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Wetting Characteristics of a Nano Y-TZP Dental Ceramic by a Molten Feldspathic Veneer

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Abstract

The purpose of this study was to evaluate the wetting behaviour of a molten feldspathic glass-ceramic which is used as a veneering layer on dental Y-TZP cores. The grain size effect of the zirconia substrate on the wettability of the veneering material was also studied. It is suggested that the presence of a weak bond at the interface could be attributed to the poor wetting of ZrO2 surface by the molten veneer. Result of the sessile drop analysis showed high contact angles of more than 110˚ at the initial states of the test. The contact angles were affected by increasing the grain size. An about 6% increase in mean of the contact angles of micro Y-TZP was determined when compared to the nano-structured bodies. It is suggested that the fine microstructure which was observed in the nano Y-TZP body enhances the physical wetting behaviour due to a probable increase in surface energy which is considered as the driving force of wetting. The enhancement which was observed in wettability of the nano-sized Y-TZP at longer times may also be originated from a chemical wetting assisted by the diffusion of the atoms through the increased defects of surface such as grain boundaries and triple junctions.

Keywords: Dental Ceramics; Nano-Yttria Stabilized Zirconia; Pheldspathic Veneer; Chipping; Interface; Wettability; Contact Angle.

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1. Introduction

Due to their excellent mechanical properties, perfect biocompatibility and appropriate esthetic properties yttria stabilized zirconia ceramics are receiving great attention to be used in dental and biomedical applications, Vagkopoulou et al. (2009). A nano-structure makes Y-TZP better stabilized and toughened, Angela et al. (2011). By development of several CAD/ CAM systems, zirconia has become one of the most advantageous materials for core materials in all ceramic dental restoration systems. For instance, zirconia is widely used as single crowns, fixed partial dentures, or different parts of dental implants, Koutayas et al. (2009) in restorative dentistry. In application of zirconia as the core material in all-ceramic dental restorations, a glassy feldspathic veneer which is fused at < 1000 °C is applied to the surface of the zirconia. Veneer mainly enhances esthetic properties of the restoration in addition to its stability in wet conditions. However, chipping at the interface of zirconia cores and veneering materials have been reported as the main restriction in clinical use of Y-TZP in dentistry, Komine et al. (2010). The origin of chipping is still unknown but it can be contributed to the presence of a weak bond at the interface of the zirconia core and the veneering material, Aboushelib et al. (2005). The following parameters have been suggested to be the most influencing factors in this regard: mismatches in coefficients of thermal expansion between zirconia and porcelain veneers, residual thermal stresses, differences in modulus of elasticity between zirconia and veneer, porcelain firing shrinkage, addition of coloring pigments, and poor wetting conditions, Komine et al. (2010), Koutayas et al. (2009), Vagkopoulou et al. (2009). Many researches have directed towards the chipping issue in their experimentally oriented studies. Hence, the literature have mainly been focused on evaluating the bond strength between the zirconia cores and various types of veneers or studying the effect of diverse processing parameters and surface treatments on the bond strength, Aboushelib et al. (2008), Aboushelib et al. (2005), Doi and Atsuta (2011), Fischer et al. (2008), Mosharraf et al. (2011), Omori et al. (2013).

Authors of the present paper believe that in order to diagnose such interfacial complications, studying the wettability of the system could help in better understanding of the interactions between these materials at high temperature. Wetting in ceramic – glass interfaces seems to include a complicated combination of chemical and physical phenomena. Proper chemical wetting conditions are achieved when the porcelain firing time and temperature enhances the bulk diffusion of atoms toward the interface. The active sessile drop method is known to be a generally accepted way to study the wetting in liquid/solid systems, Marshall et al. (2010). The measured contact angle from the sessile drop analysis represents the wettability of the solid surface by the liquid. The favorable wetting behaviors are maintained at the minimum contact angles, where the limit of wetting and non-wetting conditions of two materials is assumed at $\theta = 90^\circ$.

2. Experimental Procedure

Pre-sintered dental zirconium oxide blocks (Zirconzahn®–ZRAB0912) where cut into six $15\times15\times5$ mm$^3$ substrates. The cutting was performed using a micro cutting machine with a steel disc. The impure, uneven surface of the cut samples were polished with sand paper at the green state. The prepared substrates were densified in two different firing schedules; the first program was performed at 1500 °C for 1hr, while the time dedicated to the second program (1500 °C, 5hrs) was extended in order to observe a significant growth in zirconia grains. The sintered samples where characterized in terms of density, phase, and microstructural evaluations using Archimedes method, XRD (Inel®, EQ 3000) and SEM (ZEISS®, DSM 960A).

The active sessile drop analysis was used to study the wetting behavior of a feldspatic dentin (Zirconzahn®–KEAA0801) on the prepared substrates. The test was carried out in air and the temperature was set at 990 °C. The contact angles were directly measured from the images which were captured by a CCD camera. In order to eliminate the experimental errors, each test was done four times and the average contact angles of the three similar results were reported as a function of time from 0 to 120 minutes.

3. Results and Discussion

Both firing procedures (1500 °C for 1h and 5hrs) resulted in fully dense and stabilized zirconia ceramics according to density measurements and XRD analysis, carried out after firing. The relative density of the sintered
bodies was measured to be more than 99.7% of the theoretical density. The tetragonal phase is the only phase which can be seen in the XRD pattern of fig. 1. SEM images shown in Fig. 2 reveals that the shorter sintering period made the Y-TZP grains nanometric, while an obvious grain growth is observable at the same body when it is fired at the same temperature for 5 h. When both sample groups are fully dense and stabilized with the same chemical composition, this observed difference between their grain sizes makes them suitable for a comparative wetting study.

![XRD pattern of the sintered Y-TZP samples at 1500°C.](image)

**Fig. 1.** XRD pattern of the sintered Y-TZP samples at 1500°C.

![SEM images of Y-TZP samples sintered at 1500°C.](image)

**Fig. 2.** Effect of sintering time on the grain size of the Y-TZP samples sintered at 1500°C (A) for 1 h; (B) for 5 h.

Figure 3 demonstrates the time dependence of wetting angle, measured at 990 °C for the molten feldspathic veneer on the nano Y-TZP substrate, as well as on a Y-TZP substrate with larger grains. At the initial times of the experiment, relatively high contact angles of more than 110° was observed for both Y-TZP with different grain sizes. Because of the high amount of flux in the veneer composition, it could be assumed that the feldspathic glassy systems should show notable reactivity at their liquid interface with oxide ceramics such as alumina, Denry and Kelly (2008). In case of zirconia and by taking the aforementioned data into account the wetting between these materials should be considered as poor at shorter annealing periods. This could be attributed to a high mismatch of
the lattice parameters between tetragonal phase of zirconia and leucite crystallites within the veneer, Ji et al. (2013), lack of similarity in chemical composition between Y-TZP and the Al₂O₃-SiO₂-K₂O system of the veneer, high surface energy of ZrO₂ as a ceramic hard material, a weak interdiffusion at the interface, Kawai et al. (2010), and/or any other possible reasons that are still unknown. During longer annealing times the contact angles reasonably reduced until it reached values of less than 90°. This gradual decrease in contact angle is normal in systems with high temperature due to the activated chemical wetting mechanism. However, for better controlling the mechanical and esthetic properties of the restoration, dedicating long times of porcelain firing should be avoided. Hence, it would be demanded to reach enhanced wetting behaviors at possible short times. By using a nano-sized Y-TZP, the time required for the veneer drop to wet the substrate (θ < 90°) was measured to be about 10 minutes, while it was three times greater in case of testing the micronized Y-TZP (30 minutes). Furthermore, it seems that the poor wettability of dental zirconia could even get worse by an increase in grain size. As a clue, a difference of about 6% in the contact angles of the nanostructured and microstructured zirconia was determined according to the data given fig. 3.

Due to a relatively great decrease in grain boundaries by over sintering the samples, the surface energy of zirconia would change. Under equilibrium condition, the Young’s equation, Eustathopoulos (1983), is used to describe a physical balance between surface tensions:

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]

where \( \gamma_{sv} \) is the interfacial energy, \( \theta \) is the measured contact angle, and the subscripts s, v, and l refer to the solid, vapor, and liquid phases. According to this equation, the main driving force of physical wetting of a surface by a liquid is its surface energy. In other words, when \( \gamma_{sv} \) is not high enough, the solid phase does not have the enough thermodynamic tendency to further lower its s-v energy by means of spreading a liquid on it. If we assume that \( \gamma_{sl} \) is independent of the microstructure and associated with the surface chemistry, it can be favorable to use fine
structures to get a better wetting. The effect of microstructure on wetting is also studied by XU et al. (2003). They have shown huge differences in wetting behavior of molten Bi on polycrystalline Cu substrates. They have claimed that in Cu/Bi interface, the grain boundaries plays key role for an activated chemical wetting which is assisted by diffusion of atoms through the interface. In case of Y-TZP, in addition to the surface energy effects, this claim can be considered to explain the average 6% difference in contact angles which can be obvious even at longer annealing times of about 90 minutes. By further extending the contact time the equilibrium contact angles of both systems was measured to be about 60°.

4. Conclusion

Wetting characteristics of a molten veneer on a Y-TZP dental ceramic was studied using the sessile drop method. The high contact angles of > 90˚ which was measured at the initial times showed poor physical wetting of the substrate materials with different grain sizes. A continuous decrease of θ by passing time proved activation of chemical wetting mechanism at 990 °C in longer times. The grain size of Y-TZP clearly influenced wettability as mean of the contact angles in zirconia with nano-sized grains decreased by 6% compared to the micronized substrate. The time required for achieving contact angles of less than 90˚ in nano-sized Y-TZP was measured to be about 10 minutes, while this time was about 30 minutes for the microstructured bodies. In other words, by using a nano-sized zirconia core better wetting behaviors was recorded in shorter porcelain firing times.

References