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The effect of nano-structured alumina coating on the bond strength of resin-modified glass ionomer cements to zirconia ceramics

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Abstract

The purpose of this study was to evaluate the effect of Y-TZP ceramic surface functionalization with a nano-structured alumina coating on bond strength of the resin modified glass ionomer dental cement. A total of 160 disc-shaped specimens were produced and randomly divided into two groups of 80. Half of the discs in each group received an alumina coating which was fabricated by exploiting the hydrolysis of aluminum nitride (AlN) powder. The shear bond strengths of the resin-modified glass ionomer cement FUJI+ (GC Japan) and the composite resin luting agent RelyX Unicem (3M ESPE, USA) were then studied for the coated and uncoated surfaces The SEM analyses revealed that the application of an alumina coating to the Y-TZP ceramics created a highly retentive surface for bonding. The bond strengths for the coated groups in both cements were significantly higher than the uncoated groups.

Keywords: Zirconia; Adhesion; Resin-bonding; Surface functionalization; Alumina coating

1. Introduction

The growing demand for aesthetic restorations in dentistry has led to the development of tooth-colored, metal-free systems. In most cases, yttria partially stabilized tetragonal zirconia (Y-TZP) is used as the core material, owing to its superior mechanical properties, chemical stability and biocompatibility.[1,2] It has been shown that the long-term survival rate of zirconia-based dental restorations depends largely on the adhesive bond strength and that a stronger bonding to the core would be advantageous for many clinical applications. Unfortunately, establishing a durable chemical or mechanical bond to zirconia has been proven to be difficult because of its surface stability. Although superior in terms of mechanical, aesthetic and biological properties, bonding zirconia still remains a challenge. With silica-based ceramics, a reliable bond can be achieved with hydrofluoric acid (HF) etching followed by silanization.[3] In contrast, chemically stable, silica-free Y-TZP ceramics are acid-etch resistant, and the bonding protocols that are successfully used in silica-based ceramics cannot be employed. For this reason, various mechanical and chemical conditioning methods have been proposed to enhance the bonding between the resin and the ceramics. Of these, airborne-particle abrasion has often been used to increase the surface roughness,[4,5] thereby creating micro-retentions.

Another key feature when establishing a durable bond to Y-TZP ceramics is the appropriate choice of luting cement. Several types of luting agents with different retention mechanisms can be used for the fixation of fixed partial dentures made from Y-TZP. The retention of conventional zinc–phosphate cements is based on the micromechanical interlocking on the intaglio surface of the restorations. In contrast composite resin cements exhibit chemical bonding to Y-TZP ceramics. Composite resin luting agents containing 10 MDP (10-methacryloyloxydecyl dihydrogen phosphate) are currently advocated, since the phosphate ester monomers are capable of a chemical interaction with the hydroxyl groups of the Y-TZP ceramics.[6–8] Adhesive bonding, however, is a time-consuming, multistep clinical procedure. Furthermore, a dry operating field is required during this operation, which is difficult to maintain when the preparation extends below the cemento-enamel junction. As a result, glass ionomer cements (GICs) are being considered as an alternative to composite luting agents. Their use is less complicated and time consuming, since any acid etching can be avoided. GICs are water-based dental

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materials that consist of an acid-decomposable glass and a water soluble acid. They set on the basis of an acid–base or neutralization reaction.[9] They have become widely used because they release fluoride ions over prolonged time periods and thus introduce a certain degree of cariostatic activity. In addition, they do little harm to the dental pulp and are considered to be biocompatible. One of their most favorable properties is an ability to bond chemically to hard dental tissues. This is achieved by an ion exchange between the cement and the apatite minerals.[10] A stable bond is formed that is able to withstand the biting forces that are exerted on the restoration. To overcome the problems associated with early water sensitivity and long setting times a new group of materials named resin-modified glass ionomer cements (RM-GICs) were developed.[11] They are hybrid materials that combine the properties of conventional GICs and composite resins. Curing is the result of both a free-radical polymerization and a neutralization reaction. In these cements part of the water is replaced by hydroxyetilmethacylate (HEMA). RM GICs have two setting reactions: (i) the acid–base reaction and (ii) the polymerization of HEMA.[12,13] The free radical polymerization of HEMA is usually begun with visible light (photopolymerization), but it can also be initiated chemically, as is the case with the frequently used FUJI + luting cement (GC, Japan). The penetration of light through the layers of prosthetic work is limited, but via the chemical activation of HEMA it is also possible to harden the deepest areas of the luting agent.

Despite the user-friendly nature of RM-GICs, their use in bonding to Y-TZP ceramics has recently been questioned.[14] The "in vitro" bond-strength values were found to be significantly lower than those of resin cements and the specimens debonded spontaneously during thermal cycling.[15] A clinical evaluation also revealed higher failure rates for fixed partial dentures, cemented with the RM-GIC: the loss of retention being reported as a the main cause of failure.[16]

In our previous work we proposed a solution to improve the bonding of composite resin luting cements to dental Y-TZP ceramics. It involves a non-invasive functionalization of the core ceramic surface that is based on applying a thin, nanostructured alumina coating. The preparation of the coating, based on exploiting the AlN powder hydrolysis, was described in detail.[17] This method already proved to be very effective in improving the resin-bond strength to Y-TZP ceramics.[18,19]

The purpose of this "in-vitro" study was therefore to evaluate the effect of Y-TZP ceramic surface functionalization with a nano-structured alumina coating on the bond-strength of the resin-modified glass ionomer dental cement. After the synthesis, the coating was characterized using scanning electron microscopy and the shear bond strength of a RM-GIC to a coating–substrate complex, before and after thermal cycling, was evaluated.

2. Materials and methods

2.1. Specimen preparation

The ceramic substrates were fabricated from commercially available, ready-to-press, biomedical-grade, TZ-3YB-E zirconia powder (Tosoh, Tokyo, Japan) containing 3 mol% of yttria in the solid solution to stabilize the tetragonal structure, 0.25 wt% of alumina to suppress the $t \rightarrow m$ transformation during aging, and 3 wt% of an organic binder. This material is most commonly used in the fabrication of biscuit-sintered zirconia blanks. Uni-axial dry pressing at 147 MPa in a floating-head die was used to shape green pellets that were 20 mm in diameter and 3.5 mm thick. These pellets were subsequently pressure-less sintered at 1520 °C for 2 h. After firing, 160 disc-shaped specimens (15.5 ± 0.03 mm in diameter and 2.6 ± 0.03 mm thick) were produced, randomly divided into two groups of 80, and subjected to the following surface treatments.

AS: Left in the as-sintered condition to serve as a control.
APA: Airborne-particle abraded with 110-μm fused-aluminum-oxide particles at 4 bar for 15 s. The discs were mounted in a sample holder at a distance of 30 mm from the tip of the air-abrasion unit, equipped with a nozzle of 5 mm in diameter.

All the specimens were ultrasonically cleaned in acetone, ethanol and deionized water for 2 min in each solvent. Half of the specimens in each group received an alumina coating. The coated groups were designated as AS-C and APA-C.

2.2. Coating preparation

The AlN powder used for the adhesive coating was AlN Grade C (H.C. Starck, Berlin, Germany) with a median particle size of 1.2 μm, a surface area of 6 m^2/g, and an oxygen content of 2.5 wt% O_2. A diluted aqueous suspension containing 3 wt% of AlN powder was prepared by dispersing 7.5 g of AlN powder in 250 ml of deionized water, preheated to 75 °C. Immediately after dispersing the AlN powder, the as-sintered and air-particle abraded Y-TZP substrates were immersed in the suspension for 15 min. Once exposed to hot water, the dispersed AlN powder starts decomposing following reaction (1), resulting in the formation of a nanostructured boehmite coating onto the surface of the immersed substrates. The coated substrates were subsequently air-dried in an oven for 2 h at 110 °C, and thermally treated by heating in an electric resistance furnace in atmospheric air at 900 °C for 1 h. The heating rate was 10 °C/min. The morphology of the representative samples before and after the thermal treatment was analyzed using field-emission scanning electron microscopy (FE-SEM) (Supra 35 LV, Carl Zeiss, Germany). The fine structure of the coating and its interface with the luting cement were analyzed using transmission electron microscopy (TEM) (JEOL, JEM 2010 FX, Japan). The cross-sections were prepared by mechanical polishing and ion etching.

2.3. Shear bond strength testing

Composite resin cylinders were fabricated by filling quartz tubes (inner diameter of 4 mm and height of 3 mm) with a Filtec Z250 composite resin (3 M ESPE, USA) in two increments. Each increment was light polymerized for 20 s with a light source

(Elipar II, 3 M ESPE, USA) positioned immediately above the specimen. The light curing was also applied to the bottom surface, so that each cylinder received a total of 60 s of polymerizing radiation. After this light polymerization the composite cylinders were bonded to different zirconium oxide ceramic surfaces. Two commercially available dental luting cements were used: a resin-modified glass ionomer cement FUJI+ (GC Japan) and a self-adhesive composite resin luting agent RelyX Unicem (3M ESPE, USA). Both cements were in capsule form and the capsules were activated and mixed for 10 s using a mechanical mixer (Capmix, ESPE, Seefeld, Germany). After mixing, the cements were extruded to the bonding surface and the composite resin blocks were luted with the finger pressure. Any excess cement was removed with the cotton pellets and the composite cement was polymerized for 40 s radially along the ceramic-composite cylinder interface. All the bonding procedures were performed by the same operator to ensure that all the specimens were subjected to similar bonding conditions. The bonded specimens were then left for 10 min at room temperature. Each surface-treated Y-TZP ceramic group was divided into two subgroups of 10 each and either stored in distilled water at 37 °C for 24 h or thermally cycled (TC). The latter samples were subjected to 12,000 cycles between 5 °C and 55 °C with a dwell time of 15 s (Thermocycler THE 1200C, SD Mechatronic, Germany). The shear bond strength was tested with a universal testing instrument (Model 4301, Instron Corp. USA) at a crosshead speed of 1 mm/min. The bond strength (S) in MPa was calculated using the formula:

$$S = \frac{L}{A} \quad (1)$$

where L is the load at failure in N and A is the adhesive area in mm^2. The data were analyzed by a two-way analysis of variance (ANOVA). In the case of a significant interaction effect, the Tukey HSD post hoc test was performed. A T-test was used to compare the effect of the thermal cycling in the APA group. p Values below 0.05 were considered to be statistically significant. The statistical analysis was performed using R software, version 2.9.

3. Results and discussion

3.1. Coating characterization

A typical SEM micrograph of a synthesized alumina coating on a Y-TZP ceramic surface before thermal treatment is shown in Fig. 1a. The coating has a uniform thickness and it exhibits a good surface coverage. No cracks and delaminations were observed. Nano-structured lamellas can be seen growing perpendicular to the substrate during the process of AlN powder hydrolysis in an aqueous suspension. According to the SAED pattern obtained from the coating during the TEM analysis, the interlocked nano-sized lamellas consist of poorly crystalline boehmite (AlOOH). During a subsequent thermal treatment at 900 °C, the aluminum hydroxide was converted to a transient δ alumina, while the original coating morphology was preserved, as illustrated in Fig. 1b. In this way a large micro-retentive area

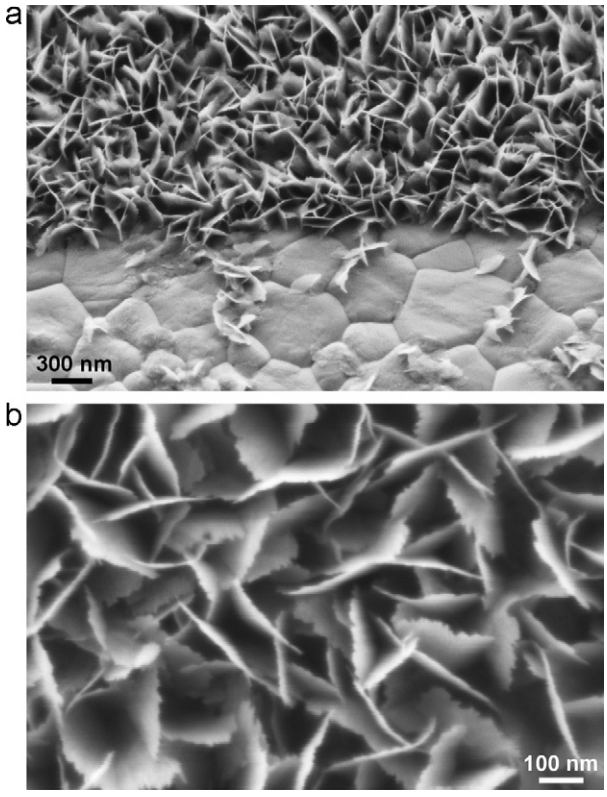

Fig. 1. FE-SEM micrographs of nano-structured alumina coating on a polished Y-TZP surface. (a) Before thermal treatment. (b) After thermal treatment at 900 °C.

was created on the Y-TZP substrate, with the potential for promoting resin bonding. The thickness of the individual lamellas after the thermal treatment is around 6 nm. This was further confirmed by the TEM analysis of the resin-coating interface (Fig. 2), also revealing that the coating–substrate contact is firm, without voids and air inclusions. The resin matrix filled all the inter-lamellar spaces, forming an intermediate structure that was designated as the hybrid layer. The resin was determined to have a good wetting ability.

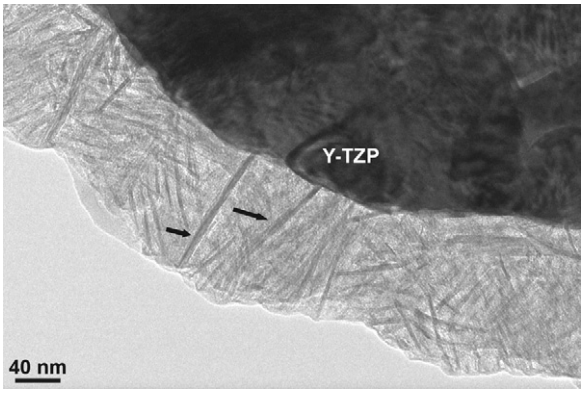

Fig. 2. TEM micrograph of the coating–luting agent interface. Resin matrix filled nano dimensional inter-lammelar spaces and a hybrid layer was formed.

Table 1
Shear-bond strength in MPa (SD) of composite resin luting cement RelyX Unicem and resin-modified glass ionomer cement FUJI+ to Y-TZP ceramic after different surface-conditioning methods.

Surface treatment	Rely X Unicem		FUJI +	
	24 h in water	12,000 thermal cycles	24 h in water	12,000 thermal cycles
As sintered	5.15 ± 0.73	Spontaneous debonding	5.86 ± 1.14	Spontaneous debonding
Air-particle abraded	10.15 ± 1.04	10.16 ± 1.57	8.95 ± 1.37	3.27 ± 1.35
As sintered + coating	24.05 ± 2.90	27.46 ± 3.89	20.07 ± 3.14	20.18 ± 3.83
Air-particle abraded + coating	27.44 ± 3.23	27.32 ± 3.89	17.86 ± 2.04	21.52 ± 3.31

3.2. Shear bond strength

The shear-bond strength values for two different cements and four different surface treatments are presented in Table 1. The application of the surface coating significantly increased the resin-bond strength following 24 h of water storage in the RM-GIC FUJI+ and RelyX Unicem, regardless of the original surface treatment ($p \leq 0.001$). In the uncoated groups, the lowest bond strengths before the TC were obtained with the AS group in both cements. These values were significantly lower than those obtained with the APA groups ($p \leq 0.001$). All the specimens in the as sintered groups, bonded either with the RM-GIC FUJI+ or with the composite resin cement RelyX Unicem debonded spontaneously during thermal cycling (12,000 TC). This is in agreement with the results of previous studies, where spontaneous debonding was also reported for the as-sintered Y-TZP specimens bonded with a composite resin cement[20] and RM-GIC.[21] On the other hand, thermal cycling, did not affect the bond strength of the two coated groups. As seen in Table 1, all the coated specimens survived the TC without any significant reduction in the strength. In addition, with reference to the results presented in Table 1, the air-particle abrasion of the substrate prior to the coating does not seem to play any major role in the bonding, despite all the well documented morphological differences between the as-sintered and air-particle abraded Y-TZP surfaces.[22,23] It can thus be assumed that, regardless of the original surface treatment, the application of the alumina coating is the main factor in the increase of the surface area.

The retention of the cemented restorations is influenced by a number of different parameters. The abutment size (height and width), the convergence angle between the walls, the cements and the materials selected for the FPD fabrication have been shown to play an important role in the performance of the restoration. Providing appropriate size and angle of the abutment conventional surface pretreatments such as airborne particle abrasion and silanization might be utilized prior to bonding. There are, however clinical situations where retention might be compromised due to the reduced bonding area.

Firstly, minimally invasive restorations based on the adhesive approach may offer an alternative to conventionally retained full coverage fixed partial dentures (FPD) which require more tooth preparation. Due to good mechanical properties, Y-TZP ceramics is often selected for inlay retained zirconia FPD. As bonding area is significantly reduced in this type of restorations, the proposed surface functionalization technique offers several advantages over conventional surface treatments.

Secondly, dental implants have gained acceptance in replacing missing teeth and their long-term predictability is well documented. The success of oral rehabilitation with dental implants depends not only on osseointegration but also on the integrity of the abutment-FPD interface. Implant restorations can be screw retained or cemented, whereas luting is a preferable treatment option currently. In the aesthetically demanding areas of the dental arch zirconia abutments are commonly used. It has been shown, that abutment height strongly influences the bonding ability. In reduced interoclusal space, where abutment height is below 5 mm, short abutments are more likely to demonstrate significant differences in retention dependent on cements. Thus for example, significantly lower bond strength values were reported when glass ionomer cement was used compared to the composite cements.[24,25] Applying a nano-structured alumina coating in these clinical situations might improve reliability of the restorations

This is in agreement with the results of this study where significantly higher values after the TC that were obtained for the self-adhesive composite cement, compared to RM-GIC. This could be ascribed to the lower mechanical properties of the RM-GIC.[26,27] The failure mode in the RM GIC is predominantly cohesive within the cement,[18] also indicating that the strength of the cement might be a predominant factor. Another possible explanation is related to the hydrothermal bond degradation that is characteristic of both cements.[28] In RM-GIC, however, it might be more pronounced, since this type of the material absorbs water that might contribute to bond degradation.[29]

4. Conclusion

The goal of our work was to apply a new method to chemically modify the surface of Y-TZP ceramics in order to improve bond-strength to glass ionomer cements. The bond strength data strongly support this new process for non-invasive surface functionalization. The application of a nano-structured alumina coating can improve the resin-bond strength of the RM GIC by a factor of 2–4, which is a remarkable increase. Within the limits of this "in-vitro" study, the application of an alumina coating significantly improves the bond strength compared to an air-abrasion pre-treatment. The proposed technique is simple and can be transferred to dental laboratories.

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