples were prepared with a basal diameter of 5 mm and a vertical projection of 4 mm height and 4 mm diameter[17] [Figure 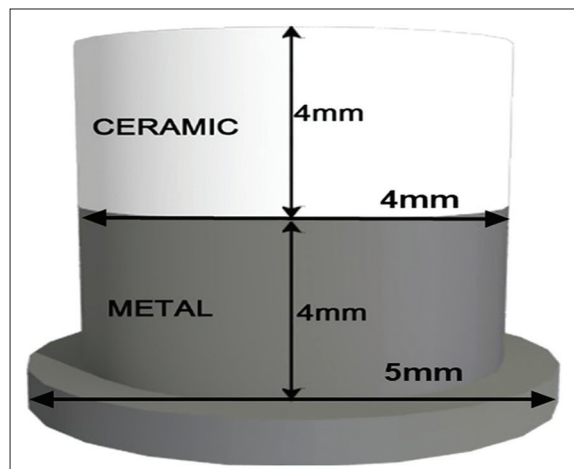1]. Cylindrical stainless steel mold was milled to the final disc shape for the fabrication of the samples. The die was milled to 20 mm length with an outer diameter of 20 mm and inner diameter of 4 mm until 19 mm length and a base diameter of 5 mm. Two cylindrical pistons of 15 mm and 20 mm length were prepared with 4 mm diameter width and 20 mm broad base, respectively. The pistons were customized to penetrate through the mold space.

Casting wax (Blue inlay casting wax, Type II; Kerr) was melted and poured into the mold with the first piston in place. The first piston acting like a base prevented the wax from flowing through the entire length of the mold space. After hardening, the wax pattern was ejected out of the mold space using the second longer piston. The wax patterns were sprued and mounted on a silicone casting ring and invested using phosphate bonded investment. (Bellasum; Bego).The set investment was burnt out in the furnace (Fire, SIRIO) and removed for casting at 1100°C. The casting of the metal was done on the induction casting machine (Fornax T; Bego).

Palladium-based Co-Cr alloy used for casting which contains Co-40%, Pd-25%, Cr-21.4%, Mo-12.7%, W <1%, B <1%, Ta <1% (CallistoCP++; IvoclarVivadent). The completed castings were divested and cleaned using air-bone particle abrasions using 50 µm Al_2O_3. After which samples were placed in an ultrasonically cleaner for 15 min. A total number of 40 samples were prepared and evenly distributed into four groups. Group A samples were not subjected to any form of surface treatment (control), Group B sample was treated with 50 µm aluminum oxide abrasion at a pressure of 60 Psi for 30 s, Group C was coated with TiNi [Figure 2], and Group D were coated with titanium aluminum nitride (Ti, AlN) using cathodic arc plasma deposition (CAPD) [Figure 3].

CAPD method was used to deposit ultrathin hard layer of 99.9% pure Ti and TiAl composite alloy target (purity = 99.9%, Ti/Al– 50:50 at %) in an N_2 and argon atmosphere for deposition. Presputtering with TiAl and pure Ti was performed on the substrate for 5 min to serve as an interlayer between the metal substrate and nitride implantation. Nitrogen gas was introduced next along with argon gas for final sputtering, and the substrate

Figure 1: Schematic diagram of sample

Figure 2: Titanium nitride coated sample

temperature of 300°C was maintained. The nitrogen and argon flow rate of 2.0–2.5 sccm in the ratio of 1:1 was maintained with the voltage of −200 V, at <1 × 10⁻⁶ torr for 2 h. The D.C. substrate voltage was maintained at 100V and the substrate temperature was 300°C. The total pressure of mixed gas (Ar and N_2) was fixed at 80 m torr. The coating of 2.0 µm Ti and TiAl metallic films was achieved by the implantation of nitrogen ions. After which the samples were ultrasonically cleaned (Sonic Clean; Transkit system).

Surface oxidation was done by raising the temperature to 980°C with 140°C rise in temperature per minute. (IPS d. sign; Ivoclar Vivadent) ceramic was used as the veneering material. Two layers of opaque ceramic (thickness: 0.1 mm each) were applied onto the metallic surface and fired at 890°C. The dentin body ceramic was condensed and gradually fired up to 920°C with a holding time of 1 min in Programmed P100 ceramic furnace (Ivoclar Vivadent) [Figure 4]. Shear bond strength test was evaluated using Instron 3382. The 10 KN of the load was applied on the metal-ceramic interface at a constant test speed of 0.5 mm/min until fracture. The specimens were analyzed using scanning electron microscope (SEM) (QUANTA 200 F), and the images were digitally recorded [Figures 5-8].

Statistical analysis

To analyze the data software SPSS version 22.0 Armonk, NY: IBM Corp. was used, and power analysis was performed with a confidence interval of 99%. (α-0.01) Comparisons within the groups were statistically analyzed using one-way ANOVA. The analysis revealed that the $P < 0.001$ suggestive of statistically significant groups.

Results

The mean shear bond strength for Group A (control) was 172.994 ± 3.739 N, Group (sandblasted) was 209.485 ± 5.913 N, Group C (TiNi coated) was 176.536 ± 4.780 N and Group D (TiAl) Ni coated) was 260.576 ± 16.351N, respectively [Table 1].

One-way ANOVA shows significant value $P < 0.001$; hence, the shear bond strength were statistically significant within the groups [Table 2]. Multiple comparisons was made using Tukey's honestly significant difference *Post hoc* test that showed the $P < 0.001$ for all the samples except Group A compared to Group C. This is suggestive of the absence of significant difference between these two groups [Table 3].

On evaluating the mode of failure, it was found that Group A showed 80% adhesive failure and 20% adhesive and

Figure 3: Titanium aluminum nitride coated sample

Figure 4: Ceramic coated alloy

10.0kV 9.2mm x60 SE   500um

Figure 5: Scanning electron microscope image of control sample

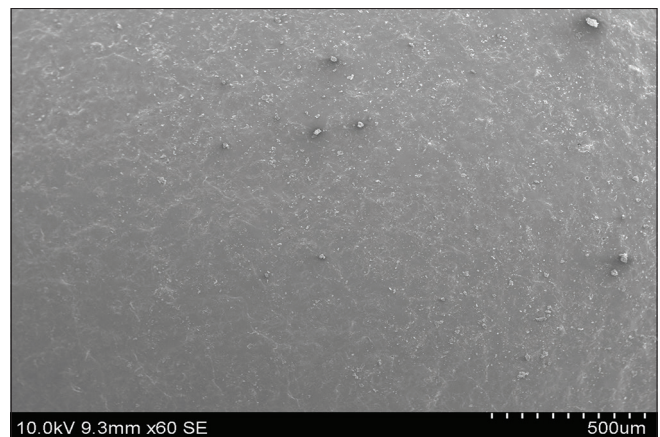10.0kV 9.3mm x60 SE   500um

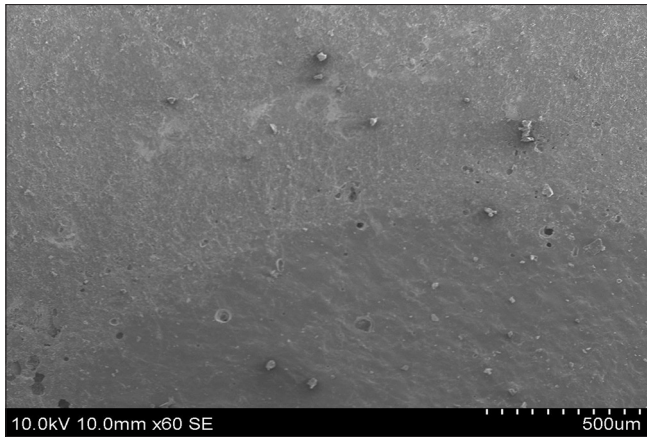Figure 6: Scanning electron microscope image of sandblasted sample

Figure 7: Scanning electron microscope image of titanium nitride coated sample
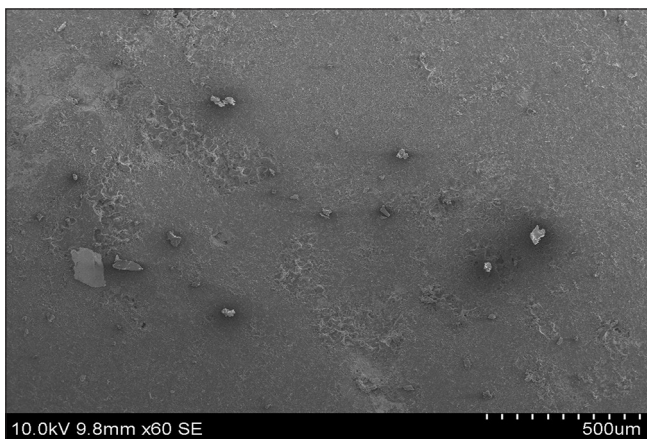

Figure 8: Scanning electron microscope image of titanium aluminum nitride coated sample
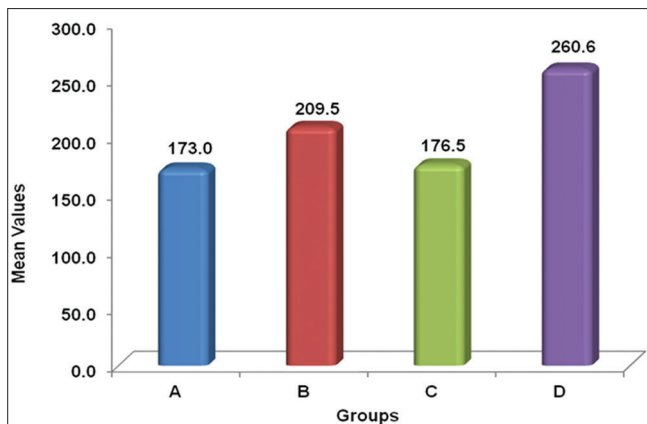

Figure 9: Comparison of mean shear bond strength between Palladium Cobalt Chromium and ceramic after various surface treatments

cohesive type of failure. Group B showed 90% adhesive and cohesive type of failure and 10% adhesive failure. Group C displayed 75% adhesive failure with 25% of the adhesive and cohesive type of failure. Group D displayed 99% adhesive and cohesive type failure and 1% cohesive failure [Table 4].

Table 1: Mean and standard deviation of shear bond strength values between groups

Group	n	Mean±SD	Minimum	Maximum	P
Group A	10	172.994±3.739	165.620	177.610	<0.001
Group B	10	209.485±5.913	200.500	221.060	
Group C	10	176.536±4.780	170.000	185.320	
Group D	10	260.576±16.351	233.600	287.590	
Total	40	204.898±36.685	165.620	287.590	

SD: Standard deviation

Table 2: One-way ANOVA for comparison within the groups

	Sum of squares	Df	Mean square	F	P
Between groups	49433.458	3	16477.819	194.341	<0.001
Within groups	3052.376	36	84.788		
Total	52485.834	39			

Df: Degrees of freedom

Table 3: Tukey honestly significant difference *post hoc* tests for pairwise comparisons

Pair	Mean difference	P
Group A		
Group B	36.491	<0.001
Group C	3.542	0.825
Group D	87.582	<0.001
Group B		
Group C	32.949	<0.001
Group D	51.091	<0.001
Group C		
Group D	84.040	<0.001

Table 4: Type of failure

Group	Adhesive (%)	Cohesive (%)	Adhesive and cohesive (%)
Group A	80	0	20
Group B	10	0	90
Group C	75	0	25
Group D	0	10	90

Discussion

The bond strength of the metal and ceramic determines the quality of the restoration. Palldium-based Co-Cr alloy is an alternative to expensive gold-based alloys and its elastic modulus is the most favorable of all noble metal alloys.[18] Co-Cr alloys have found to be of lighter weight in comparison to other alloys.[19] The addition of Copper and Indium reportedly decrease the solid solubility of Gallium in Palladium, causing a eutectic effect.[20]

The literature revealed ceramo-metal interface without surface treatment produced the lowest shear bond strength values. Increasing the surface roughness by Al_2O_3 air

abrasion, increases the retention by micro-mechanical action by increased surface area.[16] Adachi *et al*. attributed the poor bonding of Ti alloys to the degradation of the oxide layer during porcelain firing, which made the previously adherent layer nonadherent. This was because of the large negative Gibbs (used to predict whether a reaction will be spontaneous in the forward or reverse direction) energy of oxidation that results in the reduction of oxides in the porcelain through displacement reactions.[13,19,21] Tanaka *et al*.[13] demonstrated the absence of micro-gaps as TiNi coating filled the interface of Au-Pd-Ag alloy and the veneering composite. They concluded that the greater shear bond strength of TiNi coated group alloy to the absence of micro-gaps in comparison to the metal conditioned alloy.

Chung *et al*.[14] elicited the deterioration of TiNi in TiNi coated dental alloys during porcelain firing due to its 550°C evaporation point. Whereas (Ti, Al) Ni film has stable pyrochemical properties with the evaporation point being higher than 800°C, thereby better stability during porcelain firing. TiNi coated groups revealed mean bond strength values of 176.536 ± 4.780 N similar to the noncoated groups 172.994 ± 3.739 N validating the evaporation of TiNi during porcelain firing. This explains the weaker bond strength in the TiNi coated alloys. Hence, this study rejected the null hypothesis. SEM analysis of TiNi coated alloy shows disintegrated and irregular coating suggesting the instability of TiNi coating at higher temperatures similar to that of noncoated alloy with absence of coating [Figure 7].

Application of microlayered coatings such as chromium, silver, gold silicon nitride, and TiNi on the metal surface to improve the bond strength has been analyzed.[12] Barshilia and Rajam elicited that TiNi was unstable at above 500°C due to the displacement of N in Ti.[15] High oxidation nature of titanium has been postulated as the main cause of poor bond strength, as continuous oxidation reaction takes place during porcelain firing resulting in an unstable TiO_2 oxide layer.[12] This TiO_2 formed continues to oxidize with displacement reaction and disintegrates at higher temperatures. Therefore TiNi has very severe limitations for higher temperature applications.[13] Peroxidation of milled titanium under vacuum is found to efficiently improve the metal-ceramic bond strength in pure Titanium.[22]

The substitution of Ti by Al in TiNi lattice to form (Ti, Al) Ni improved the thermal stability. The appearance of TiO_2 and Al_2O_3 at 800°C indicates the onset of oxidation. Better stability of the surface coating at higher temperatures and the ability to block adverse oxidation effects of the underlying metal substructure; hence, better bond strength was obtained.[23] The superior behavior of (Ti, Al) Ni is also likely due to the strongly different Gibbs free energy for oxide formation; also Al_2O_3 is much more stable than TiO_2.[24,25]

SEM analysis of the TiAlNi coated alloy (Fig. reveals a dark uniform stable layer of TiAlNi of 1.9 μm thickness on the metal substructure. This coating masked the porosities and diffused on the underlying substructure. The EDX cross-sectional analysis of TiAlNi coated alloy reveals peaks of TiO_2 and Al_2O_3 on the coating showing the stability of TiAlNi at higher temperature [Figure 8].

Chung *et al*. demonstrated higher flexural bond strength values ranging from 278.0 ± 12.3 N in (Ti, Al)Ni coated groups when compared other noncoated groups whose values where 159.0 ± 11.7 N. Furthermore, the highest bond strength values was observed in groups prepared with both air abrasion plus (Ti, Al) Ni coating.[14] (Ti, Al) Ni group in this study demonstrated mean shear bond strength values ranging from 260.576 ± 16.351N, which was followed by sandblasted, TiNi coated and noncoated groups. Furthermore, (Ti, Al)Ni groups demonstrated values which were significantly higher than the sandblasted group 209.485 ± 5.913 N [Figure 9].

The mode of failure was examined using SEM. The majority of the samples in (Ti, Al)Ni coated group and sandblasted group showed both adhesive and cohesive type of failure. Noncoated and TiNi coated samples presented an adhesive type of failure. Classification of the mode of failure for deboned specimens is a complicated task and in some instances, the limit between mixed and cohesive failure becomes merely subjective. Rather than an indication of a strong bond, cohesive failure is explained by the mechanics of the test and the brittleness of the materials used for the study.[26]

The distribution and thickness of TiNi and (Ti, Al)N particles coating is uncertain and unpredictable. Further studies needed to standardize the samples surface with uniform distribution of TiNi particles.

Clinical implication

The application of (Ti, Al)N on metallic surfaces improved the bond strength between palladium-based Co-Cr alloys and ceramic, which enhances the longevity, success, and esthetics of the restoration. This enables the clinician to provide superior ceramic bonded restorations to the patient.

Conclusion

Palladium-based Co-Cr alloy coated with (Ti, Al)N by cathodic plasma arc deposition showed maximum shear bond strength with feldspathic ceramic compared to noncoated, sandblasted, and TiNi coated alloy.

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Conflicts of interest

There are no conflicts of interest.

References

1. Merriam-Webster Dictionary Online. Available from: http://www. merriam-webster.com. [Last accessed on 2019 May 22].

2. Glossary of prosthodontic terms. 9th Edition. J Prosthet Dent 2017;117:e1-105.

3. O´Brain WJ, Kring JE, Ryge G. Heat treatment of alloys to be used for the fused porcelain technique. J Prosthet Dent 1964;14:955-60.

4. Baran GR. Phase changes in base metal alloys along metal-porcelain interfaces. J Dent Res 1979;58:2095-104.

5. Barreto MT. Failures in ceramo-metal fixed restorations. J Prosthet Dent 1984;51:186-8.

6. Knap FJ, Ryge G. Study of bond strength of dental porcelain fused to metal. J Dent Res 1966;45:1047-51.

7. Swartz ML, Phillips RW. A study of adaptation of veneers to cast gold crowns. J Prosthet Dent 1957;7:817-22.

8. Kontonasaki E, Kantiranis N, Papadopoulou L, Chatzistavrou X, Kavouras P, Zorba T, *et al*. Microstructural characterization and comparative evaluation of physical, mechanical and biological properties of three ceramics for metal-ceramic restorations. Dent Mater 2008;24:1362-73.

9. Johnson A, Winstanley RB. The evaluation of factors affecting the castability of metal ceramic alloy – Investment combinations. Int J Prosthodont 1996;9:74-8.

10. Serra-Prat J, Cano-Batalla J, Cabratosa-Termes J, Figueras-Àlvarez O. Adhesion of dental porcelain to cast, milled, and laser-sintered cobalt-chromium alloys: Shear bond strength and sensitivity to thermo cycling. J Prosthet Dent 2014;112:600-5.

11. Ting S, Li KC, Waddell JN, Prior DJ, van Vuuren LJ, Swain MV. Influence of a tungsten metal conditioner on the adhesion and residual stress of porcelain bonded to cobalt-chromium alloy. J Prosthet Dent 2014;112:584-90.

12. Khung R, Sukjai SN. Effect of gold sputtering on the adhesion of porcelain to cast and machined titanium. J Prosthet Dent 2013;110:41-6.

13. Tanaka K, Kimoto K, Sawada T, Toyoda M. Shear bond strength of veneering composite resin to titanium nitride coating alloy deposited by radiofrequency sputtering. J Dent 2006;34:277-82.

14. Chung KH, Due JG, Shin D, Cagna DR, Cronin RJ Jr. Characteristics and porcelain bond strength of TiAlN Coating on Dental Alloys. J Biomed Mater Res 2002;63:516-21.

15. Barshilia HC, Rajam KS. Raman spectroscopy studies on the thermal stability of TiN, CrN, TiAlN coatings and nanolayered TiN/CrN, TiAlN/CrN multilayer coatings. J Mater Res 2004;19:3196-205.

16. Draddy RE. Chrome cobalt alloy pontics in fixed partial denture. J Prosthet Dent 1971;25:638-41.

17. Metal ceramic dental restorations. Int Stand Org 9693:1999/2005;18:64-72.

18. Yao L, Peng C ,Wu J. Wettability and bond strength between leucite-reinforced dental porcelains and Co-Cr alloy. J Prosthet Dent 2013;110:515-20.

19. Asgar K. Casting metals in dentistry: past, present and future. Adv Dent Res 1988;2:33-43.

20. De Melo RM, Travassos AC, Neisser MP. Shear bond strengths of ceramic systems to alternative metal alloys. J Prosthet Dent 2005; 93:64-69.

21. Winings JR. Using aluminum oxide abrasives in porcelain bonded to metal fabrication. J Prosthet Dent 1981;46:345-47.

22. Anusavice KJ. Phillip´s Science of Dental Materials. 10th ed., Saunders, Philadephia, PA, 1996:442-43.

23. Shillingburg HT, Hobo S, Whitsett LD, Jacobi R. Fundamentals of fixed prosthodontics. 3rd ed., Illinosis;Quintessence Publication, 1997:456-57

24. Zhang C, Ye J, Zhang Y, Liao J, Li J. Effect of titanium preoxidation on wrought pure titanium to ceramic bond strength. J Prosthet Dent 2013;109:106-12.

25. Rosenstiel SF, Land MF, Fujimoto J. Contemporary fixed prosthodontics. 2nd ed. St.Louis; Mosby year book, Inc. 1995:505-7.

26. Braga RR, Meira JB, Boaro LC, Xavier TA. Adhesion to tooth structure: A critical review of macro test methods. Dent Mater 2010;26:e38-49.