SEM ANALYSIS ZIRCONIA-CERAMIC ADHESION INTERFACE

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SUMMARY
Objectives. Modern dentistry increasingly tends to use materials aesthetically acceptable and biomimetic. Among these are zirconia and ceramics for several years, a combination that now has becoming synonym of aesthetic; however, what could be the real link between these two materials and especially its nature, remains a controversial topic debated in the literature. The aim of our study was to "underline" the type of bonding that could exist between these materials.
Materials and methods. To investigate the nature of this bond we used a SEM microscopy (Zeiss SUPRA 25). Different bilaminar specimens: "white" zirconia Zircodent® and ceramic "Noritake®", after being tested with loading test in bending (three-point-bending) and FEM analysis, were analyzed by SEM. Fragments' analysis in closeness of the fracture's point has allowed us to be able to "see" if at large magnifications between these two materials, and without the use of linear, could exist a lasting bond and the possible type of failure that could incur.
Results. From our analysis of the specimens' fragments analyzed after test Equipment, it is difficult to highlight a clear margin and no-adhesion zones between the two materials, although the analysis involving fragments adjacent to the fracture that has taken place at the time of Mechanical test Equipment.
Conclusions. According to our analysis and with all the clarification of the case, we can assume that you can obtain a long and lasting bond between the zirconia and ceramics. Agree to the data present in the literature, we can say that the type of bond varies according to the type of specimens and of course also the type of failure. In samples where the superstructure envelops the ceramic framework Zirconium we are in the presence of a cohesive failure, otherwise in a presence of adhesive failure.

Key words: sem-analysis, zirconia, adhesion, interface, failure, ceramic.

Introduction

The modern dentistry increasingly tends to be associated with the physical characteristics of the materials used also aesthetic needs. In the aesthetic areas have almost disappeared traditional metal-ceramic crowns. Passage of time here it is from traditional materials with time spent in new, so to speak, materials such as zirconia. Roe Garvin, who first tried to rationalize the characteristics of this material, called it in his famous 1979 "Ceramic-stell". Since then, several researchers of international caliber have described the various features in an increasingly detailed such us: Picconi and Maccauro, Chevalier et al., WF Smith, Denry, etc. The qualities of this material are different: the ability to self toughing at different stages, the large flexural capacity and biomimetism, however the bond that this material may establish with the ceramic remains a moot point. A lot manufacturers associated with the presence of a liner or a means adhesive whenever it wants to establish a long and lasting bond between the ceramic and zirconia. Some findings have revealed failures at 8% of the dental porcelain-to-zirconia interfaces over a period of 36 months compared with 13% over 38 months (1, 2). Another study revealed failures at 15% of the dental porcelain-to-zirconia interfaces over a period of 24 months and 25% over 31 months (3). However, a low failure rate (2.7-

5.5%) has been revealed for metal-ceramic systems over periods of 10 and 15 years (4, 5). Above all it is certainly to investigate the failure mode that incurs the system: if it is of type adhesive or cohesive. Researchers experts in the field such Aboushelib et al. (12) evaluating the bond between core-veener, compare a method for each veener, with a manual layering, obtained significant differences; however SEM studies of these structures show that the structures to CAD, are subject to a cohesive failure, while the structures subjected to a manual layering have a failure mainly in the interface. The CAD method, in this study, shows that the two materials fail to provide a good interface, while a manual stratification demonstrates the presence of bubbles. Aboushelib et al. (2009) (13), re-evaluating the link between a core zirconia and veneers, confirm the data of the previous year, highlighting the possibility of bubbles in a structure to CAD.

SEM

The Scanning Electron Microscopy (SEM) has becoming a technical investigation of the most modern and avant-garde that finds application in many areas of materials science.
The principle on which it is based is to send a beam of primary electrons of known intensity of a sample conductor and gather, by appropriate scanning on the corresponding area is selected by the magnification operator, the image of two-dimensional and enlarged of the same surface, by converting the signal, by means of suitable detectors, the various phenomena resulting (emission of secondary electrons, back-scattering of the primary electrons, cathodoluminescence, etc.). These signals are then reproduced on a screen which cathode electron beam must be in phase with that of the SEM column, or sometimes are reprocessed using appropriate software packages to obtain chemical data quality or quantity. The image that are obtained have an excellent depth of field (a wide range of distances around the focus of the image, where it is still clear because the blur is imperceptible or at least tolerable), for which one can observe in detail the surface roughness, the morphological characteristics of a single element or crystal and the cavities of the surface.
The scanning electron microscope is an electro-optical instrument; essentially consists of a vacuum chamber and an electron gun that produces a thin beam of electrons of high energy (8).

Material and methods

According to ISO 6872 we prepared 12 bars zirconia-ceramic, (Ceramic-Noritake ® Czr) (zirconium-Zircodent®); the choice of this legislation was not casual but dictated by two reasons: the first one was an indication of the producer company (Zircodent®) specifying this legislation, as a reference; the second reason was that alternative such regulations 9693 (2001), have prevented us obtaining specimens that could respond to the excellent technical requirements under test Equipment. In fact, we made the specimens according to standard 9693, although of different colors, have undergone a considerable bending stress during sintering, which made them unusable.

Synthesis of specimens

First phase - CAD design specimens (Figure 1).
Section of the sample (Figure 2): c = chamfer: 0.09 to 0.15 mm;
Zr Thickness: 1.5mm b = height: 3.0 +/- 0.2 mm;
Ceramic thickness: 1.5mm l = length: 40.0 mm.
Second phase - implementation according cad-cam technology of zirconia samples (Figure 3): length 40mm, width 4mm, 1.5m thick, with rounded corners at the base according to ISO 6872.
Third phase - sintering of samples and size control. According to the information of the parent company structure milled shrinks by about 20%

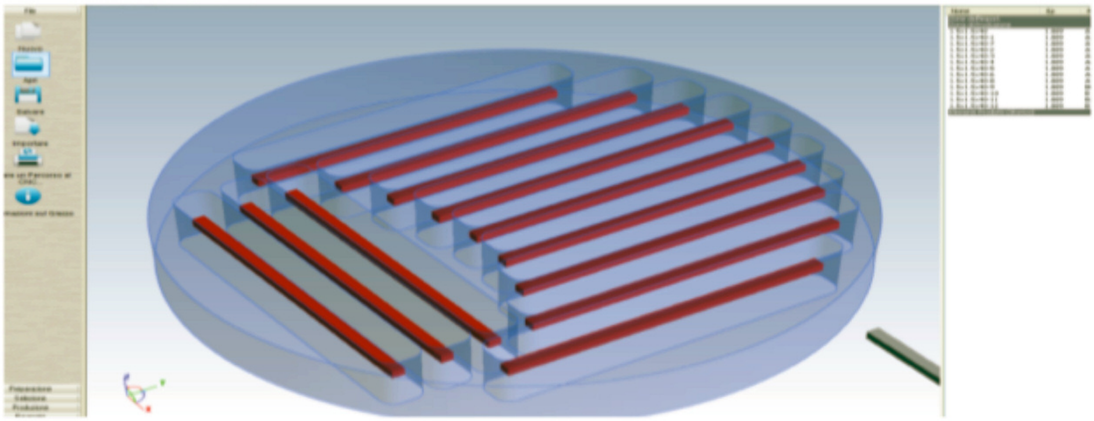

Figure 1
CAD project.

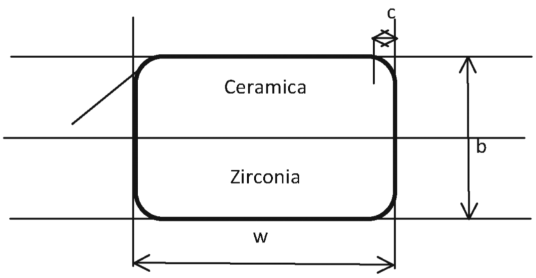

Figure 2
Section's specimen.

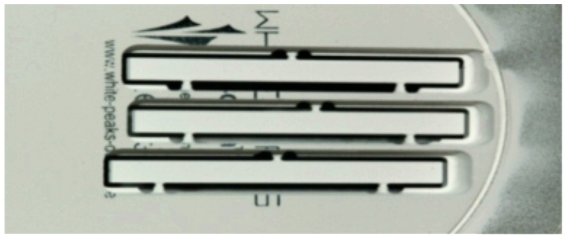

Figure 3
Zirconium after cam processing.

during the sintering oven to 15000 C, therefore we recommend the use of suitable supports that support the structure without impeding the movement (Figures 4-6).
Fourth phase - sandblasting interface zirconia-ceramic (EUROCERAM machine) with ALO2 50µm, 2.5 Bar distance of 3-5 cm. After sandblasting, clean the surface with vaporizer (distance 5-10cm).
Fifth phase - layering porcelain on the artifact.
Sixth step: cooking (Tables 5-7).
The artifact will undergo three firings, two for the ceramic and the third as polishing with vitrification, without the use of glaze (Figure 7).
Our specimens before SEM analysis are subjected to a three point bending test (9), so our analysis has sought to highlight some structural defects and physical of these two materials, using SEM.

Three-point bending test

In the three-point bending test (5, 6) the presence of the cut can cause the fractures to delamination of the material, rather than to bending, thus making impossible the correct determination of the resistance to bending. This phenomenon can also occur in the specimen to four

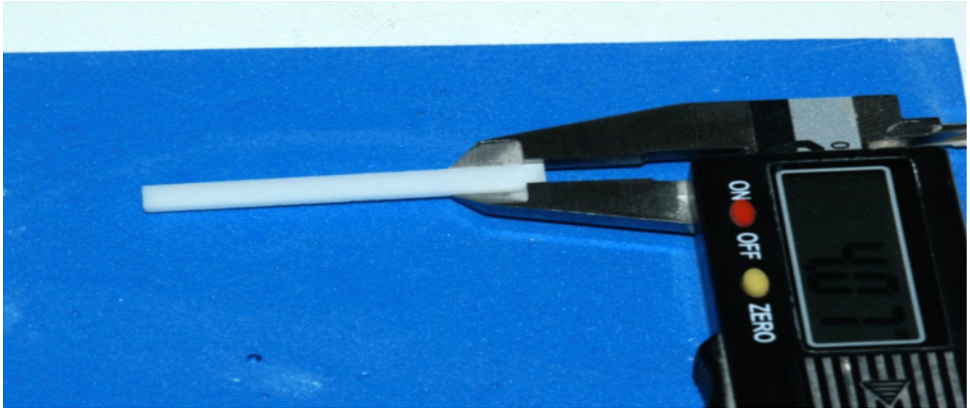

Figure 4
Specimen width.

Figure 5
Specimen's thickness.

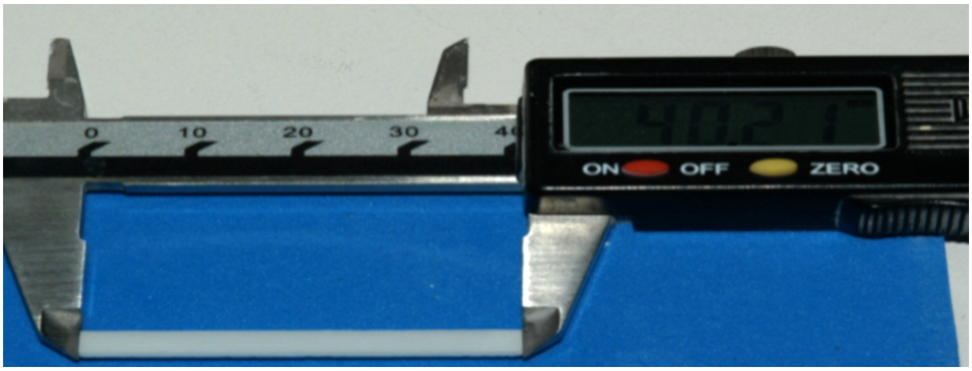

Figure 6
Specimen's length.

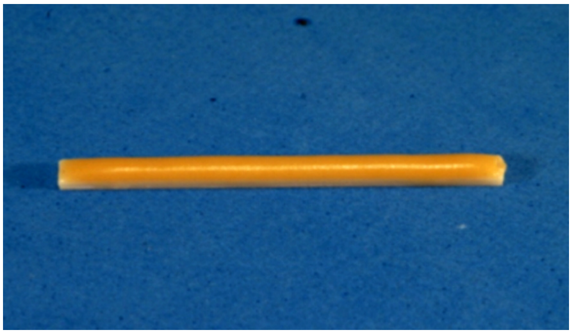

Figure 7
Specimen.

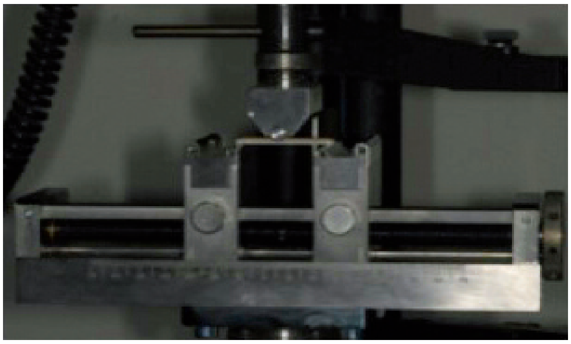

Figure 8
Three point bending test.

points, limited to the two lateral zones. To avoid this drawback, it is necessary to increase as much as possible the ratio R f / t between the maximum bending stress (which occurs on the surface) and the maximum shear stress (which occurs at the neutral axis), i.e.:

$$R\frac{f}{t}=\frac{\sigma max}{\tau max}=\frac{6M/(bh^2)}{3P/(2bh^2)}=\frac{4M}{Ph}= \quad \frac{L/2h}{(L-l)/2h} \frac{(3\ punti)}{(4\ punti)}$$

$$\sigma_f = \frac{M_f\ Y}{I}$$ **Navier formula**

The use of ratios too high may result in excessive arrows with ratios too high and with the emergence of abnormal horizontal binding reactions. In order to avoid such problems, it is good to use values of R = f/t not exceeding 16. In the case of non-symmetrical lamina test bending and twisting tests can be complicated by partial detachments of the specimen from the supports, caused by the torsional deformation. In such cases, in order to minimize the effects on the outcome of the test, you must use relatively large specimens (10-12, 15).
Using a machine from Test Equipment Instron 5566®, three point bending tests were performed on 12 specimens zirconium-ceramic (Figure 8).

Specimens' characteristics

- The specimens shall be longer than two millimeters of the length of supports and the relationship between the thickness and the length should be ≤0.1.
- The roller support have dimensions ranging from 1.5 to 5mm (+/-) in diameter and must be positioned with a distance from both ends of the sample varies between 12.0mm to 40.0mm (+/- 0.5), the load must be applied at the midpoint of the sample.
- The load results to be perpendicular to the section of the specimen. The machine must act with a Speed's boost (1 +/- 0.5) mm / mines must be able to measure how the load applied from 10N to 1000N (+/- 0.1) (7).

Graphical representation of the values obtained in Table 4

In blue σ max zirconia, red σ max ceramic and green and yellow respectively averages about the specimens. From the graph appears that zirconia focuses on a higher values than the porcelain: in fact the average of the voltages of the zirconia is higher than ceramic. All values are correlated with the largest accumulation of tension on zirconia because it is more rigid and consequently the deformations are prevented compared to porcelain. The zirconia has a modulus of elasticity higher than ceramic. The zirconia has a modulus of elasticity of 210 GPa while ceramic veener of only 70 GPa (14) Table 1, Table 2, Table 3.

SEM analysis submitted four specimens: respectively four bars bilaminar fragments realized according to ISO 6872 (2, 7). Our choice has been on four samples:

1) Bar# 1 in Test Equipment which gave the worst values.
2) Bar# 9 Test Equipment which gave values above average.
3) Bar# 13 which gave the worse values.
4) zirconium bar.

Specimens were placed on a metal adhesive base and subsequently fixed with a glue based metal silver. Subsequently they were placed in stove at 70°C for a few minutes.
Specimens were not metallized except number 9, which was metallized with a veneer of gold of 12 μm, to ensure the best microscopic vision.

Table 1 - Specimens' bending stress.

	Bending stress (MPa)
1	279.631
2	298.995
3	426.196
4	248.738
5	341.113
6	314.948
7	435.038
8	346.969
9	505.881
10	436.596
11	477.689
12	389.593

Discussion

From our microscopic analyzes all the specimes that we analyzed show a perfect adhesion in the interface, although there has been analyzed locations very close to the loading zone and consequently places of fracture zirconia-ceramic interface (Figures 8, 9). Specimens were classified under their failure mode as adhesive, cohesive or mixed: (1) adhesive, if no remnants of porcelain were found in the metal or zirconia surface; (2) cohesive, if fractures occurred within the porcelain side; (3) mixed, if remnants of porcelain were found in the metal/zirconia surface. The continuity between the two structures is present

Table 2 - The three point bending results.

ID specimen	width (mm)	thickness (mm)	maximum bending load (kN)
1	4.13	3.05	0.199
2	4.05	3.03	0.206
3	4.15	2.92	0.279
4	4.10	2.95	0.164
5	4.12	2.91	0.220
6	4.02	2.95	0.204
7	4.06	3.00	0.294
8	4.08	2.96	0.230
9	4.13	2.71	0.284
10	4.12	2.86	0.272
11	4.11	2.84	0.293
12	4.04	2.90	0.245

Table 3 - FEM analysis results.

		Zirconium	Ceramic
n	C	2,0652	1,1844
1	199	410,9748	235,6956
2	206	425,4312	243,9864
3	279	576,1908	330,4476
4	164	338,6928	194,2416
5	220	454,344	260,568
6	204	421,3008	241,6176
7	294	607,1688	348,2136
8	203	419,2356	240,4332
9	284	586,5168	336,3696
10	272	561,7344	322,1568
11	293	605,1036	347,0292
12	245	505,974	290,178
	average	492,7223MPa	282,5781MPa
	%	31,39261	-24,6458

C= proportionally constant between effort and flexion.%= shift between FEM analysis results and Table 1.

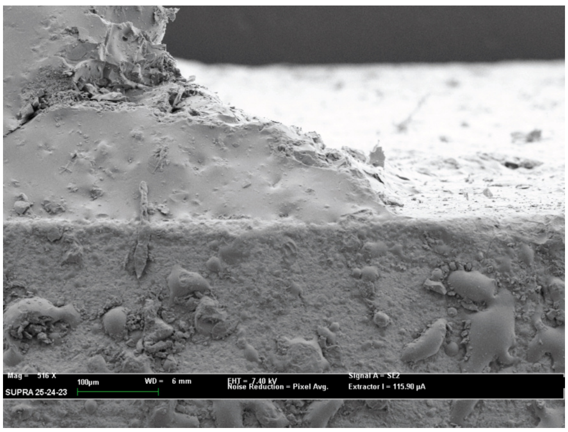

Figure 9
SEM analysis zirconium bar #9.

in all specimens, from the bar with reduced values (flexion) to those with very high values. Therefore we can support a good connection that the adhesion between these two materials has certainly excellent values. Structural defects and not places of secondment vary in size between 1 micron (μn) and 450 nm (nanometre), which can be detected only at high magnification (Figure 10), have been identified in the structure of zirconia, but we believe that such "defects" are a direct result of ceramic porosity. In the Figures, in fact, we see direct continuity between the two structures, so that at high magnification (as reflected by the specimens #9) (Figures 9, 11) the limit tends to be less and less clear, since residual melting of ceramic harness into the pores of the zirconia. Aside from the fact that the geometry of the specimens used in *in-vitro* studies do not reflect the geometry of dental crowns, the failure mode demonstrated in clinical situations and *in-vitro* experiments are both related to the problem of poor cohesion strength of the porcelain (21).

The bond between the metal and ceramic works with threefold mechanism, which provides a mechanical retention by a surface roughness, the exploitation of the coefficients of thermal expansion and the consequent phenomenon of compression, and a chemical bond due to oxides. "With the zirconia instead there is a true chemical bond, but our observations we saw with the microanalysis one thing never yet shown: zirconia ceramic is formed at the interface a sort of

Table 4 - Sigma fracture.

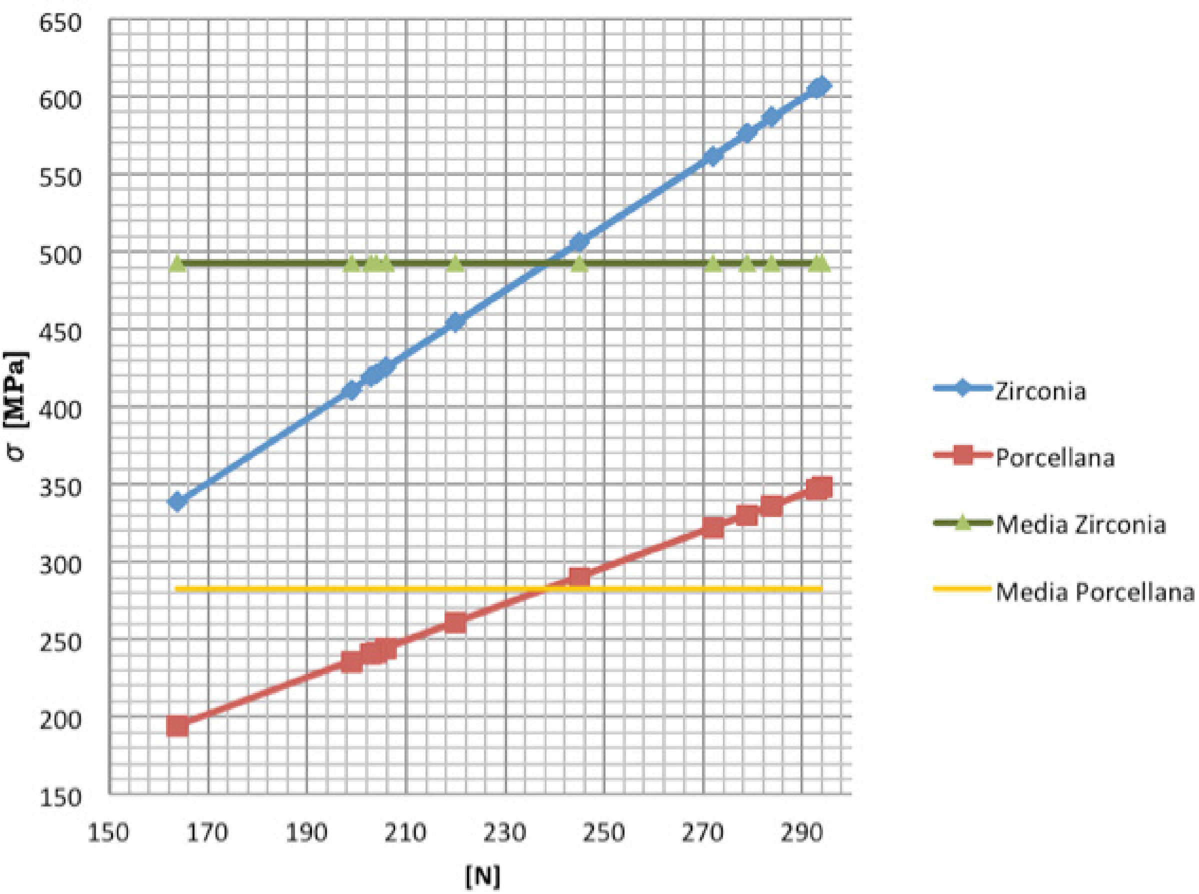

Table 5 - First cooking.

low temperature	600°C	vacuum level	-740mmHg
rising time	06:00	high temperature	945°C
Preheating time	02:00	maintenance temperature	
Degrees / min	45°C/min	final temperature	945°C
departure /vacuum	600°C		
end vacuum	895°C	down time	02:00

Table 6 - Second cooking.

low temperature	600°C	vacuum level	-740mmHg
rising time	10:00	high temperature	940°C
Preheating time	02:00	maintenance temperature	
Degrees / min	45°C/min	final temperature	940°C
departure /vacuum	600°C		
end vacuum	900°C	down time	04:00

Table 7 - Third cooking.

low temperature	600	vacuum level	
rising time	02:00	high temperature	940°C
preheating time	01:00	maintenance temperature	
degrees / min	46°C/min	final temperature	940°C
departure /vacuum			
end vacuum		down time	02:00

hybrid layer of a few microns which is very similar to a bond chemical. These are the considerations of scholar experts in the field as the Prof. Scotti". According to our SEM analysis, we can admit that zirconium specimens after sandblasting have a high porosity surface (Figure 11).
According to literature, ceramic rich in leucite have high adhesion values compared to those that do not have it. Evaluating SEM failures that are obtained with these ceramic, we can maintain that it is a cohesive failure.

Conclusion

In conclusion, the mode of detachment found in literature agree to our evaluations with SEM and FEM (Figure 12). The fracture of zirconia was found on the surfaces of detachments adhesive interface at the highest adhesion values show that if the coating is adequately valid, it can develop a good bond. In our opinion, the problem does not lay on the compatibility between the two materials but on their inherent brittleness and therefore imputable to the different nature of the interface that can be achieved, compared to a ceramic metal. It is apparent from our experimentation, the need to have a great technical skill, in order to obtain a perfect the bond. The technical expertise must try to obtain surfaces as homogeneous as possible, in order to ensure an uniform distribution of stress. In fact, as is clear from our studies on the fingers with the same thickness and material, the fingers that had surface uniforms fail to convey the most stress and to support high loads during Test Equipment.
Aboushelib et al. (2008) (13) evaluating bond between core-veener, comparing a method for each veener, with a manual layering, get significant differences; however SEM studies of these structures show that the structures to CAD are subject to a cohesive failure, while the structures subjected to a manual layering have a failure mainly in the interface. The method cad, in this study, shows that the two materials fail to provide a good interface, while a manual stratification demonstrates the presence of bubbles.
Aboushelib et al. (2009) (13), re-evaluating the adhesion between a core zirconia and veneers, confirm the data of the previous year, highlighting the possibility of bubbles in a structure in CAD.
In a recent comparison regarding the chipping resistance between MCR (metal-ceramic-crown) and Y-TZP, bar-shaped specimens were tested with no difference between groups (Quinn et al., 2010). These Authors concluded that clinical differences in chipping between MCR and Y-TZP should exist only if residual stresses or interface flaws may occur. In contrast, the mouth-motion fatigue testing of anatomically correct molar crowns in the present study revealed MCR failures occurring as a function of load and not fatigue. In contrast, both Y-TZP systems' failures were accelerated by fatigue (16-19).
The fracture surface analyses of the all-ceramic systems revealed mainly a mixed failure mode, cohesive in the porcelain and adhesive at the interface. Also in other studies, where has been

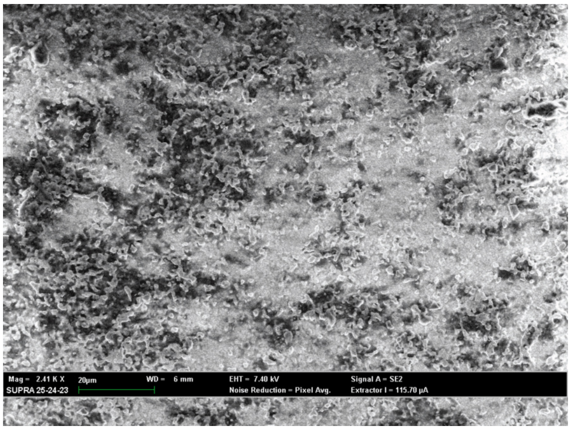

Figure 10
SEM analysis zirconium bar, after sandblasting.

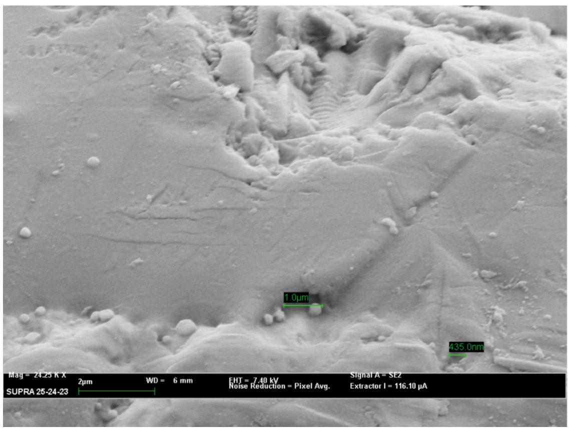

Figure 11
SEM analysis zirconium bar #9-detail.

evaluated fracture and shear bond strenght results that: the fracture surface analyses of the all-ceramic systems revealed mainly a mixed failure mode, cohesive in the porcelain and adhesive at the interface (20). However, the literature has suggested that chipping or debonding of vennering ceramic from the zirconia core is a common complications. A very important observation in that: if we use laser method as a surface treatment, we reduce monoclinic content compared to the airbone particle abrasion (21). Taking into account that the stress distribution on layered composites is considerably influenced by the elastic moduli of the materials involved, frameworks with higher elastic modulus (Inceram-Zirconia and TZP) are preferred for all-ceramic posterior bridges, since they are able to reduce the stress developed on the weaker veneer layer and thus increase the composite load bearing capacity (19).

Recently, to avoid chipping, dopant segregation was found to be a key factor to design hydrothermally stable and high-translucent 3Y-TZP ceramics and the cation dopant radius could be used as a controlling parameter. A large trivalent dopant, oversized as compared to Zr4+, exhibiting strong segregation at the ZrO_2 grain boundary was preferred. The introduction of 0.2 mol% La_2O_3 in conventional $_{Al2O3}$-doped 3Y-TZP resulted in an unique combination of high

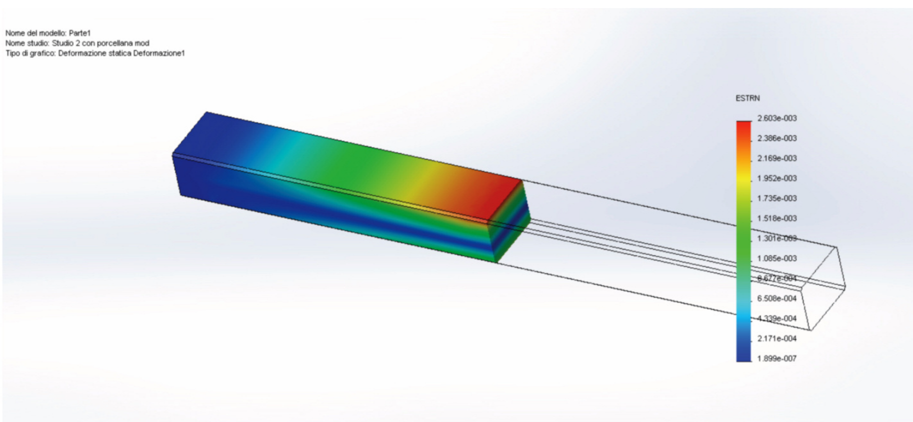

Figure 12
FEM analysis stress distribution upon bar.

translucency (42% increase compared to conventional 0.25 wt.% alumina-doped 3Y-TZP) and superior hydrothermal stability (no transformation up to 120 h of hydrothermal aging at 134 _C), while maintaining excellent mechanical properties (22).

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