Optimization of bond strength between gold alloy and porcelain through a composite interlayer obtained by powder metallurgy

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1. Introduction

Metal–ceramic restoration, in the dentistry field, is still the most reliable method in dental prosthetics, especially when a good adhesion of the ceramic to the metal substrate is achieved [1]. The recent trend for all ceramic restorations do not accomplish, yet, for the necessary longevity and clinical failure is often reported prematurely [2,3]. Despite its cost, within the available metals used in PFM restorations, a well-approved high gold alloy is still the best option in terms of longevity, functionality, aesthetics, and biocompatibility, together with ease of manufacture [4]. Also, it is no coincidence that in all testing and development of competing materials, gold is always defined as standard material to be judge against. Therefore, for this study was used a high gold content dental alloy (Keramit 750, Nobilmetal, Villafranca d’Asti, Italy). Nevertheless, with the recent increase in gold’s price, reduced-gold content and Palladium-based dental alloys are becoming very popular. Also, in some particular economic contexts, base metal alloys constitute the solutions for low cost dental restorations.

As referred above, metal–ceramic dental restorations strongly depend on the success of the bond between porcelain and the metal substrate [1–14]. This is achieved by attaining to the characteristics of compatibility of the materials involved, e.g. choose the metals and ceramics with the proper CTEs (coefficient of thermal expansion). Using metals and ceramics with different CTEs, means that when cooling down from processing (sintering) temperature, both materials will contract at different rates and strong residual stresses will form across the interface. Depending on their magnitude, these stresses can lead the ceramic to crack or even to separate from the metal substructure. Despite PFM restorations longevity, when compared to all-ceramic restorations, clinical failures sometimes occur and the failure rate, due to fracture and exfoliation of porcelain, represents 59.1% of the whole clinical failure [7,8]. In this study, it is proposed the presence of a composite interlayer in the metal–ceramic interfacial zone. This interlayer will eliminate the sharp transition between the materials and, consequently, of their properties. For instance, the Young Modulus of the gold alloy and Ceramo3 are different (100 GPa and 83 GPa, respectively) causing an elastic mismatch that can lead to the microcracks generation and finally to failure.

The specimens produced for this study were obtained through the hot pressing powder metallurgy (PM) technique. Powder metallurgical (PM) processing was the chosen route in this study because of the ease in controlling the composition and microstructure, as well as shape forming of the specimens. Hot pressing allowed avoiding undesired residual porosity and small cracks, together with a better and quicker compaction and full densification. PM used in rapid manufacturing, in the dentistry field, is starting to

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Table 1
Gold alloy chemical composition (Wt%).

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>Pt</th>
<th>Pd</th>
<th>Ag</th>
<th>In</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>75</td>
<td>4.3</td>
<td>8.5</td>
<td>9</td>
<td>1.7</td>
<td>Fe, Ir</td>
</tr>
</tbody>
</table>

Table 2
Ceramic chemical composition (Wt%).

<table>
<thead>
<tr>
<th></th>
<th>SiO2</th>
<th>Al2O3</th>
<th>K2O</th>
<th>SnO2</th>
<th>ZrO2</th>
<th>CaO</th>
<th>P2O5</th>
<th>Na2O</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>41.3</td>
<td>14.5</td>
<td>14.0</td>
<td>11.9</td>
<td>5.8</td>
<td>4.1</td>
<td>4.1</td>
<td>3.0</td>
<td>MgO, SO3, ZnO, Cr2O3, Fe2O3, CuO, Rb2O</td>
</tr>
</tbody>
</table>

The processing of the metal-composites comprised three steps: first, a metal green compact was produced through the pressing of metal powders in a stainless steel die with 4.5 mm of diameter under a load of 3000 N; the second step consisted in producing the composites, blending the proper metal/ceramic powders ratio in a rotary machine at 40 rev/min for 10 min; the final step consisted in inserting both metal green compact and composite powders in the graphite die for hot pressing (Fig. 1a). A similar procedure was used in the manufacturing of ceramic-composite specimens, though with a slight difference. Instead of being pressed separately in a stainless steel die, like in metal powders, ceramic powders were initially stacked in the graphite die. After that, composite powders were also inserted into the graphite die and then the set was hot pressed (Fig. 1a and b). Hot pressing was performed in vacuum (5 × 10⁻⁴ mbar) till a temperature of 970 °C (as suggested by the ceramic supplier technical data for the porcelain) and at a constant pressure of 20 MPa. The heat rate was approx. 60 °C/min and after reaching 970 °C, the power of the induction heating furnace was shut down and the die was left to cool down naturally (Fig. 1c).

2.3. Shear tests

The test selected to assess metal-composite and ceramic-composite (Fig. 2a) bond strength was the shear test due to its recognized reliability based on minimal experimental variables and lower residual stresses induced at metal–ceramic interface [1]. Minimum acceptable values for metal–ceramic bond strength are present in standards ANSI/ADA Specifications N 38 (2000) and ISO Standard 9693 (1999), and is indicated as 25 MPa. This value refers to a three-point bending test that measures bond strength. Due to geometrical differences of the specimens used in both tests (shear and three-point bending), no direct comparison should be made of the results of different tests.

Shear bond strength tests were carried out at room temperature and performed in an universal testing machine (Instron 8874, MA, USA), with a load cell having 25 kN capacity and under a crosshead speed of 0.5 mm/s. Tests were performed in a custom-made stainless steel apparatus consisting in two sliding parts A and B (Fig. 2b), each one with a hole perfectly aligned to the other. After alignment of the holes, the specimen 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 a fracture occurs due to shear loading. Shear bond strength (MPa) was calculated by dividing the highest recorded fracture force (N) by the area of adherent composite (mm²).

3. Results

Shear bond strength for PMCC (pressed metal–ceramic composites), specimens are presented in Fig. 3 and exhibited a range of values between 162.1 ± 45.4 MPa and 235.1 ± 13.0 MPa. The 20Met80Cer composite bonded to the metal base showing a shear bond strength of 162.1 ± 45.4 MPa whereas when bonded to the ceramic substrate showed a strength of 189.7 ± 24.8 MPa. In the case of 40Met60Cer and 60Met40Cer results obtained were quite similar being slightly higher in the latter case. 40Met60Cer composite exhibited a shear bond strength of 215.1 ± 13.0 MPa, whereas when bonded to a metal substrate and 227.1 ± 16.7 MPa when bonded to a ceramic one. Regarding 60Met40Cer composite the values recorded are already available commercial equipments that produce precious metals dental copings using PM. Using laser assisted methods one can achieve fully dense parts with good mechanical properties, as well as a dynamic and continuous transition in material composition when desired. This leads to a smooth transition in materials properties, e.g. Young Modulus, thus reducing or even avoiding critical stress concentrations in the component. Some work has been reported in multi-material dental restoration using laser assisted densification of powders [15], although no actual fabrication of dental prostheses has been reported yet.

The purpose of this study was to determine whether the use of a metal–ceramic graded interface would result in a more resistant one compared with the conventional sharp transition interface or not. So, studies were performed to find which was the best composition of the interlayer composite that simultaneously best adhered to ceramic and to the metal substrate, resulting in an enhanced mechanical strength metal–ceramic interface. Once the ideal composition for the interlayer was identified, some metal/interlayer/ceramic specimens were produced and tested with encouraging results.

2. Materials and methods

The compositions of the dental gold alloy (Keramit 750, Nobilmetal, Villafranca d’Asti, Italy) and the dental opaque ceramic (Ceramco3, Dentsply, York, USA) (batch number: 08004925) used in this study are presented in Tables 1 and 2, respectively, as obtained from supplier catalogues. The gold alloy was used in irregular powder form, with dimensions of 170 mesh. The chemical compositions of the gold alloy and opaque ceramic are presented in Tables 1 and 2, respectively, as well as their mechanical properties in Table 3.

2.2. Processing

In order to obtain PMCC (pressed metal–ceramic composites), which is the designation for our obtained specimens, several different metal–ceramic composites were bonded by hot pressing them to a metal green compact and to a ceramic framework.

Tested composites had the following compositions [%Vol.]: 80Met20Cer; 60Met40Cer; 40Met60Cer; 20Met80Cer.

Table 3
Base materials properties.

<table>
<thead>
<tr>
<th></th>
<th>Density g/cm³</th>
<th>Melting range [°C]</th>
<th>CTE [25–600 °C]</th>
<th>E [GPa]</th>
<th>Hardness</th>
</tr>
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<tbody>
<tr>
<td>Keramit750 [17]</td>
<td>16.2</td>
<td>1160–1230</td>
<td>14.8</td>
<td>100</td>
<td>HV200(self-hardened)</td>
</tr>
</tbody>
</table>

in the shear test were $217.0 \pm 27.9$ MPa in the connection to the metal and $235.1 \pm 13.0$ MPa in the connection to the ceramic substrate. Finally, the shear bond strengths registered for 80Met20Cer composite were $207.2 \pm 23.3$ MPa and $201.1 \pm 17.6$ MPa to metal and ceramic substrates, respectively.

The analysis of the fracture surfaces of PMCC (pressed metal–ceramic composites) specimens showed remnants of the interlayer composites in all tested specimens. After these tests, and attending to the results obtained (Fig. 4), some metal-composite–ceramic specimens (Fig. 4a) were produced using a 50Met50Cer composite interlayer and tested like all

![Fig. 3.](image) Shear bond strength results for the metal and ceramic bonding to different pressed metal–ceramic composites (PMCC) and comparison to alternative processing methods [24].

![Fig. 4.](image) Cross section view of metal–ceramic specimen’s with 50Met50Cer composite interlayer. (a) Fracture zone showing remnants of the composite interlayer in the metal surface. (b) Schematic of the specimen’s cross-section.
the other specimens before. To produce these specimens, a small amount (enough to produce an approx. 0.5 mm interlayer) of pre-mixed metal–ceramic powders were placed on the metal green compact, previously inserted in the graphite die, and stacked to turn the layer uniform. Ceramic powders were then inserted in the graphite die, and the set was hot pressed in the conditions described in Section 2.2.

Shear bond strength obtained for 50Met50Cer composite interlayer specimens was 201.8 ± 11.4 MPa. The fracture typology observed for these specimens exhibited the same behavior registered before for the other tested specimens, with remnants of the composite interlayer in both metal and ceramic substrates (Fig. 4b).

Fig. 5 presents a SEM/EDS analysis of the metal–ceramic interface [27]. Inter-diffusion of some elements was verified between the two materials. Elements constituting of the gold alloy (e.g. Au, Pt, Pd, Ag and In) were found in the vicinity of the interface, and stacked in a very small range (Fig. 5a). On the other hand, elements of porcelain (e.g. O, Sn, Al, Si, Ca, Na and K) were the ones that diffused the most and with the biggest range. A remark should be made relatively to Oxygen, which was the ceramic's element with the highest concentration found in metal's side (Fig. 5b).

4. Discussion

4.1. Materials

This study aims to evaluate the influence, in bond strength, of a composite in the interface of a gold alloy–porcelain restoration. Keramit 750 is a gold based alloy with several elements (Pd, Pt, In, Fe and Ir), each of them playing different roles. The significant presence of Pd and Pt 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 are also used to decrease the melting point and recrystallization temperature of gold alloys, an important fact in metaloceramic prosthetics. This alloy also contains In in its composition which is used to improve the bonding strength between porcelain and metal, and the mechanic properties of the metallic framework [20–22]. Elements like Fe and Ir help in grain refinement and consequently, mechanical properties enhancement. As reported in the literature [1,3,5,6,12,13] dental restorations involving gold alloys present more longevity than others performed with base materials (CoCr and NiCr alloys).

Due to its mechanical properties as well as its good adhesion to dental gold alloys [18], Ceramco3 Opaque was the selected porcelain to carry out this study [1,5,6].

4.2. Metal–ceramic sharp transition vs smooth transition

Reporting to a previous study [24], hot pressing (pressure + temperature) proved to enhance, in over 50% (up to 120 ± 25.4 MPa), the bond strength between this gold alloy and porcelain relative to a conventional PFM (porcelain fused to metal) (83.7 ± 14.0 MPa) (PFM is a firing process without pressure). This was explained by a more intimate contact between the materials to bond, due to pressure, leading to an enhancement of diffusion mechanisms and avoidance of undesired interface defects like porosity and cracks.

The increase on the surface roughness also proved to positively influence the metal–porcelain bonding strength (128.5 ± 4.9 MPa). In this case, an approximately 7% higher bond strength was registered for a 10 times higher surface roughness. Surface roughness contributes to a better mechanical interlocking and to a higher adhesion surface area. This means that when one combines temperature with pressure and surface roughness the bond strength of metal–ceramic composite is highly improved.

Based on these outputs, the presence of a smooth interface between metal and ceramic was considered and studied, through the use of a metal–ceramic composite interlayer. Fig. 6 is an example of a metal–ceramic smooth transition using a 50Met50Cer composite interlayer. The interlayer was obtained by powder metallurgy technique, which is a very simple way to tailor a metal–ceramic composite through the blending of differ-
ent volume fractions of the desired materials for the interface [15,25–28].

In a conventional PFM (porcelain fused to metal) restoration, there is a sharp transition between metal and ceramic which induces a properties mismatch (Young Modulus, hardness, chemical composition, etc.) between materials involved. A Young Modulus mismatch causes 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, thus avoiding a sharp transition of material properties. This feature is something that nature already provides for natural teeth in dentin–enamel-junction (DEJ), for instance. Dentin and enamel are the two materials that constitute natural teeth. Enamel with ∼65 GPa Young’s Modulus and dentin with ∼20 GPa Young’s Modulus are bonded by DEJ. In DEJ, the Young’s Modulus changes linearly from that of enamel to that of dentin reducing dramatically the stress in the enamel or crown layer [29]. The use of a functionally graded material (FGM) layer between ceramic crowns and cements proved to significantly reduce interface stresses between crown and cement [29]. Stresses are regarded to be responsible for many dental restorations failures (dental ceramic + cement) mainly due to sub-surficial radial cracks [30,31].

Shear strength results registered for PMCC (pressed metal–ceramic composites) specimens were substantially higher than those referred in literature for sharp transition interfaces [24] even when hot pressed techniques are employed [1,5–7,11,22–24]. From Fig. 3 it is possible to see that the range of results go from ∼160 MPa 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.

The higher bond strength results obtained in PMCC (pressed metal–ceramic composites), relatively to PPMP (porcelain pressed to metal powders), are explained by the introduction of the smooth transition zone between the base materials. This allows a smooth transition of the materials’ properties along the interface (Fig. 6). Stresses in the interface are also very different from a conventional PFM (porcelain fused to metal) and PPMP (porcelain pressed to metal powders) restoration, as indicated in Fig. 7. A smooth transition, instead of a sharp one, provided by the presence of a composite interlayer allows a reduction of stress mismatch in the vicinity of the interface (obtained by the combined effect of the reduction of the stress maximum level obtained at sharp interface (τ₂ < τ₁ in Fig. 7) and by the distribution of the developed stresses by a higher volume of material).

Also, the presence of a composite interlayer increases the bonding area between the two materials.

4.3. Toughening mechanisms of the metal–ceramic composite interlayer

In fact the metal–ceramic composite interlayer is nothing more than a metal matrix composite (MMCp). It is generally recognized that two types of strengthening may occur in MMCp: direct and indirect [32]. Direct strengthening results from load transfer from metal matrix to the reinforcing particles (phase) whereas indirect strengthening results from the influence of the reinforcement on matrix microstructure or deformation mode. Therefore, strain hardening phenomena might be occurring in the metal and the restriction to its plastic deformation due to the presence of ceramic particles (enhancing mechanical resistance). Simultaneously, the presence of a metal phase surrounding the ceramic phase avoids a premature fracture of ceramic particles due to the capacity of the metal to accommodate their strain. Considering Fig. 4, the increase of the shear strength from composition 20Met80Cer to 50Met50Cer is explained by the increase of the metal phase with the hardening effect being predominant. From the 80Met20Cer to 50Met50Cer, the increase in ceramic particles is responsible for the deformation constraint of the metal phase, leading to increased shear strength.

In MMCp toughness depends on a complex interaction between the constituent phases. Fracture toughness is a measure of resistance to crack propagation. When a crack propagates through a particulate reinforced composite there are many mechanisms which may, to a larger or smaller extent, hinder the crack growth (Fig. 8). Each of these mechanisms absorb energy, whereby requiring more work to be done by the external load [33]. They are: (1) deformation within plastic zone, (2) formation of voids along fracture surface, (3) fracture of reinforcement particles along crack.
path, (4) interfacial separation between matrix and reinforcement, 
(5) fracture of reinforcement with plastic zone, (6) tortuous fracture 
path, increasing fracture surface area and (7) matrix crack near, but 
not continuous with the main crack.

Detrimental effects of an increased amount of metal–ceramic 
interface, like fragile intermetallic phases, porosity, stress concen-
tration, etc., must also be considered. However, obtained results 
show that these effects are not predominant for the studied 
metal–ceramic system.

The analysis of the fracture surfaces of PMCC (pressed 
metal–ceramic composites) specimens showed remnants of com-
posites in all tested specimens which indicates a good adhesion 
of the composites to the substrates, whether they are metal or 
ceramic.

With the introduction of the transition zone, in the case of 
40Met60Cer composite, there was an improvement of 70% in bond 
strength, relatively to results obtained for hot pressed specimens 
with metal–ceramic sharp transition, and 160% relatively to the 
conventional PFM (porcelain fused to metal) [24].

Attaining to experimental results presented in Fig. 4, one can 
conclude that shear bond strength is maximized for composites 
with similar metal:ceramic [%Vol.] content. Hence, several metal 
ceramic specimens were produced with a 50Met50Cer composite 
interlayer. Shear strength results obtained were very promising 
(201.8 ± 11.4 MPa) proving that the interlayer had the expected 
effect of improving metal/ceramic bond strength. The fracture zone 
of the specimens showed remnants of the interlayer’s composite 
(Fig. 4) as observed previously for metal–composites and ceramic-
composites specimens. Composites showed, once more, a very good 
adhesion to metal and to ceramic substrates.

4.4. Practical application

In what concerns to practical application of the outputs of this 
study, a method that can be used to create a composite interlayer in 
a metal ceramic interlayer is painting the metal framework with a 
slurry of blended metal and ceramic powders prior to the ceramic 
veneering. This can be done using the traditional PFM (porcelain 
fused to metal) technique. However, in order to reduce the inter-
face defects (porosity, microcracks, etc.), it can be used a uniform 
pressure during sintering. Therefore, it might be used a laboratorial 
Hot Isostatic Pressing (HIP) furnace using inert gas, such as argon.

Another approach is using rapid manufacturing (RM) tech-
niques. Recently, great advances in RM of dental prostheses using 
powder metallurgy have been made, and the commercial manu-
facturing of multi-material parts is not very far in time. It has 
already been developed multi-material laser-assisted densification 
processes for dental restorations, in which dental restorations are 
built with powders (dental alloy and porcelain) delivered by slurry 
extrusion, followed by laser densification of these extruded slurries 
[34–37]. Because this is a layer-by-layer process, it can be easily 
used to create the complete coping with a metal base, followed by 
a composite interlayer and finally the ceramic veneer. All this can 
be done with no human intervention, once it is produced directly 
from a computer model.

5. Conclusions

From this study, the following conclusions can be drawn:

1. The metal–ceramic composites showed better bond strength to 
metal and to ceramic frameworks than those observed in a sharp 
transition between metal and porcelain. Improvements in bond 
strength can reach 160% when compared with a conventional 
PFM;

2. Powder metallurgy based dental restoration appears to be a fea-
sible method and can, inclusively, produce better results than 
those obtained by other methods.

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