J.-W. Kim¹, N.S. Covell¹, P.C. Guess²,
E.D. Rekow³, and Y. Zhang^{1*}

¹Department of Biomaterials and Biomimetics, New York University College of Dentistry, 345 East 24th Street, New York, NY 10010, USA; ²Department of Prosthodontics, University Hospital, Hugstetter Strasse 55, 79106 Freiburg, Germany; and ³Office of the Provost, New York University, New York, NY, USA; *corresponding author, yz21@nyu.edu

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ABSTRACT

Zirconia-based restorations are widely used in prosthetic dentistry; however, their susceptibility to hydrothermal degradation remains elusive. We hypothesized that CAD/CAM machining and subsequent surface treatments, *i.e.*, grinding and/or grit-blasting, have marked effects on the hydrothermal degradation behavior of Y-TZP. CAD/CAM-machined Y-TZP plates (0.5 mm thick), both with and without subsequent grinding with various grit sizes or grit-blasting with airborne alumina particles, were subjected to accelerated aging tests in a steam autoclave. Results showed that the CAD/CAM-machined surfaces initially exhibited superior hydrothermal degradation resistance, but deteriorated at a faster rate upon prolonged autoclave treatment compared with ground and grit-blasted surfaces. The accelerated hydrothermal degradation of CAD/CAM surfaces is attributed to the CAD/CAM machining damage and the absence of surface compressive stresses in the fully sintered material. Clinical relevance for surface treatments of zirconia frameworks in terms of hydrothermal and structural stabilities is addressed.

KEY WORDS: zirconia (Y-TZP), surface treatments, phase transformation, low-temperature degradation (LTD), fatigue strength.

Concerns of Hydrothermal Degradation in CAD/CAM Zirconia

INTRODUCTION

High aesthetic demands of patients and excellent biocompatibility have driven the growing use of ceramics in restorative dentistry (Raigrodski, 2004). A major problem with all-ceramic restorations is low fracture resistance. Due to an unusual combination of high strength and toughness, yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) has become the material of choice for ceramic crown/bridge restorations, implant abutments, and so forth. (Jeong *et al.*, 2002; Pilathadka *et al.*, 2007; Kohal *et al.*, 2008).

Zirconia occurs in 3 polymorphs: cubic (*c*), tetragonal (*t*), and monoclinic (*m*). When stabilized with yttria, the high-temperature tetragonal zirconia structure can be retained at room temperature. External stresses can return the metastable tetragonal particles to a stable monoclinic phase. This *t*→*m* phase transformation is accompanied by a shear strain of ~0.16 and a volume expansion of ~5% (Hannink *et al.*, 2000). The shear strain and the volume change induce compressive stresses and microcracks around the transformed particles, which effectively oppose the opening of cracks and increase the resistance to crack propagation (Garvie *et al.*, 1975). This so-called 'transformation toughening' mechanism results in the superior mechanical properties of Y-TZP. The *t*→*m* phase transformation can also occur at low temperatures, especially in the presence of water. This is commonly known as aging or low-temperature degradation (LTD). Aging occurs by a nucleation and growth process, which initiates from isolated surface grains, gradually spreads along the surface, and proceeds into the bulk, resulting in surface roughening and reductions in strength, toughness, and density (Hirano, 1992; Piconi and Maccauro, 1999; Zhang *et al.*, 2004a).

Recently, the introduction of Computer-aided Design/Computer-aided Manufacturing (CAD/CAM) has become an increasingly popular alternative to traditional manufacturing techniques (Strub *et al.*, 2006). To reduce processing time and wear of the cutting instruments during the milling process, many CAD/CAM systems use partially sintered Y-TZP blocks instead of fully sintered ones (Raigrodski, 2004). After CAD/CAM milling, the partially sintered framework/core is then subjected to final sintering. Because of this process, CAD/CAM-prepared surfaces inherently possess micro-defects. In addition, adjustments of the intaglio surface (cementation surface) of Y-TZP framework by grinding and/or polishing to achieve better fit are commonly performed by dental practitioners and technicians (Aboushelib *et al.*, 2009). Airborne abrasion of the Y-TZP cementation surface is widely recommended to increase micromechanical retention and durability of resin bond strength (Wolfart *et al.*, 2007).

Although the grinding and abrasion behaviors of zirconia (especially their effects on strength) have been studied (Kosmac *et al.*, 1999, 2000; Zhang *et al.*, 2004b, 2006), the hydrothermal stability of Y-TZP subject to abrasive machining and grit-blasting has not been systematically investigated. In

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Figure 1. SEM micrograph of polished (1 μm finish) and thermally etched (1400°C for 20 min) Y-TZP surface, showing a homogenous microstructure with an average grain size of 0.5 μm .

Figure 2. SEM micrographs showing representative features of (a) as-received CAD/CAM-machined, (b) grit-blasted, and (c) 120-grit ground surfaces of Y-TZP before subsection to steam autoclave treatments. Images are of both surface and sectional views.

addition, little attention has been paid to the low-temperature degradation behavior of CAD/CAM-machined Y-TZP. This study investigated the hydrothermal stability of CAD/CAM Y-TZP blanks with and without post-sintering surface modifications, namely, grinding and alumina abrasion.

MATERIALS & METHODS

Fifteen Y-TZP plates (10 x 10 x 0.5 mm in dimension) were CAD/CAM-machined with 64- μm burs from pre-sintered blocks and then sintered to full density by the manufacturer (IPS e.max[®] ZirCAD, Ivoclar-Vivadent, Schaan, Liechtenstein). Specimens were randomly divided into 5 groups. A control group of 3 specimens ($n = 3$) received no additional treatment. The remaining 4 groups received various surface treatments: grit-blasted with 50- μm alumina particles at a compressive air pressure of 0.5 MPa for 5 sec at a standoff distance of 10 mm ($n = 3$); or ground with resin-bonded diamond discs of various grit sizes—80-grit (~200 μm , $n = 3$), 120-grit (~162 μm , $n = 3$), and 600-grit (~30 μm , $n = 3$). These grit sizes were carefully selected to simulate dental diamond burs: 80-grit represents a super-coarse diamond bur (Black, 181 μm , Komet, Stuttgart, Germany); 120-grit correlates to a coarse diamond bur (Blue, 151 μm); and 600-grit mimics an extra-fine diamond bur (Yellow, 25 μm).

Low-temperature aging was carried out in a steam autoclave (Amsco Steris SG-120 Gravity Sterilizer, Mississauga, ON, Canada) at 122 (± 1)°C under 2 bars of pressure for predetermined durations. Since the $t \rightarrow m$ phase transformation in Y-TZP is thermally activated and is accelerated by the presence of water, steam autoclave treatments at elevated temperatures can effectively induce phase transformation. Since the thermal activation energy required for this phase transformation is ~106 kJ/mol, it is possible to estimate that 1 hr of steam autoclave treatment at 122°C under 2 bars has the same effect as 1 yr *in vivo* (Chevalier *et al.*, 1999).

We used scanning electron microscopy (SEM, Hitachi S-3500N, Tokyo, Japan) to observe the surface (surface view) and subsurface (section view) features in specimens before and after aging. Prior to SEM examination, the specimens were gold-coated to prevent charge accumulation.

Quantitative analysis of the phase transformation on the surfaces of Y-TZP plates following each successive autoclave treatment was made with the use of an x-ray diffractometer (XRD) equipped with Cu-K α radiation (Philips X'Pert X-ray Diffractometer, Philips Analytical Inc., Natick, MA, USA). X-ray diffraction spectra were collected over a 2 θ range between 27° and 33° at a scan speed of 1°/min and a step size of 0.02°. The monoclinic phase fraction was calculated according to the Garvie-Nicholson method (Garvie, 1972).

RESULTS

A SEM micrograph of polished (1 μm finish) and thermally etched (1400°C for 20 min) sections of Y-TZP revealed a homogenous microstructure (Fig. 1). The specimen possessed an average grain size of 0.5 μm , as determined by the linear intercept method (Wurst and Nelson, 1972).

The representative features of the as-received, grit-blasted, and ground surfaces of Y-TZP before subsection to steam autoclave treatments are presented in the SEM micrographs (Fig. 2). Images were taken in both surface and sectional views. Damage sustained was quite different for each group studied. The as-received CAD/CAM surfaces (control group) were covered with flakes of

smeared materials coupled with a high incidence of microcracks and wear debris [Fig. 2(a)]. A sectional view revealed that the CAD/CAM surfaces were quite rough and consisted of microcracks penetrating 4–6 μm beneath the surface [indicated by arrows in Fig. 2(a)].

The grit-blasted surfaces contained a high area fraction of plastically deformed zones with high incidence of randomly oriented plough marks or grooves [Fig. 2(b)]. A previous study with nanoindentations revealed an increased microcrack density associated with the plastically deformed regions on grit-blasted Y-TZP surfaces (Zhang *et al.*, 2004a). The sectional view showed subsurface cracks, typically 2–4 μm below the surface, propagating laterally (in a direction parallel to the specimen surface) and eventually intersecting with the surface.

The morphology of 80-, 120-, and 600-grit ground surfaces consisted mainly of long scratches [Figs. 2(c)]. However, the width of these scratches was wider in 80- or 120-grit ground surfaces than in 600-grit surfaces. Detailed inspection revealed that zirconia surfaces ground with coarse diamond grits (80- or 120-grit) contained characteristic features associated with scratch grooves composed predominantly of plastically deformed materials at the bottoms of the grooves and microcracks, deformed materials (side flow across the scratches), and wear debris at the edges of the grooves. Similar features were observed on the zirconia surfaces ground with a 600-grit diamond wheel, but the occurrence of microfracture and wear debris was less compared with that on 80- or 120-grit ground surfaces. Section view micrographs showed that 120-grit grinding generated lateral cracks 2–4 μm beneath the surface, extending several tens of microns laterally [Figs. 2(c)]. No significant microcracks were observed on 600-grit ground surfaces. Further, the surface roughness was much greater following 80- or 120-grit grinding than following 600-grit grinding.

The representative features of the as-received, grit-blasted, and ground surfaces of Y-TZP, after subjection to steam autoclave treatments at 122°C under 2 bars for 20 hrs, are presented in the SEM micrographs (Fig. 3). Compared with unaged specimens (Fig. 2), the surfaces of aged specimens had a grainy appearance, especially along the edges of the scratch grooves [Figs. 3(a), 3(c)]. Sectional view revealed a surface grainy layer in all specimens: being ~4–6 μm thick for as-received and grit-blasted surfaces; ~1–3 μm for 120-grit ground surfaces; and less than 2 μm for 600-grit ground surfaces.

The relative amounts of monoclinic (*m*) zirconia detected by XRD on the specimen surfaces were plotted as a function of cumulative autoclave treatment duration (Fig. 4). Before thermal aging, as-received surfaces contained negligible amounts of *m*-phase, while grit-blasted and ground surfaces consisted of ~5% *m*-phase. After 2 hrs of aging in a steam autoclave (122°C, 2 bars), grit-blasted surfaces showed ~12% *m*-phase, and ground surfaces exhibited ~7–8% *m*-phase. Again, no *m*-phase was detected on the CAD/CAM-machined (control) surfaces. As the aging time accumulated, the amount of *m*-phase increased steadily in grit-blasted and ground surfaces. The amounts of *m*-phase, in descending order, were: grit-blasted, then 80- and 120-grit ground (no significant difference between the two), and

Figure 3. SEM micrographs showing representative features of (a) as-received CAD/CAM-machined, (b) grit-blasted, and (c) 120-grit ground surfaces of Y-TZP after subjection to steam autoclave treatments at 122 ($\pm$ 1)°C under 2 bars of pressure for 20 hrs. Again, images are of both surface and sectional views.

then 600-grit ground. The *m*-phase in as-received surfaces ranked the lowest up to 10 hrs of aging, but eventually caught up with that in the ground surfaces. Interestingly, the amount of *m*-phase in the as-received surfaces increased dramatically after 10 hrs of aging and outpaced that in the other groups. After 20 hrs of autoclave aging, the CAD/CAM-machined control surfaces contained over 55% *m*-phase, while grit-blasted surfaces had ~30%, 80- and 120-grit ground surfaces had ~20%, and 600-grit ground surfaces had a low 15% *m*-phase.

DISCUSSION

Our results demonstrate that surface treatments, *i.e.*, CAD/CAM machining with or without subsequent grit-blasting or grinding, have pronounced effects on the hydrothermal degradation behavior of Y-TZP. The present CAD/CAM zirconia frameworks were prepared with pre-sintered Y-TZP blocks, followed by a final sintering stage (Sindel *et al.*, 1998; Raigrodski, 2004). CAD/CAM machining of pre-sintered Y-TZP blocks induced compressive stresses (both from the *t*→*m* phase transformation and from a plastically deformed surface layer) and microcracks at the surface. The final densification of partially sintered Y-TZP frameworks at temperatures between 1350 and 1550°C resulted in over 20% volume shrinkage. This sintering process partially healed microcracks and eliminated voids and flaws. It also facilitated the *m*→*t* phase transformation and relieved surface

Figure 4. The relative amount of monoclinic (*m*) phase detected by XRD on Y-TZP surfaces following steam autoclave treatments at 122 (± 1)°C under 2 bars of pressure for 20 hrs. Note that the equivalent *in vivo* time was estimated based on the thermal activation energy (~106 kJ/mol) required for *t*→*m* phase transformation (Chevalier *et al.*, 1999).

compressive stresses derived from the CAD/CAM milling process (Raigrodski, 2004). This is supported by our SEM observations, demonstrating that the surface and subsurface microcracks are not fully healed by the final-sintering process. The current XRD analyses revealed no detectable monoclinic phase in as-received CAD/CAM specimens and in specimens subjected to short-term aging tests (up to 2 hrs at 122°C under 2 bars of steam, equivalent to 2 yrs *in vivo*). However, the rough surfaces, which consist of microcracks without the presence of any compressive stresses, eventually lead to increased low-temperature degradation of CAD/CAM Y-TZP surfaces.

Post-sintering grinding and grit-blasting induce mechanical damage as well as compressive stresses on Y-TZP surfaces. Grit-blasting produces grain boundary microcracks (resulting from high-impact energy and the volume expansion associated with *t*→*m* transformation), lateral cracks, cutting grooves, and plastic deformations of the surface material (Zhang *et al.*, 2000, 2001; Zhang, 2006). Grinding, in contrast, could introduce damage varying from deep scratches associated with penetrating median cracks (under coarse grit and high loads), to subsurface lateral cracks to shallow scratches, depending on the grit size, applied load, and grinding speed (Yin *et al.*, 2003, 2006; Quinn *et al.*, 2005). A scratch groove consists of zones of two types of stresses (Yin *et al.*, 2003). Along the scratch edges, where the displaced grains exist, is a region of tensile stress. Under the central valley of the scratch is a plastically deformed zone with associated compressive stress (Rainforth, 2000). The plastically deformed surface layer resulting from grit-blasting and grinding, together with *t*→*m* phase transformation, produces compressive stresses. It has been well-documented that surface compressive stresses suppress the LTD process (Deville *et al.*,

2006), while microcracks facilitate the LTD process by providing passage for water (Chevalier, 2006). As a result, only the grains along the scratch edges (where the tensile stresses are located) were extensively transformed into *m*-phase; the remaining surface area contained only isolated monoclinic particles. Therefore, despite the presence of microcracks, the residual stresses are able to suppress the LTD process, resulting in ~15 to 30% *m*-phase in the grit-blasted and ground Y-TZP surfaces following cumulative aging tests at 122°C under 2 bars of steam for a total of 20 hrs (equivalent to ~20 yrs *in vivo*), which is much lower than that (~55% *m*-phase) of as-received CAD/CAM-machined surfaces. A previous study has shown that Y-TZP surfaces containing ~70% *m*-phase caused ~30% reduction in fatigue strength compared with their polished counterparts (Zhang *et al.*, 2006).

The concept of utilizing grinding- and grit-blasting-induced compressive stresses to enhance the LTD resistance and thus flexural strength of metastable tetragonal zirconia was suggested by Chevalier (Deville *et al.*, 2006) and Kosmac (Kosmac *et al.*, 1999). It was proposed that if the microcracks are confined within the plastically deformed compressive layer, both the LTD resistance and flexural strength can be improved. This may be true for the immediate load flexural strength. For long-term fatigue loading, our study showed that although there are no large median or lateral cracks in 600-grit ground Y-TZP and only shallow lateral cracks in grit-blasted Y-TZP, the as-received CAD/CAM-machined Y-TZP exhibits higher long-term flexural strength than do 600-grit ground and grit-blasted Y-TZP. In addition, our study showed that microcracks (~0.5 μm, induced by nanoindentation on polished surfaces) in the range of Y-TZP grain size, are capable of propagating under cyclic stressing, resulting in long-term strength degradation (Zhang and Lawn, 2005). It has been well-established that shear-driven plastic deformation of ceramics due to indentation with hard, sharp objects is associated with a zone of diffused microscopic shear cracks (Lawn, 1993). We introduced a zone of diffused shear cracks onto polished (1 μm finish) Y-TZP surfaces (without introducing any median or lateral cracks), using a spherical tungsten carbide indenter (*r* = 1.5 mm) at 3000-N load (Zhang *et al.*, 2004a). We then subjected these diffused zones to cyclic stressing and demonstrated that microscopic shear cracks can coalesce and evolve into strength-limiting cracks under fatigue loading, especially in wet environments (which is pertinent to dental applications) (Zhang *et al.*, 2004a). Therefore, utilizing compressive stresses to suppress the LTD of Y-TZP by grinding or grit-blasting inherently compromises its long-term strength.

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