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RESISTANCE EVALUATION OF A METAL-CERAMIC DENTAL FUNCTIONALLY GRADED RESTORATION

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ABSTRACT

Restoration of Porcelain Fused to Metal (PFM), which is widely used in dental field, relays on the strength of the bond between porcelain and metal substructure. PFM restorations failure occurs fundamentally in the metal-ceramic interface vicinity. The purpose of this work was to study the interface between metal and ceramic. To overcome problems associated with metal-ceramic sharp transition in metal-ceramic dental restorations, a new method is proposed, based on a powder metallurgy technique and in a smooth transition of chemical composition between metal and porcelain (FGM – Functionally Graded Biomaterial). The graded transition was obtained by different volume fractions of metal and ceramic in the interface. The strengthening effect of the graded interface was investigated by the means of shear test, optical microscope, stereomicroscope, SEM/EDS. Results were compared with a conventional PFM restoration. Experimental results showed that the resistance of the metal-porcelain interface can be substantially improved by using a graded metal-ceramic transition rather than a sharp one. This new processing approach of graded interface can prevent or even avoid many PFM restorations failures.

Keywords: *Porcelain fused to metal restorations, powder metallurgy, hot pressing*

1. INTRODUCTION

Metal-ceramic restorations still the most reliable method in dental prosthetics, especially when a good adhesion of the ceramic to the metal substrate is achieved (Vásquez and Kimpara 2009). All ceramic restorations is a alternative, although it is not accompanied of the desired life span and premature clinical failure is often reported (Donovan and Swift 2009; Kelly 1997). Many dental alloys are available for metal-ceramic dental restorations. Despite its cost, a well-approved high gold alloy stills the best option in terms of longevity, functionality, aesthetics, and biocompatibility, together with ease of manufacture (Knosp et al. 2003). Also, it is no co-incidence that all testing and development of competing materials, gold is always defined as standard material to be judge against. Metal-ceramic dental restorations strongly depend on the success of the bond between porcelain and the metal substrate (Donovan and Swift 2009; Vásquez and Kimpara 2009; dos Santos et al. 2006; Liu et al. 2006; Anusavice 2003; Knosp et al. 2003; Ozcan 2003; Chang et al. 2002; Haselton et al. 2001;Kelly 1997; Shell and Drummond et al. 1984; Eames et al. 1977; Lavine and Custer 1966; Nielsen 1962;). This is achieved by attaining to the characteristics of compatibility of the materials involved, e.g. choose the metals and ceramics with the proper Coefficients of Thermal Expansion (CTEs). Despite PFM restorations longevity compared to all-ceramic restorations, clinical failures can occur and the failure rate due to fracture and exfoliation of porcelain is 59.1% of the whole clinical failure (Liu et al. 2006; Ozcan 2003).

So, there is still some work to do in increasing the bond strength between metal and ceramic.

In this study is evaluated the effect of a smooth transition, between metal and porcelain, in the bond strength of this two materials. An interlayer with mixed properties of the metal and porcelain to bond eliminates the sharp transition between them and their properties. For instance, the Young Modulus of the gold alloy and ceramco3 are different (100GPa and 83GPa, respectively) causing an elastic mismatch that can lead to the microcracks generation and finally to failure.

This study introduces powder metallurgy in dental prosthetic restorations. The tested specimens were obtained by this process since this is a rising technology in the dental prosthetic field. With the advance of medical imaging technologies, such as X-ray radiology, computerized tomography (CT), magnetic resonance imaging (MRI) and laser digitalization, is nowadays possible to have detailed three-dimensional pictures of the anatomy of the area of interest and to build a physical model of it (Liu et al. 2006). Today are already available in the market equipments that produce precious metal dental copings from metal powders (Strauss 2009). Using laser assisted methods one can achieve fully-dense parts with good mechanical properties, as well as a dynamically and continuous transition in material composition when desired. Based on this, it is relevant to introduce this new method in comparative studies since it starts to be a valid option in what concerns to dental restorative field.

Hot pressing was employed in the processing of the specimens. The appliance of pressure and temperature promotes a more intimate contact of the powders enhancing the diffusion of the elements and contributes to a better and quicker compaction, leading to the desired full densification. Also helps in the avoidance of undesired residual porosity and cracks.

The purpose of this study was to evaluate the shear bond strength of hot pressed gold dental alloy-ceramic composites, obtained by powder metallurgy (PM), when compared to conventional Porcelain Fused to Metal (PFM) restorations.

2. MATERIAL AND METHODS

For this work was used a dental gold alloy (KERAMIT 750, Nobilmetal, Villafranca d'Asti, Italy) and a dental opaque ceramic (Ceramco3, Dentsply, York, USA) (batch number: 08004925). The gold alloy was used both in powder (170 mesh) and cast form. The chemical compositions and mechanical properties of the gold alloy and opaque ceramic are presented in the tables 1, 2 and 3, respectively.

Table 1 – Gold alloy chemical composition (Wt%)

Au	Pt	Pd	Ag	In	Others
75	4,3	8,5	9	1,7	Fe, Ir

Several metal-ceramic composites specimens were produced by two routes: hot pressing and furnace firing. The specimens fired in the furnace were used as standards to be compared with those processed by hot pressing. Former specimens were obtained by fusing porcelain onto a gold alloy substrate (Porcelain Fused to Metal – PFM). Regarding hot pressing, two types of connections were made: one type consisted in hot pressing porcelain powders onto a metal substructure (Porcelain Pressed to Metal – PPM), and another type consisted in hot press porcelain powders onto metal powders previously compacted, i.e. in a green state (Porcelain Pressed to Metal Powders – PPMP).

Table 2 – Ceramic chemical composition (Wt%)

SiO_2	Al_2O_3	K_2O	SnO_2	ZrO_2	CaO	P2O5	Na2O	Others
41,3	14,5	14,0	11,9	5,8	4,1	4,1	3,0	MgO, SO3, ZnO, Cr2O3, Fe2O3, CuO, Rb2O

Another approach was tested and consisted in evaluate the effect of a metal matrix composite interlayer in the shear bond strength of a metal-ceramic composite when compared with a conventional Porcelain Fused to Metal (PFM). To identify which was the best composition for the interlayer, different composites were bonded to metal and to ceramic substrates - Pressed Metal-Ceramic Composites - PMCC) and tested.

PFM specimens were obtained through the following manner: metal bases to bond the porcelain were produced from a casted rod approximately 30 mm in length and 4mm in diameter used as a pattern. From the rod were obtained 3 bases of 3mm height. These specimens were polished with 1200-grit SiC sand-paper, ultrasonically cleaned in an alcohol bath for 10 min and rinsed in deionized water for another 10 min to remove contaminants. Then they were dried with adsorbent paper towels. No initial oxidation step was performed on the base metal specimens before applying the porcelain. Each metal base was placed in one of the holes of a special acrylic device that allowed a uniform height porcelain veneer (aprox. 4mm). To form the ceramic veneer, deionized water was added to the ceramic powder in the ratio of 2:1 (porcelain:water) creating a creamy paste which was left to condense in the acrylic device. Metal-porcelain sets were then carefully removed and sintered under vacuum (1mBar) in a furnace (Termolab, Braga, Portugal) at 970ºC at a heat rate of aprox. 10ºC/min. Power was shutted down after reaching 970ºC and vacuum removed at that point. Specimens cool down slowly inside the furnace.

In PPM specimens, ceramic powders were placed over a metallic framework, like the ones used for PFM, and hot pressed in a graphite die, in vacuum (5x10-1mbar) at a temperature of 970ºC and a constant pressure of 20 MPa. The heat rate was 60ªC/min and after reaching 970ºC, the power of the induction heating furnace was shut down and the die was left to cool down naturally.

In PPMP specimens, metal powders were first stack in a stainless steel die of 4mm of diameter at a load of 3000N to obtain a green compact. Then the green compact was inserted in a graphite die, together with the ceramic powder and both were hot pressed in the same conditions described above.

In order to obtain PMCC specimens, several different metal matrix composites were bonded by hot pressing to a green compact of a metal and to a ceramic framework. To obtain the green compact, metal powders were first stack in a stainless steel die of 4mm of diameter at a load of 3000N. The tested metal matrix composites had the following compositions [%Vol.]: 80Met20Cer; 60Met40Cer; 40Met60Cer; 20Met80Cer.

Table 3 – Base materials properties

	Density g/cm^3	Melting Range [ºC]	CTE [25-600ºC]	E [GPa]	Hardness
Keramit750 [17]	16,2	1160-1230	14,8	100	HV200 (self-hardened)
Ceramco3 Opaque	2,82		13,2	83	

In order to obtain the metal-composite specimens, composites were manually blended prior to their insertion into the graphite die where the green compact framework had been already placed. Same thing happened for the ceramic-composite specimens. Ceramic powders were previously inserted and slightly stacked in the graphite die, after which, the metal-matrix composite were putted in contact with ceramic and then hot pressed.

Processing cycle was the same used in PPM, PPMP and PMCC. The processing parameters for these routes, PPM, PPMP and PMCC, are presented in figure 1a) and hot pressing schematic in figure 1b).

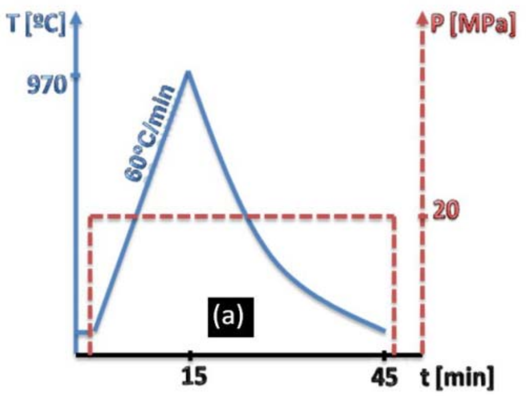

Fig. 1 a) - Temperature and pressure conditions during the hot pressing cycle.

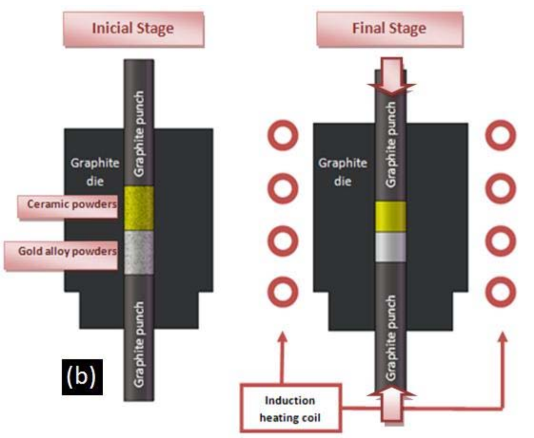

Fig. 1 b) – Hot pressing apparatus. Hot pressing schematic.

2.1. Shear tests

The shear bond strength tests were carried out at room temperature and performed in a universal testing machine (Instron 8874, MA, USA), with a load cell having 25 kN capacity and under a crosshead speed of 0.5mm/s.

Tests were performed in a custom-made stainless steel apparatus consisting in two sliding parts A and B (Figure 2 a) , which one with a hole perfectly aligned to the other. After alignment of the holes, the specimen (figure 2b) is inserted into it and the specimen's interface is moved to the sliding plane with the help of the adjusting screws. A compressive force is then applied in the upper side of part B until fracture occurs due to shear loading. The shear bond strength (MPa) was calculated by dividing the highest recorded fracture force (N) for the area of adherent porcelain (mm^2).

2.2. Analysis of a gold alloy-ceramic interface

The metal-ceramic interface as well as representative fracture surfaces were evaluated by stereomicroscope (SMZ-2T, Nikon, Japan), optical microscope (Axiotech, Carl Zeiss, USA) and SEM/EDS (Nova 200, FEI, Oregon, USA). For interface analysis, the specimens were embedded in auto-polymerizing resin, ground finished to 1200 grit SiC sand-paper and polished with diamond paste first in 6µm and finally in 1µm felt disc. Morphology and chemical analysis were carried out. The interface chemical analysis was made by the means of 20 perpendicular to the interface points allowing to obtain the chemical composition profile through the interface, comprising metal, interfacial zone and ceramic. Of these 20 aligned points, 10 were in the metal zone and 10 in the ceramic zone.

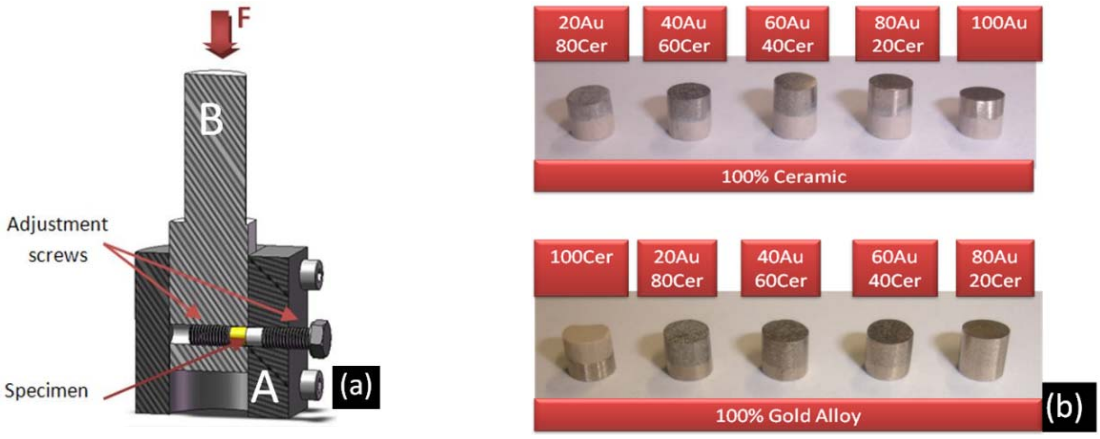

Fig. 2 – Test apparatus. (a) Cross-section schematic of the shear test device (b) Specimens: composites bonded to ceramic and metal frameworks

3. RESULTS

Shear bond strength of tested specimens are presented in table 4 for sharp transition methods and figure 3 for smooth transition in the interface. Conventional PFM results appeared in line with the upper range of literature data (83±14 MPa) for gold alloys-ceramic composites (Drummond et al. 1984). For both PPM and PPMP processing techniques there is a significant increase of the shear bond strength values (120±25.5 MPa, 128.5±4.9 MPa, respectively) highlighting the effect of the process parameters temperature (T), pressure (P) and roughness (R) in the interface.

Table 4 – Results for metal-ceramic sharp transition methods

Bonding Methods	Shear bond Strength [MPa]	Standard Deviation
PFM	83,7	14,0
PPM	120	25,4
PPMP	128,5	4,9

Highest values, thought, were registered for PMCC (>200), where shear bond strength reached values approximately 3 times higher than those registered in the conventional PFM. The highest values were registered for the 60Met40Cer and 40Met60Cer composites composition with preponderance to the second one. This composite exhibited a shear bond strength of 235.1±13MPa when bonded to ceramic and a 217±27.9MPa shear bond strength when bonded to metal, revealing that the best results are achieved for composites with similar quantities of metal and ceramic.

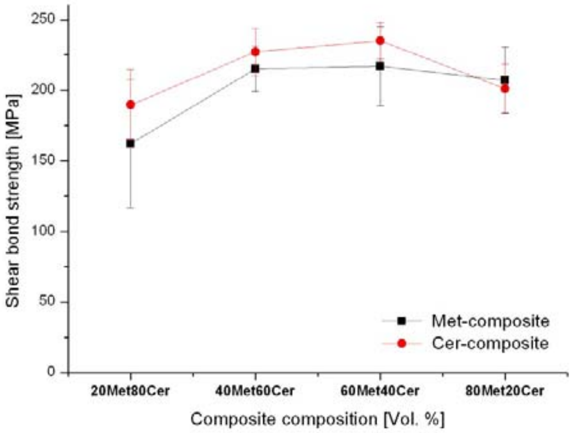

Fig. 3 - Shear bond strength results for the metal and ceramic bonding to different metal-matrix composites (PMCC).

The specimens were classified under their failure type as adhesive or cohesive. The PFM specimens exhibited a mixed-failure mode. Some remnants of ceramic were present at the fracture surface of these specimens.

All other specimens showed adhesive failure with no remnants of ceramic in the surface.

Figure 4 illustrates the metal/ceramic interface and line a-b through which the EDS analysis was made for a PPMP specimen. In this picture is possible to distinguish two different phases in the diffusion zone of the metal side. The darker phase (zone 1) is rich in O, Pd, In, Sn and Pt while the lighter phase (zone2) is rich in Au, Ag and Pd. In the porcelain side, the darker phase is mainly SiO_2 and the lighter one is mainly $SnO_2$and Al_2O_3. These results are presented in table 5.

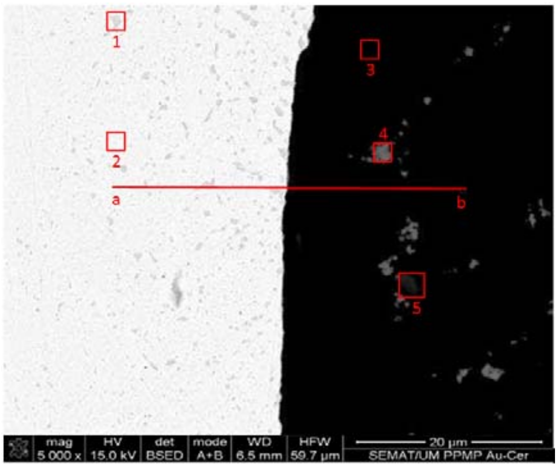

Fig. 4 – EDS line analysis of metal/ceramic interface processed by the PPMP technique.

Results of the EDS analysis have shown the interdiffusion of atoms occurring during firing for some elements. Elements constituting the gold alloy (e.g. Au, Pt, Pd, Ag and In) barely or nothing diffuse into porcelain. On the other hand, we assisted to an extensive diffusion of almost all elements of the porcelain (e.g. O, Sn, Al, Si, Ca, Na and K) with special relevance to the O_2 detected in a higher concentration.

Since PPM, PPMP and PMCC had the same hot pressing cycle, this data refers to both processes. These results are also applicable to the case of PFM specimens but one should take into account that, despite of the fusing temperature had been the same (970ºC), both heating and cooling rate were slower, allowing more time for elements to diffuse in the latter case.

Table 5 – Elemental composition (wt.%) of different phases present in metal and ceramic

Points / Elem.	Metal		Ceramic		
	1	2	3	4	5
Au	39,46	84,66	0,00	0,00	0,00
Pd	15,62	7,34	0,14	0,00	0,00
Pt	24,06	0,00	0,13	0,00	0,00
Ag	3,34	8,00	0,09	0,00	0,00
In	2,70	0,00	0,08	0,00	0,00
O	2,96	0,00	71,25	44,43	46,30
Si	0,00	0,00	16,82	8,00	15,74
Al	0,00	0,00	4,31	1,97	1,54
K	0,00	0,00	2,43	1,43	1,77
Sn	6,87	0,00	0,92	40,98	8,35
Zr	0,00	0,00	0,06	0,00	24,57
Ca	0,00	0,00	0,47	1,28	0,49
P	5,00	0,00	0,00	0,00	0,00
Na	0,00	0,00	1,94	1,91	1,24

4. DISCUSSION

This study focuses the enhancement of metal-ceramic bonding strength for different joining techniques. Conventional and hot pressed bonding methods were tested and compared.

The gold alloy used in the study was Keramit 750 (Au-Pd-Pt), a 18ct dental gold alloy (table 1). It's a type 2 alloy (ISO 1562:1995). Every alloying element plays a specific role in the alloy. The significant presence of Pd and Pt in this alloy, contributes for a considerable solution hardening and leads to a widening of the separation between the solidus and the liquidus line of the solid solution phase diagram. These elements also increase the melting point and recristalization temperature of gold alloys, a fact that is important for metaloceramic restorations.

The presence of In is to improve bonding strength between porcelain and metal and the mechanic properties of the metallic framework (Hautaniemi 1995; Liu and Wang 2007; Fisher 2002).

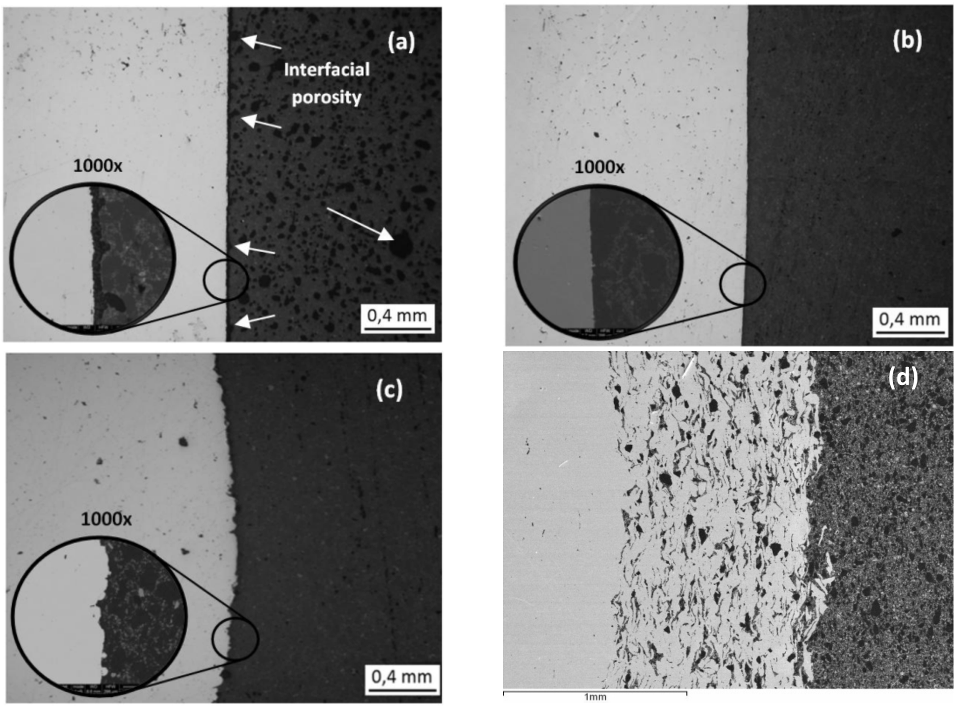

Fig. 5 – Interface appearance for PFM (a), PPM (b) and PPMP (c) specimens. High porosity in the ceramic side and interface at PFM technique a). Interlayer 50Met50Cer (d).

The rest of elements such as Fe and Ir is for grain refinement and thus mechanical improvement too. Bonding between gold alloys and feldspatic porcelains generally presents higher bonding strength than base metal alloys and feldspatic porcelain. Moreover, a well-approved high gold alloy still the best option in terms of longevity, functionality, aesthetics, and biocompatibility, together with ease of manufacture (Knosp et al. 2003). Ceramco3 Opaque was the chosen ceramic to carry out this study due to its overall good mechanic properties (Rizkalla and Jones 2004) traduced in a good adhesion to gold dental alloys (Vásquez and Kimpara 2009; Drummond et al. 1984;Shell and Nielsen 1962).

The results obtained for the PFM standard specimens were in line (~80 MPa) with other data taken from the literature, showing a good adhesion between the metal and ceramic. Hot pressing obtained specimens exhibited increased bond strength, relatively to PFM specimens, in a magnitude of approximately 50%. This highlights the influence of the simultaneously application of pressure and temperature in the process which promotes a more intimate contact between the materials to bond, enhancing diffusion mechanisms and avoiding undesired interface defects like porosity and cracks. Figure 5 a) to c) shows the interface aspect for the three types of joining tested techniques where is possible to see the improvement on the interface quality for hot pressed specimens relatively to conventional PFM ones.

Comparing the PPM and PPMP techniques, the slightly higher bond strength and lower results dispersion values found in PPMP specimens can be explained by an increased roughness of the surface (**PPM**: R_a = 0,7μm; **PPMP**: R_a = 6,8μm), which contributes to a better mechanical interlocking and to a higher adhesion surface area (see figure 5c). This interface roughness is a consequence of the joining technique which allows interpenetration between the metal and ceramic powders during the pressing step. Although chemical bonding is regarded to be the responsible for metal-ceramic adherence, mechanical interlocking plays also an important role in the bonding

process.

There is no consensus about the magnitude of this role, but there is no doubt about the importance of this mechanism (Lavine and Custer 1966). In this work an improvement of ~7% was obtained between the samples processed from PPMP and PPM techniques. According to literature (Shell and Nielsen 1962), increased surface roughness also leads to a better wetting of the metal by the molten ceramic enhancing the diffusion reactions between both parties. The arithmetic roughness values (R_a) were obtained based on the analysis of the micrographs of the two kinds of specimens using the expression (1).

$$R_a = \frac{1}{n}\sum_{i=1}^{n}|y_i| \qquad (1)$$

Regarding fracture type for the tested specimens, analysis of the fracture surfaces revealed two types of failure modes: mixed failure and adhesive failure. PFM specimens showed mixed failure mode, partly adhesive in the interface and partly cohesive with some remnants of porcelain at the fracture surface. In PPM and PPMP specimens exhibited adhesive failure, ie, no remnants of ceramic can be found in the metallic surface. This means that the bonding of the metal to the substrate was not as effective as the cohesive strength of the ceramic. This is a typical mechanism failure of ceramic when bonded to noble alloy substrates (dos Santos JG et al. 2006; Haselton et al. 2001; Eames et al. 1977).

Results registered for PMCC specimens were well superior to those registered for PFM, PPM and PPMP specimens. From figure 3 is possible to see that the range of results goes from ~160 to 230 MPa, to Cer-Composite(20Met80Cer) and Met-Composite(60Met40Cer), respectively. Composites, regardless of their composition, showed a generally better adhesion to ceramic substrate than to a metal one. The highest values were registered for the 60Met40Cer and 40Met60Cer composites composition with preponderance to the second one. This means that the best results are obtained for composites with a composition of similar metal/ceramic quantities. This higher bond strength results are explained for the same reasons of PPM and PPMP and additionally by the smooth transition of materials properties along the interface. The smooth transition in the case of 40Met60Cer composite is responsible for an improvement of 70% in bond strength, relatively to PPMP specimens, and 160% relatively to the conventional PFM (with no roughness nor pressure). In a conventional PFM restoration, there is a sharp transition between metal and ceramic which induces a properties mismatch (E, hardness, chemical composition, etc) between materials involved. A Young Modulus mismatch cause different elastic behaviors of the two materials in the interface, upon loading, that can cause failure of the system. Using a composite interlayer, composed by the two materials to bond (metal+ceramic), we are introducing in the interface a material that has mixed properties between metal and ceramic ones.

This study shows the importance of using pressure combined with temperature in the improvement of bond strength between metal and porcelain. If we add to these factors an intentionally rough surface of a powder metallurgy obtained part (Strauss 2009) then we can increase this strength even more. Combining all these aspects in an interlayer that allows a smooth interface between metal and ceramic (figure 5 d), the bond strength comes maximized.

As fatigue is also a requirement for these applications, future studies will include mechanical fatigue, preferably in a wet environment, since it better reproduces the clinical behavior.

5. CONCLUSIONS

From this study, the following conclusions can be drawn:

1. Generally, Ceramco3 opaque presents a very good adhesion to Keramit750.
2. PPM and PPMP techniques showed a great improvement in metal-ceramic bond strength (~50%), showing the positive influence that hot pressing can have in the enhancement of the metal-ceramic adhesion, with a slight contribution of the interface roughness in the case of PPMP.
3. Metal matrix composites showed better bond strength to metal and to ceramic frameworks than those observed in a sharp transition between metal and porcelain.
4. A composite interlayer, in the metal-ceramic bonding, can enhance the bond resistance in 160% relatively to a conventional PFM.
5. Powder metallurgy based dental restoration appears to be a feasible method and can, inclusively, produce better results than those obtained by other methods.

6. ACKNOWLEDGEMENTS

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