Surface treatments of dental ceramics: The state of the art

B. MAFTOUH, I. BOUJOUAL, A. ANDOH

Fixed Prosthesis Department, Faculty of dentistry of Casablanca, University Hassan 2 of Casablanca, Morocco.

Abstract: The durability of prosthetic restorations is conditioned by the ultimate clinical step which is the assembly. The multitude of ceramic materials and bonding products on the market can mislead us as to the correct implementation of the protocol. There is no universal bonding protocol; while vitreous ceramics are easily etchable and react well to acid etching, crystalline ceramics, on the other hand, are not suitable for acid etching and therefore require rather heavy surface treatments, such as: laser, selective infiltration-etching technique, Argon plasma cleaning...

Therefore, for each type of ceramic material a suitable surface treatment must be adapted to achieve an effective and durable bonding.

The aim of our work is to highlight the current surface treatment processes for dental ceramics depending on the type of material, as well as the main rules to be observed, for achieving a durable adhesive bond.

***Key words*:** dental ceramics, prostheses, surface treatment, bonding

The term ceramic comes from "keramos", a Greek word meaning pottery. They are inorganic materials, composed of oxides, carbides, nitrides and borides. Ceramics have strong chemical bonds of an ionic or covalent nature. Ceramics are shaped from a powder of suitable grain size which is agglomerated. Then a second step consists of densifying and consolidating this agglomerate by a heat treatment called sintering, in which a system of individual particles or a porous body changes some of its properties in the direction of an evolution towards a state of maximum compactness. Currently, it is considered that the consolidation treatment can also be a crystallization or hydraulic setting.

For a long time, ceramics have been used mainly for the manufacture of artificial teeth for removable prostheses and the production of metal-ceramic crowns and bridges (MCC). Since the 1980s, however, the development of these materials has made it possible to design veneers, inlays and onlays and even crowns and bridges without metal frameworks. Today's ceramics have a wide range of indications ranging from partial tooth restoration, to the replacement of missing teeth with metal-free bridges and abutments for implant-supported prostheses.

Conventional dental ceramics are composite structural materials comprising a glassy structure known as a glass matrix reinforced with different crystalline phases which allows the thermal expansion coefficient of the material to be adapted. Manufacturing is done by heating the mixture above the melting temperature of the glass matrix and below that of the crystals. The crystalline phase increases strength and reduces fractures. The nature of the crystalline phase present in the ceramic mainly conditions the physical, mechanical and optical properties (light reflection and color) of the final restoration. In particular, it prevents the propagation of surface dislocations and microcracks within the material. Currently, some types of dense ceramics are essentially crystalline without any glass phase.

Developments in laboratory techniques, the improvement of adhesion especially dentine adhesion and the development of new bonding cements have made it possible to strictly codify clinical and laboratory protocols so that this system can become established in our daily practice.

Classification of ceramics:

The old classification classifies ceramics according to their fusion temperatures (figure 1), chemical composition, shaping process and microstructure (Saadoun and Ferrari). Recently, a new classification has been proposed by Gracis et al in 2015 and allows new materials to be placed in the main existing families. This new classification system classifies ceramic restoration materials into three families (figure 2) (16):

1) glass matrix ceramics

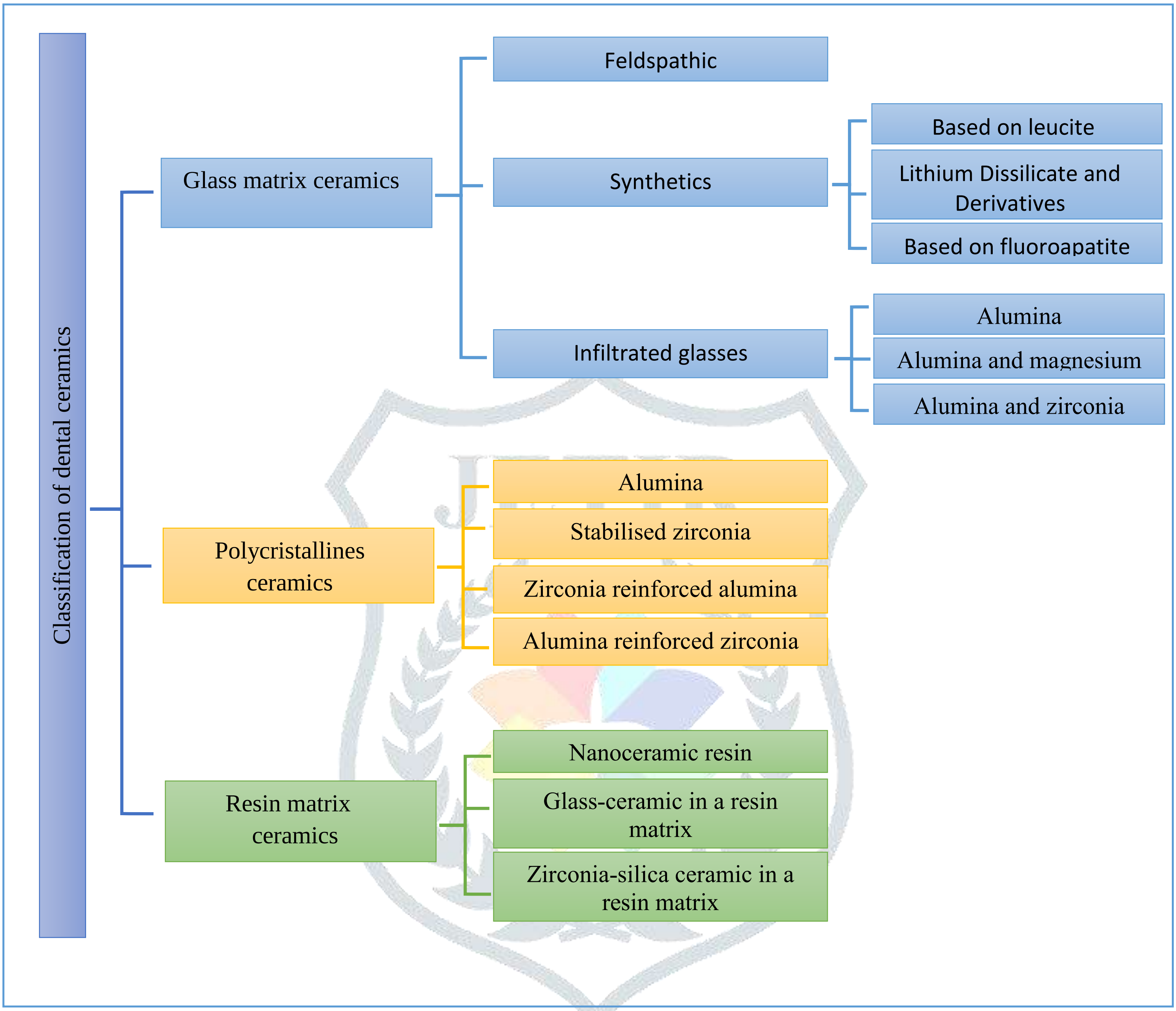
2) polycristallines ceramics

3) resin matrix ceramics

figure 1: Classification of ceramics according to their melting range (M. Sadoun 1995) (16, 5)

Types of ceramics	Fusing temperature	Indications
High-fusing ceramics	1280 °C – 1390 °C	Removable prosthesis
Medium-fusing ceramics	1090 °C – 1260 °C	Jacket prosthesis on platinum matrix
Low-fusing ceramics	870 °C – 1065 °C	Ceramo-metal prosthesis for metal glazing
Very low-fusing ceramics	660 °C – 780 °C	Ceramo-metal prosthesis for titanium and gold glazing

Figure 2: Classification of ceramics Gracis et coll 2015 (16)



Surface treatments of dental ceramics:

In general, the quality of the bond depends on the surface energy and the wettability of the substrate to be bonded. Strong adhesion is achieved when the bond combines a micromechanical and chemical bond, which requires roughness and purity for better surface activation.

1- Glass matrix ceramics:

Feldspathic ceramics:

These are the traditional ceramics used for glazing metal-ceramic copings. New feldspathic ceramics with a high leucite crystal content, have improved mechanical resistance and an increased coefficient of thermal expansion. They can be used without a framework in certain clinical situations. (13, 5)

Synthetic Ceramics:

The ceramics industry has started to use synthetic materials. The composition varies according to the manufacturer, but generally includes silicon dioxide (SiO2), potassium oxide (K2O), sodium oxide (Na2O) and aluminum oxide (Al2O3). Their glass phases can be combined with apatite crystals, lithium dissilicate and derivatives and leucite, for thermal expansion compatibility with metals and for improved strength. (16,5)

Ceramics with infiltrated glass:

The glass is infiltrated in a porous magnesium aluminate or alumina and partially stabilized zirconia to reinforce the ceramic. The use of this class of materials is being reduced due to the increased advancement of lithium Dissilicate and zirconia, particularly for CAD/CAM fabrication. (16)

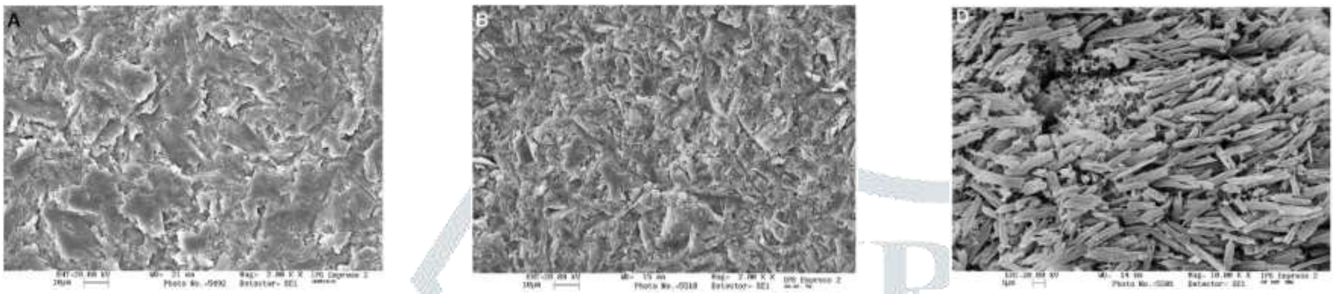
⇨ Surface treatments for glass matrix ceramics (11,6):

The steps for preparing the intaglio of a prosthetic reconstruction with a continuous glass matrix are as follows:

- The prosthetic parts are prepared beforehand using an aero-abrasion technique. This consists of the projection of alumina particles (Al 2 O 3) from 50 µm at a pressure of 2.5 bars. This pressure blasting produces a rough surface and results in the appearance of an opaque whitish color on the prosthetic intrados.
Particular attention must be paid to ultra-fine veneers (less than 0.6 mm with risk of cracks).
- They are then etched with 5% hydrofluoric acid (e.g. Porcelain Etch®) for 1 to 2 minutes. This etching modifies the morphology and surface appearance of the ceramic with the aim of creating micromechanical retentions between the ceramic and the bonding composite. Hydrofluoric acid appears to be the best way to achieve a reliable bond to the ceramic because it dissolves the silica in the glass phase and exposes the crystal structures (Figure 3). This results in an increase in the surface area, which becomes porous and irregular. This facilitates the penetration of the resin into the micro-retentions. This etching can be carried out in the laboratory before delivery of the ceramics or by the practitioner.
- The intaglio of the prosthetic part is then rinsed thoroughly. The etching residues are removed in a 90° alcohol bath in an ultrasonic tank. In this way, the parts are cleaned and degreased after clinical fitting.
- Subsequently, the intaglio of the prosthetic part is silanized using single-component liquid silane (e.g. Silane®). This is a coupling agent that allows the creation of a chemical interaction between the ceramic and the bonding composite, thus reinforcing the adhesion between the two materials. Silane also reduces the

hydrolytic degradation of the bond, improves the wettability of the treated surface, and reduces the surface energy of the ceramics to which it is applied until it becomes lower than that of the adhesive resins. Clinically, silane is applied with a small brush to coat the totality of the ceramic surface.

- After a waiting period of 2 minutes, the intaglio is dried using the air/water syringe, or better a hair dryer (heating improves the action of the silane) so that the solvent contained in the silane evaporates.
- An amelo-dental adhesive is then applied to the intaglio of the prosthesis. Excesses are removed with an air spray. The adhesive prevents the silane layer from hydrolyzing. This final clinical step is optional. It is not light-cured and the prosthetic parts are placed away from the light.



Microscopic view of glass matrix ceramics (IPS Empress II) before surface treatment

Microscopic view of the ceramic surface after blasting (50 µm for 5 seconds)

Microscopic view of the ceramic surface after etching with 10% hydrofluoric acid for 20 sec.

Figure 3: Surface condition of a glass matrix ceramic (IPS Empress 2) after blasting and etching with hydrofluoric acid (2)

2- Polycrystalline ceramics:

They do not have a vitreous phase. There are only alumina or zirconia oxide crystals condensed by sintering, which is a heat treatment that eliminates porosities and strongly condenses the particles, resulting in a very dense material that is therefore very resistant mechanically but remains completely opaque (figure 4). They must be layered with a cosmetic ceramic to simulate a natural shade. They can only be processed in the laboratory by CAD/CAM machining.

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Polycrystalline alumina-based ceramics

This system uses pure alumina: 99.5% agglomerated alumina grains, under high pressure. First introduced by Nobel Biocare in the mid-1990s as a base material for CAD/CAM manufacturing. It has fairly high mechanical properties and the highest modulus of elasticity of all dental ceramics (300 Gpa), making it more vulnerable to fractures. This tendency to fracture allows the appearance of materials with improved mechanical properties (zirconia) and a reduction in the use of alumina. (13,5)

Polycrystalline ceramics based on zirconia (19)

In recent years, zirconia (zirconium oxide ($ZrO2$)) has become the star of dental biomaterials. Many people use it but few really know it.

Pure zirconia HIP (Hot Isostatic Pressing) with a zirconia content of at least 93.6% is so sintered and so dense that it is very difficult if not impossible to machine for dentistry. It is still used in medicine for hip prostheses because these must be particularly resistant.

The use of zirconia in dentistry has been made possible by modifying its molecular structure by adding 3% Yttrium oxide, which stabilizes the crystals in the tetragonal phase. This is called Y-TZP zirconia (Y for yttrium, T for tetragonal, Z for zirconia and P for polycrystalline). It is very opaque and very hard (1200 Mpa bending strength). It is always used as a reference and remains indicated for prosthetic infrastructures that need to be glazed with cosmetic ceramics (except in the posterior sector).

But the major problem with glazed zirconia is the risk of chipping: shards or fractures of the cosmetic ceramic under the effect of occlusal forces. The machining of monolithic prostheses (known as monobloc or full zirconia) is a solution to try to eliminate this problem. A **2nd generation** of zirconia has then appeared: it is still a zirconia stabilized by 3% Yttrium (3Y-TZP) but for which the optical properties have been improved for greater translucency. The aesthetic appearance is improved and acceptable for posterior monolithic restorations. Also, to improve the optical properties of the material, **the 3rd generation** of zirconia has been introduced: translucent or partially stabilized zirconia because the percentage of yttrium to stabilize them increases to give 4Y-TZP and 5Y-TZP zirconia. This is accompanied by a drastic decrease in the physical properties of the material as its flexural strength falls below 700MPa for a minimum thickness of 1mm. The new zirconia will therefore not be suitable for posterior areas and will be limited to monolithic restorations in the anterior sector.

Y-TZP zirconia is a pre-sintered material, i.e. softer and easier to machine. Once machined, the workpiece is sintered again to give it its final strength, which is accompanied by a dimensional shrinkage of the material of 20-30%. It is therefore impossible to produce dental prostheses made of polycrystalline ceramics without CAD/CAM processes. After the digital impression (or digitization of the model) and the design of the prosthetic part by computer, the latter will then control a machine tool which will mill a block of Y-TZP zirconia perfectly anticipating the 20-30% shrinkage that will take place during the second sintering.

	Based on alumina	Zircone TZP	Zircone HIP
Density (g/cm3)	3,75 à 3,95	6.08	More than 6,08
Resistance to flexion (Mpa)	487-699	Sup à 1200	More than 90
Modulus of elasticity (Gpa)	300	210	210
Grain size (microns)	2	0,5	Less than 0.6
Hardness (HV)		1250	1200

Zirconia-reinforced alumina and alumina-reinforced zirconia

Figure 4: Mechanical properties of polycrystalline ceramics (19)

Since zirconia generally remains partially stabilized in the tetragonal phase and alumina has a medium toughness, there is a tendency for alumina-zirconia (zirconia-hardened alumina [ZTA]) and zirconia-alumina (alumina-hardened zirconia [ATZ]) to develop. In 1976, Claussen first described how the addition of untenderized zirconia to alumina increases the fracture resistance of alumina. The percentage of zirconia or alumina in the composite can be customised and can be changed to suit the manufacturers' requirements or handling. For classification purposes, the authors suggest that ZTA should have > 50% by weight of Al, while ATZ should have > 50% by weight of Zr. (16)

⇨ Surface treatments of polycrystalline ceramics:

The choice between a classical cement and a bonding cement will be made according to the retentive potential of the substructure and the value of the assembly.

For a good assembly, a hybrid cement of the CVIMAR type is preferred.

When the intrinsic retentive potential of the preparations is weaker and the assessment of the clinical situation suggests that the construction will be seriously solicited during the function, the choice of an adhesive method should be made. Also, with the establishment of highly translucent zirconia materials standards have evolved. The outstanding aesthetic properties of new zirconia have to be supported by an adhesive system.

However, polycrystalline ceramics are refractory to etching, and treatment with hydrofluoric acid is ineffective and does not create a relief on the surface of these ceramics suitable for bonding.

In order to improve the quality of the polymer-ceramic interface and to promote the use of adhesive systems to bond this type of ceramic, surface treatments of the intaglios of the prosthetic coping have been developed that make it possible to give it a rougher appearance in order to facilitate adhesion and therefore retention. They also allow the prosthetic surface to be decontaminated.

The precondition for a good surface treatment is first of all the cleaning and decontamination of the bonding interfaces and to rid the zirconia surface of the phosphate residues that compete with the primer. Several proposals have been cited in the literature including ultrasonic cleaning with distilled water, isopropyl alcohol, ethanol, Argon plasma cleaning or failing that, sodium hypochlorite (NaOCl) for 20 seconds. (3,4,12)

The most documented protocol giving the best results is:

- **Tribo-chemical treatment with silicates**

Silica coated alumina particles are sprayed under high pressure. The impact energy between the particles and the blasted surface causes a temperature rise that allows the silica to be incorporated into the surface of the material (to a depth of 15µm). The process is known as reactive or tribo-chemical blasting. The interest is to deposit a layer of silica on the surface of zirconia, which has no vitreous phase, in order to react with a silane which is subsequently applied (15). (Figure 5)

There are many methods of deposition, divided into chair-based methods and laboratory methods.

- SILICOATER® system: Silane deposition under the jet of a flame (150 to 200°C) (silicatisation by pyrolysis).

- ROCATEC ® system: Projection of 30µ alumina grains coated with silicates onto the target surface at a high temperature which allows the silica to be incorporated into the surface of the material. Same principle for the COJET® and Pyrosil-Pen® intra-oral tribo-chemical pen systems, which are used in the chair especially for the repair of ceramic fractures.

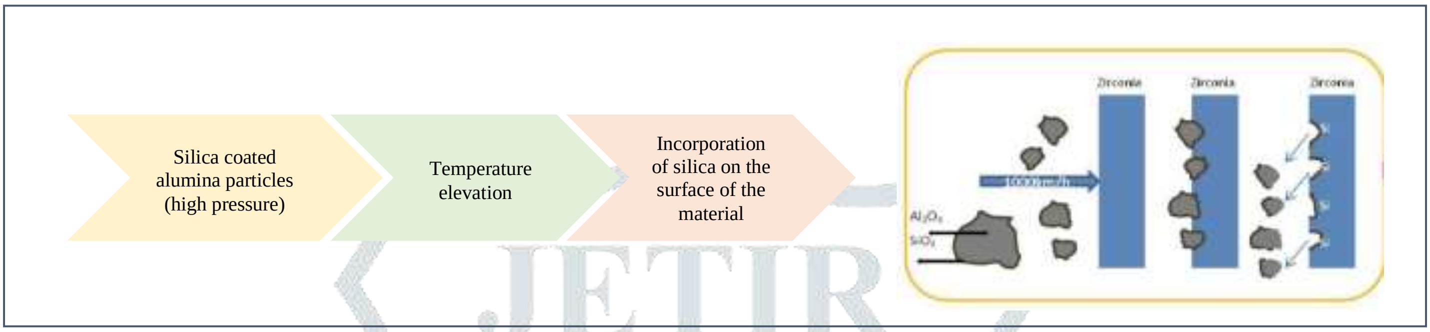


Figure 5: tribo-chemical treatment with silicates

- The alternative to the tribo-chemical treatment is **alumina blasting,** which consists of a pressure projection of alumina particles (Al_2O_3) from approximately 50µm to 110µm. (different grain sizes, 2.5 bar, 20s, at 10 mm of distance). There is a wide variation in particle size, as well as pressure and blasting distance and angle. (Preferably 45°)

Bomicke et al. 2016 (3) investigated the effect of the angle formed by the particle emission line and the surface to be blasted to determine the possible connection with the effect of material deterioration and the risk of micro-cracking on the surface of zirconia and concluded that blasting at 45° is more effective than blasting at 90°.

The aim of this process is to increase the surface roughness and therefore the mechanical adhesion properties. This surface treatment must be followed by the application of a bonding primer containing phosphate esters (10-methacryloyloxydecyldihydrogen phosphate monomer: 10-MDP). However, sandblasting runs the risk of damaging the edges and causes only a rough surface and not real micro-retentions.

➢ Primers or adhesives containing MDP in combination with alumina blasting appear to be an excellent method of bonding zirconia restorations, as is tribo-chemical treatment followed by silane application. (7)

- **Another surface treatment:**

Surface treatment by laser irradiation:

Another method for increasing surface roughness has recently been advanced. It consists of the use of lasers, which have the advantage of being carried out in the practice. Laser devices such as Er: YAG, Nd:

YAG have been used by many researchers to establish surface roughness and irregularity. Er, Cr: YSGG is another effective laser system that has been studied on these substrates.

However, the included literature (7, 9, 17) contains only limited data regarding the value of the laser in the surface treatment of Y-TZP zirconia and is highly controversial.

Erdem et al (7) concluded that Er: YAG laser treatment did not improve bond strength but created a rather smooth surface with cracks and loss of substance.

Ghasemi et al (9) assumed that sandblasting is still more effective than Er, Cr: YSGG laser, while Usumez et al (17) concluded that Nd: YAG laser would produce a rough surface and thus improve the bonding quality.

Most authors agree that the use of a short duration and low pulse of the laser could reduce the occurrence of the "crack- Effect" (7,9,17).

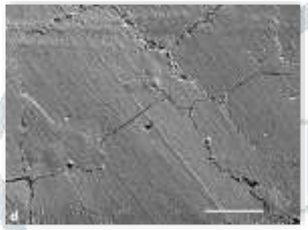


Figure A: Laser treatment Er: YAG (7)

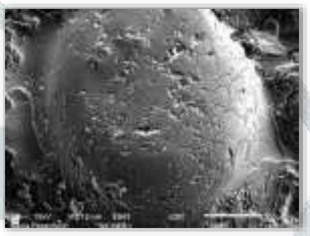
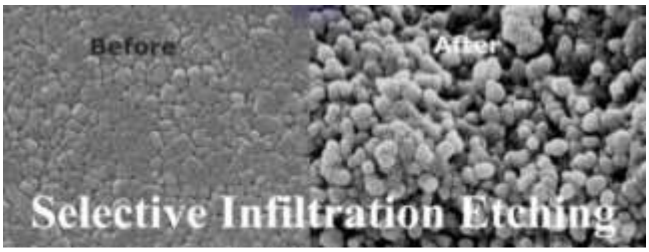


Figure B: Nd: YAG laser treatment (17)

Selective infiltration etching:

The infiltration technique by selective attack, or selective infiltration etching technique (SIE) developed by Aboushelib et al. in 2007 consists in subjecting zirconia to thermal maturation cycles (between 700 and 900°c), allowing the inter-boundary spaces to be opened and thus inducing the transformation of the dense, non-retentive structure of zirconia into a porous, highly active, retentive structure with low surface free energy, then secondarily infiltrating the intergranular network with glass (on the nanometric scale), thus improving the bond strength up to 32.4 Mpa. Some studies have suggested that the SIE technique would provide strong, stable and durable adhesion to zirconia substrates (14).



Vitrification of the intrados:

Also known as "glazing". Defined as the application of a thin layer of low-fusing vitreous ceramic to make the prosthetic intrados sensitive to etching. (Everson P 2011, Valentino 2012, Baldissara 2013). However, once it has been glazed it should be treated like a vitreous ceramic and therefore it is no longer appropriate to use MDP-based primers, on the contrary it would seem advisable to use silane and methacrylate-based primers in this case. This layer can go up to 30 microns as a maximum. (1, 8, 18)

Argon plasma cleaning:

It is carried out using a plasma reactor that emits argon gas at an intensity of 75 W and a pressure of 10 MPa for 375 to 750 seconds.

It is a non-destructive method compared to a more conventional treatment such as alumina blasting. It has been proposed to increase the wettability of zirconia and thus make it more reactive to adhesive systems containing MDP without the need for sandblasting, which can cause micro-cracks or pollute the surface of the zirconia. (4)

3- Ceramics with a resin matrix:

The third group includes resin matrix ceramics. In 2013, the American Dental Association qualified resin matrix materials as "ceramics" because they have properties similar to those of ceramics. Manufacturers suggest a wide range of indications for these ceramic-like materials in restorative dentistry.

They can be divided into several subfamilies, depending on their inorganic composition, as follows:

- ✓ Nanoceramic resin.
- ✓ Glass-ceramic in an interpenetrating resin matrix (Enamic, Vita).
- ✓ Zirconia-silica ceramic in an interpenetrating resin matrix. (16)

Nanoceramic resins

These are similar to a conventional composite with a highly hardened resin matrix, reinforced with approximately 80% by weight of mineral fillers to which nanoceramic particles are associated; formed from discrete silica nanoparticles (20 nm in diameter), zirconia nanoparticles (4 to 11 nm in diameter). These ceramic fillers are embedded in a polymer matrix composed of Bis-GMA, UDMA, TEGDMA. This group has the main advantage of having a flexural strength close to that of the natural tooth. (16)

Hybrid ceramics (glass-ceramics in a resin matrix)

Hybrid ceramics consist of a network of feldspathic ceramics of different grain sizes, compressed to create microcracks, which will then be infiltrated by the polymer matrix (UDMA). These ceramics have properties close to those of the natural tooth and can be indicated in case of bruxism and thus have a particular elasticity, mechanical strength after bonding and a perfect distribution of masticatory forces. Cementation is carried out with light-curing or dual-curing fine hybrid composites. However, these ceramics do not appear to be as esthetic as conventional ceramics for use in the anterior sector and retain more plaque than conventional ceramics, so caution should be applied when using them in patients with no rigorous hygiene. (16)

Zirconia-silica ceramics in a resinous matrix

Its mineral content comprises more than 60% by weight. (16)

⇨ **Surface treatments of resin matrix ceramics:**

The surface treatment of this type of material depends on the type of ceramic network.
However, the clinical decline is quite low on this type of ceramic, given its recent release. Long-term clinical studies need to be carried out.

Conclusion:

The simultaneous evolution of cements and ceramics has come a long way. At the present, more dense and resistant ceramics have appeared, which can be indicated as substructure in contrast to the classical ceramics with a dominant vitreous phase. The field of application of these new ceramics is wider and more adapted to the mechanical and aesthetic requirements of the mouth, but the major disadvantage of these ceramics lies in the very dense structure that gives them all their rigidity, their abundant crystalline phase is unsuitable for bonding with conventional processes, hence the appearance of new surface treatment techniques to achieve adequate adhesion like argon plasma cleaning , laser , and selective infiltration etching technique.

Bibliography:

1. Baldissara P, Querzè M, Monaco C, Scotti R, Fonseca RG.

Efficacy of surface treatments on the bond strength of resin cements to two brands of zirconia ceramic.

J Adhes Dent. 2013 Jun;15(3):259-67

2. Borges.G. A, M. Fernando, Daniel C. N. Chan,

Effect of etching and airborne particle abrasion on the microstructure of different dental ceramics.

J Prosthet Dent 2003 ;89 :479-88.

3. Bömicke.W, SchürzA, KrisamJ, RammelsbergP, Rues S.

Durability of Resin-Zirconia Bonds Produced Using Methods Available in Dental Practice.

J AdhesDent. 2016;18(1):17-27.

4. Canullo.L, P. baldissara:

zirconia composite bonding after plasma of Argon treatment.

int J Prosthodont2014; 27:267–269

5. DEJOU. J.

Les céramiques, Société Francophone de Biomatériaux Dentaires,

Date de création du document 2009-2010

6. El Yamani.A , H. Soualhi, J. El Bernoussi
système Empress et restaurations prothétiques Actualités Odonto-Stomatologiques - n° 246 - juin 2009 ; 246:167-178

7.Erdem A, Akar GC, Erdem A, Kose T.
Effects of different surface treatments on bond strength between resin cements and zirconia ceramics.
Oper Dent. 2014 May-Jun;39(3):E118-27. doi: 10.2341/12-420-L.

8. Everson P, Addison O, Palin WM, Burke FJ.
Improved bonding of zirconia substructures to resin using a "glaze-on" technique.
J Dent. 2012 Apr;40(4):347-51.

9. Ghasemi A, Kermanshah H, Ghavam M, Nateghifard A, Torabzadeh H, Nateghifard A, Zolfagharnasab K, Ahmadi H.
Effect of Er, Cr: YSGG laser treatment on microshear bond strength of zirconia to resin cement before and after sintering.
J Adhes Dent. 2014 Aug;16(4):377-82.

10. Janda. R, J.-F. Roulet, M. Wulf, H.-J. Tille;
A new adhesive technology for all-ceramics.
Dental Materials 19 (2003) 567–573

11. koubi.sa, g. weisrok, g. couderc, g. laborde, p. margossian, h. tassery , Le collage des céramiques à matrice de verre : quand méthode rime avec reproductibilité Réalités Cliniques 2010. Vol. 21, n°3 : pp. 41-51

12. Pereira. L, M. ózcan: Can
application of universal primer alone be a substitute to air-borne particle abrasion to improve adhesion of resin cement to Zirconia.
J AdhesDent 2015; 17: 169–174.

13. Poujade .J.-M, C. Zerbib, D. Serre,
Céramiques dentaires,
EMC-Dentisterie 1 (2004) 101–117

14. Samimi P, Hasankhani A, Matinlinna JP, Mirmohammadi H.
Effect of Adhesive Resin Type for Bonding to Zirconia Using Two Surface Pretreatments.
J Adhes Dent. 2015 Aug;17(4):353-9.

15. Sciasci P, Abi-Rached FO, Adabo GL, Baldissara P, Fonseca RG.
Effect of surface treatments on the shear bond strength of luting cements to Y-TZP ceramic.
J Prosthet Dent. 2015 Mar;113(3):212-9

16. Stefano Gracis, Van P. Thompson, Jonathan L. Ferencz, Nelson RFA Silva, Estevam A. Bonfante New classification system for all ceramic and ceramic like restorative materials.
The international journal of prosthodontics, volume 28, Number 3, 2015

17. Usumez, Aslıhan, Nermin Hamdemirci, BilgeYukselKoroglu, IrfanSimsek, OzgeParlar, and TugrulSari.
“Bond Strength of Resin Cement to Zirconia Ceramic with Different Surface Treatments.”
*Lasers in Medical Science*28, no. 1 (January 2013): 259–66.

18. Valentino TA, Borges GA, Borges LH, Platt JA, Correr-Sobrinho L.
Influence of glazed zirconia on dual-cure luting agent bond strength.
Oper Dent. 2012 Mar-Apr;37(2):181-7.

19. Zhang. Y and B.R. Lawn
Novel Zirconia Materials in Dentistry
Journal of Dental Research 2018 Feb; 97(2): 140-147