Scientific

Bonding to Zirconia: elucidating the confusion

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Abstract

Optimal surface preparation methods for chemical and/or mechanical bonding to porcelain substrates are critical to ensure clinical success when placing indirect porcelain restorations, as well as when repairing them intraorally. A variety of surface preparation techniques have been advocated, which includes the use of acids, particle abrasion, adhesives and silane coupling agents.

This article will discuss various methodologies currently advocated for the surface treatment of zirconia-based ceramics.

Key Words: *Zirconia, Ceramic Steel, Porcelain, Adhesion*

Short Title: *Bonding to Zirconia: elucidating the confusion*

Introduction

Ceramic materials are best able to mimic the appearance of natural teeth. As a result of the good properties of dental ceramics, such as esthetics, chemical resistance, hardness, compression resistance and biocompatibility, a significant effort has been made over the years to improve their weak points which include brittleness and low tensile strength.[1,2]

A progressive improvement in the mechanical properties of dental ceramic has led to an increase in metal free restorations. The zirconia systems currently available for use in dentistry include ceramics with a 90% or higher content zirconium dioxide, which is the yttrium, stabilized tetragonal Zirconia (Y-TZP) and glass infiltrated ceramics with 35% partially stabilized zirconia.

Though zirconia has been available for use in restorative dentistry for several years, there has been an increased interest recently in these materials. Zirconia-based restorations are versatile and can be used for crowns, bridges and implant abutments in a variety of clinical situations, if the appropriate guidelines are followed.

History

The name "Zirconium" comes from Arabic word "Zargon" which means "golden in colour". Zirconium dioxide (Zro_2) was accidentally identified in 1789 by German chemist, Martin Heinrich Klaproth, while he was working with certain procedures that involved the heating of gems. Subsequently, zirconium dioxide was used as rare pigment for a long time. The first recommended use of zirconium as a ceramic biomaterial in the form of ball heads for Total Hip Replacements (THR) has been documented.

In the early stages of development, many combinations of solid solutions (Zro2-MgO, ZrO2-CaO, ZrO2-Y2O3) were tested for biomedical application. However, in later years, research efforts concentrated more on the development of zirconia-yttria ceramic combinations, commonly known as Tetragonal Zirconia Polycrystals (TZP). TZP is being used as an application in space shuttles, automobiles, cutting tools, and combustion engines because of its good mechanical and dimensional stability, such as mechanical strength and toughness.

In vitro evaluation of the mutagenic and carcinogenic

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Table 1
TZP Technical Data

Property	TZP Material
Colour	White
Chemical compositions	Zirconium oxide and Yttrium oxide 3 mol% Hafnium oxide<2% Aluminium oxide + Silicone oxide<1% Total 100%
Density gcm^{-3}	> 6
Porosity %	< 0.1
Bending strength MPa	900-1200
Compression strength MPa	2000
Fracture toughness K_{1c}	7-10
Coefficient of thermal expansion K^{-1}	11×10^{-6}
Thermal conductivity Wmk^{-1}	2
Hardness HV 0.1	1200

capacity of high purity zirconia ceramic confirmed that it did not elicit such effects on the cells. In the 1990s, zirconium material was used for endodontic posts and as implant abutments. This heralded the use of zirconium into dentistry. Due to its excellent physical properties, white color and superior biocompatibility (Table 1), it is being evaluated as an alternative framework for full coverage all-ceramic crowns and fixed partial dentures (FPD).

Background Concepts in Y-TZP Ceramics:

Zirconia is the name given to zirconium dioxide (Zro_2). Zirconia is a polycrystalline material, which can exhibit more than one crystalline structure depending on pressure and temperature conditions.

Pure zirconia is monoclinic (M) at room temperature. This phase is stable up to 1170°C. It will transform into a tetragonal (T) phase under higher temperatures and later into a cubic phase (C) at 2370° C.

The type of zirconia used in dentistry is yttria tetragonal zirconia polycrystal (Y-TZP) material which is zirconia oxide. Yttria (Y_2o_3) is an oxide of the metallic element yttrium (atomic no. 39).

Y-TZP is a monophase ceramic material that is formed by directly sintering crystal together without any intervening matrix to form a dense, air free, polycrystalline structure. The yttria is added to zirconia to stabilize the structure and maintain the materials desirable properties (Table 2).

Another type of zirconia material available is the glass-

Table 2
Examples of Zirconia-based Ceramics.

Product	Company
Lava Crowns and Bridges	3M ESPE
Cercon	Dentsply Ceramco
CEREC inLab	Sirona
inCeram Zirconia	Vita
IPS e.max ZirCAD	Ivoclar Vivadent
KATANA	Noritake Dental Supply
Kavo Everest	Kavo
Procera AllZirkon	Nobel Biocare
Verus System	Whip-Mix
ZENO Tec System	Wieland Dental + Technik

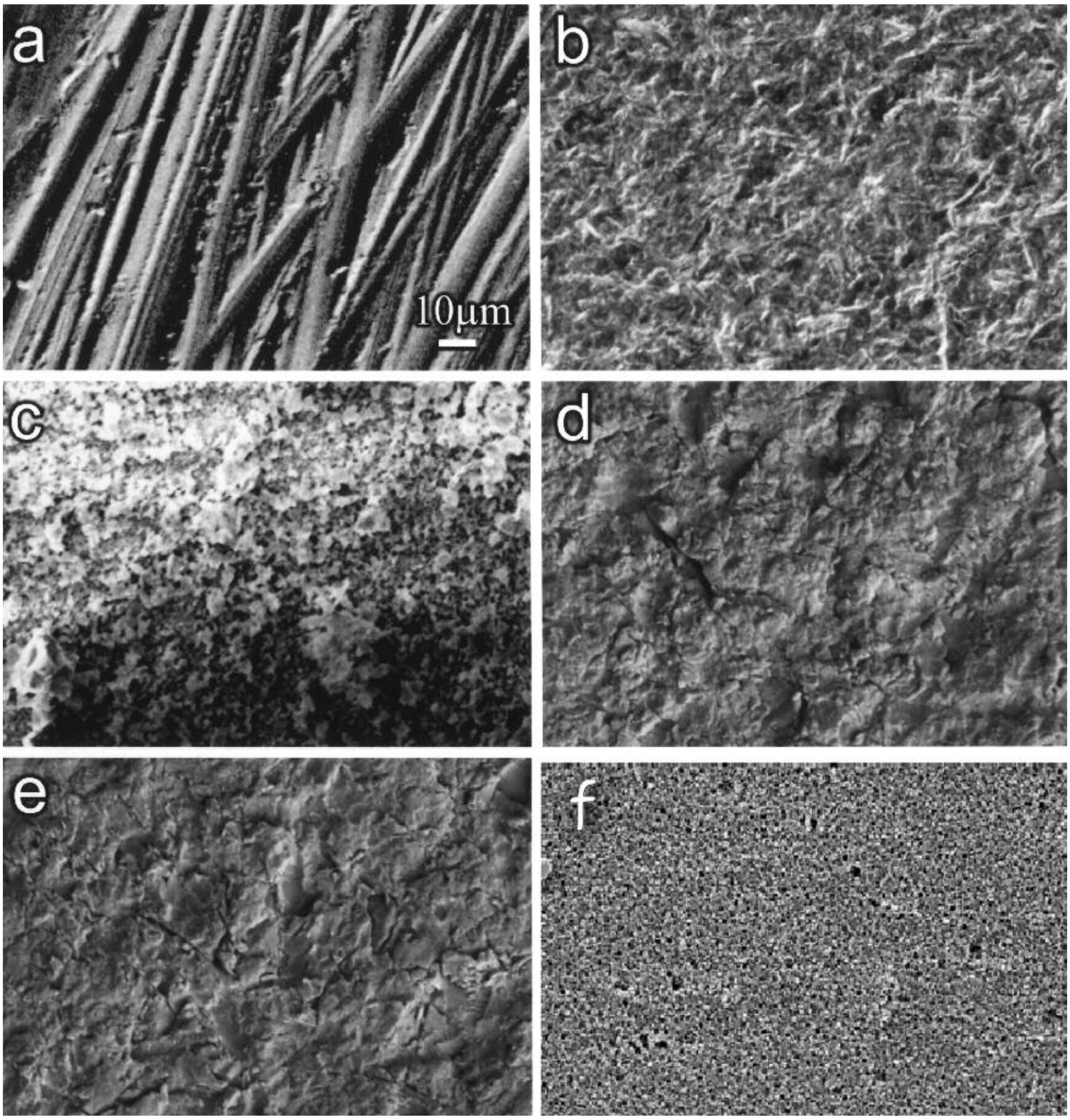

Figure 1: SEM images of the bonding surfaces on zirconia-based ceramic: (a) pretreatment with abrasive paper; (b) air brasion; (c) silica coating; (d) silica coating after 1-minute cleaning; (e) silica coating after 5 minutes cleaning.(f) SEM image demonstrating the surface of Zirconia after completion of SIE technique.Observe the intergrain porosities created on the surface where the primer and the adhesive resin can infiltrate & interlock. (Magnification 2500x).

infiltrated zirconia ceramic. This system presents a high crystal content of aluminum and zirconium oxide and a limited vitreous phase (20 wt%).

Y-TZP Ceramics have a unique characteristic of “Stress Induced Transformation”[3-6] that gives them superior mechanical properties compared with other ceramics and that is why this material is referred to as a ”Ceramic Steel” (Chevalier 1999).[4-7]

Bonding to Y-TZP Ceramics

Optimal surface preparation techniques for chemical and/or mechanical bonding to ceramic substrates are crucial to ensure clinical success when placing indirect ceramic restorations. Although the use of zirconia for dental restoration is ongoing, the best method to promote a durable bond between the ceramic and tooth structure is still unknown (Kern & Wegner, 1998).[8]

Clinicians are often confused regarding the most effective way to treat the intaglio surface of indirect ceramic restoration before placement with various adhesives and luting cements. This is not surprising, as there appears to be no clear consensus in the dental literature, from dental manufacturers, on exactly what the optimal surface treatment should be.

Table 3

The experimental zirconia primers (Contain 1 vol% functional silane in an ethanol/water solvent system)

Zirconia Primer	Functional Silane Monomer	Purity (%)
Primer 1	3-Acryloyloxypropyltrimethoxysilane	95
Primer 2	3-Isocyanatopropyltriethoxysilane	95
Primer 3	Styrylethyltrimethoxysilane	92
Primer 4	3-Methacryloyloxypropyltrimethoxysilane	> 95
Primer 5	3-(N-Allylamino)propyltrimethoxysilane	95

The lack of clear and consistent guidelines regarding the surface treatment of ceramic surfaces raises several significant questions:

1) Is it possible that various viable surface treatment options exist?

2) Is it even practical to recommend a specific "Universal" treatment protocol because of differences in materials (Not all porcelains are the same?)

An attempt to address these questions, provide some guidelines and also to raise additional questions regarding the management of porcelain surfaces should be made.

Bonding to high-content Alumina and Zirconia core-based Ceramics:

High-content Alumina and zirconia core-based ceramics are highly resistant to chemical attack from hydrofluoric acid (Kern & others)[9,10,11,12] and a different approach is required if clinician elects to bond these restorations using resin-based adhesives and luting cements (Figure 1).

A method that has shown to be quite effective in increasing bond strength to zirconia based ceramics is the technique of silica coating followed by silane application.[10,11,12] It is a simple and effective technique that uses silica-coated 30mm aluminum oxide particles (Cojet, 3M ESPE), followed by the application of silane. According to the manufacturer, sandblasting with this material uses impact energy to apply a silica coating to the target surface.[13]

It is unclear whether this transfer of silica is caused by particles actually becoming embedded in the target surface, actual mechanical/chemical transference (Tribochemistry) or both.

However, it is unlikely, that in the case of high alumina or zirconia cores, there is actual embedding of silica-coated particles because of the intrinsic hardness of the target material. It is possible that the silica-coated particles actually "bounce-off" these ceramics but before doing so there is an actual transference of silica from the particles to the target substrate (Tribochemistry).

In any case, this technique is very effective (more so than conventional sandblasting) not just with high-strength alumina and zirconia based ceramics, but also when bonding to composite[14,15] and metal surfaces.[16,17]

Silica coating of metal or composite substrates not only mechanically roughens the substrates, but also increases the number of available hydroxyl groups for surface silane coupling.

It is however, not effective or required with conventional feldspathic porcelains simply because siginificant amounts of Sio_2 and free hydroxyl groups are already present.

Tribochemical coating is less effective for zirconia ceramics than for glass-infiltrated ceramics (Ernst et al 2005; Kern M & Wegner SM 1998)[1,7] This technique uses air pressure which impregnates the ceramic with silica particles and further silane application renders the impregnated surface chemically reactive to the resin cement. (Valandro L F et al 2006).[20]

Selective infiltration etching (SIE) is a novel surface treatment developed to transform the dense and non-bonding surface of zirconia into a highly retentive surface through the establishment of inter-grain nano-porosity where the adhesive resin-composite can infiltrate and interlock.

SIE utilizes a specific glass infiltration agent that is able to diffuse in the grain boundaries and results in nano-inter-grain porosity. After rinsing off this agent, the surface of zirconia is readily capable of establishing a nano-mechanical bond with the adhesive resin-composite of choice. In a recent study, the effect of three different surface treatments on the zirconia-resin microtensile bond strength (MTBS) was investigated: selective infiltration etching, particle abrasion, and coating with MDP monomer. Beside the intial high bond strength observed for the SIE surface treatment, it was the only method that was able to maintain its bond strength value when stored in water for 4 weeks.[18]

The resin-composite-to-zirconia bond strength and

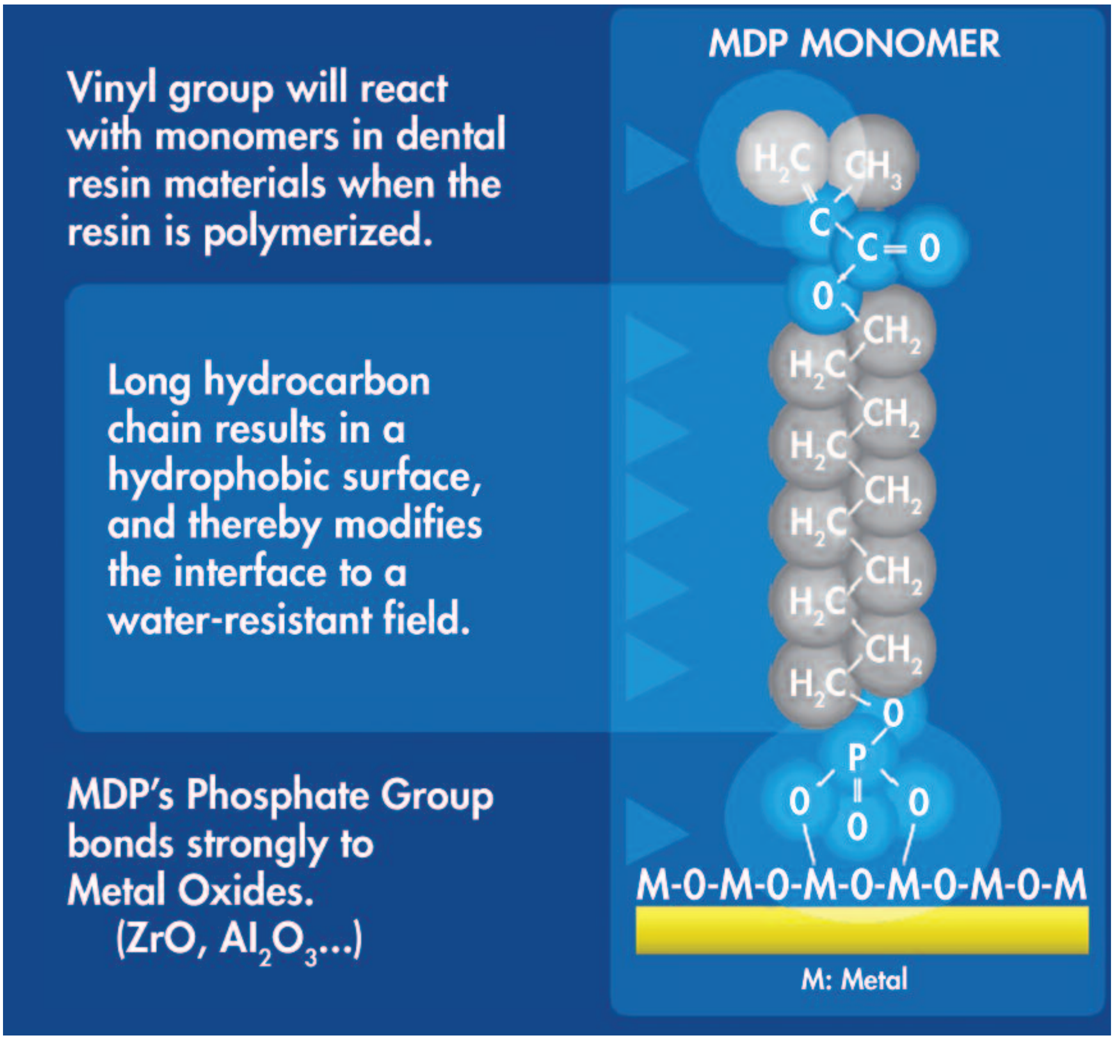

Figure 2: Chemistry of MDP monomer bonded to metal oxide.

interface quality achieved using selective infiltration etching could be further improved with specially engineered zirconia primers (Table 3). Silane coupling agents (silanes) are well-known to form covalent chemical bonds between dissimilar matrices, i.e glassy ceramics (oxides) and organo-functional monomers. In particular, the silane monomer with the methacrylate functionality, 3-methacryloyxpropytrimethoxy silane, is widely used in dentistry.[19] However, silanes cannot react directly with the chemically inert zirconia. Some other reactive functional silanes beside methacrylatesilane have recently been evaluated in bonding resins and luting cements to silica-coated zirconia.[20,21]

Considering the metallic nature of pure zirconium, recently an experimental hot chemical etching solution has been advocated for treating zirconia.[22, 23] The optimal temperature for conditioning the substrate is 100^{0} C, for a period of 10 minutes.

The action of the hot etching solution is basically a corrosion-controlled process. It selectively etches the zirconia,[24] enabling for micro-retentions by modifying the grain boundaries through preferential removal of the less-arranged, high energy peripheral atoms.

A recent study by Casucci et al [25] concluded that the effects of the chemo-mechanical zirconia surface treatments are material dependent. The application of the hot experimental etching solution increased the zirconia surface roughness of all the tested materials and created micro spaces that would optimize the overall bonding mechanism.

However, further studies are necessary to confirm the effects of this novel solution on the bond strengths of resin luting agents to pretreated zirconium ceramics.

Is there a bond to Zirconia Ceramics?

Siloxane bonds which include silica, silane and resin cement are formed only if the surface presents oxygen and silica, because both molecules present linking sites between silane and the ceramic.[26] A study by Matinlinna J P et al in 2006 showed greater hardness with Y-TZP ceramics in comparison with a glassy structure which presents the impregnation of silica onto the surface.

For this reason, silane coupling agents do not bond adequately to zirconia ceramics. However some studies have demonstrated good results with tribochemical treatment.[27,28]

There is some evidence that a good bond to Y-TZP ceramics is obtained using resin cements with phosphate ester monomers, (MDP monomer).[29,30] The phosphate ester group chemically bonds to metal oxides (Figure 2) such as zirconium dioxide. Lehmann et al evaluated the durability of the bond to zirconia with two resins cements (Bis GMA based & MDP based). The MDP based cement presented with higher bond strength to zirconia surfaces on 150 days of water storage.[30]

The anhydride group present in 4 META monomer and the phosphoric methacrylate ester also chemically bonds to zirconia ceramics.[29,33] However the bond strength of a polymethylmethacrylate (PMMA) resin cement containing META was not strong enough to resist thermal aging.[31,33]

Blatz and others[29,31] demonstrated that application of an MDP-containing bonding/silane coupling agent is the key factor for a reliable bond to zirconia ceramics and is not influenced by the resin luting agent.

Yoshida and others stated that the bond strength between zirconia and the resin cement increased significantly when the intaglio surfaces were coated with an MDP based metal primer. However this bond also could not resist thermal aging.[32,34]

Understanding bonding to Zirconia

After a fairly extensive literature reviews and research it is apparent that no single specific surface treatment protocol exists to optimize zirconia bonding.

The only consensus found in the literature is that hydrofluoric acid etching and use of silane agents are not effective for zirconia ceramics.[9,10,11] In this regard, dentists/clinicians are at the mercy of manufacturers and it should be incumbent on them to provide accurate and scientifically supported recommendations on how to optimally treat the internal surface of zirconia.

In any case, it is probably safe to make some generalizations regarding porcelain surface treatment of zirconia:-

1) High strength alumina and zirconia core based crowns cannot be etched with Hydrofluoric acid (HF). As a result, it is not possible to bond these restorations with conventional HF/silane treatment. Silica coating followed by silane application has been shown to be a viable option.

2) Proper use of hydrolyzed silane, in conjunction with warm-air drying has adequate scientific support and is advisable after silica coating of zirconia surfaces.

3) The Selective Infiltration Etching (SIE), based on ceramic infiltration by organic oxides through the creation of micro-mechanical irregularities enhances the zirconia ceramic-to-resin cement bonds.

4) The application of the experimental hot etching solution changed zirconia surface morphology and induced a significant improvement in surface roughness as comparable or higher to the well accepted surface treatment modalities.

Conclusion:

Based on the scientific evidence in this literature review the following conclusions can be drawn:

1) Silica coating with aluminum oxide particles (silanted or not) is the surface treatment of choice for improving the bonding to Y-TZP ceramics with resin cements.

2) The use of special functional monomers can chemically bond to zirconium dioxide which further improves the quality of the bond between the ceramic and resin cement.

3) Selective infiltration etching and the application of the experimental hot chemical etching solution may represent effective methods for conditioning zirconia surfaces, enhancing micro-mechanical retention.

4) Further clinical studies are necessary to evaluate the bonding or bond strength of Y-TZP ceramics and establish which technique and materials would be ideal for luting these restorations.

Undulating the confusion over bonding to zirconia requires an understanding of the involved substrates and materials as well as a logical and systemic methodology in their manipulation.

It is clear that while much is known, even more remains to be explored. It has answered some questions, raised a few and provided a greater insight into the nature of bonding to zirconia.

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