Available online at www.sciencedirect.com
SciVerse ScienceDirect
Journal of the European Ceramic Society 32 (2012) 2641–2645
www.elsevier.com/locate/jeurceramsoc

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

Peter Jevnikar[a,*], Matjaž Golobič[a], Andraž Kocjan[b], Tomaž Kosmač[b]

[a] Department of Prosthodontics, Medical faculty, University of Ljubljana, Hrvatski trg 6, SI-1000, Ljubljana, Slovenia
[b] Engineering Ceramics Department, Jozef Stefan Institute, Ljubljana, Slovenia

Available online 24 April 2012

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

* Corresponding author. Tel.: +386 1 5224242, fax: +386 1 5222504.
E-mail address: peter.jevnikar@mf.uni-lj.si (P. Jevnikar).

0955-2219/$ – see front matter
http://dx.doi.org/10.1016/j.jeurceramsoc.2012.03.037

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, nano-structured 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