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Emerging Ceramic-based Materials for Dentistry

ABSTRACT

Our goal is to give an overview of a selection of emerging ceramics and issues for dental or biomedical applications, with emphasis on specific challenges associated with full-contour zirconia ceramics, and a brief synopsis on new machinable glass-ceramics and ceramic-based interpenetrating phase composites. Selected fabrication techniques relevant to dental or biomedical applications such as microwave sintering, spark plasma sintering, and additive manufacturing are also reviewed. Where appropriate, the authors have added their opinions and guidance.

PREAMBLE

Three new ceramic-based materials have recently been introduced in dentistry: monolithic zirconia, zirconia-containing lithium silicate ceramics, and interpenetrating phase composites. These emerging restorative materials stem from very different technological approaches that are likely to lead to further developments. At this stage, it seems appropriate to provide a focused update on these new materials.

FULL-CONTOUR ZIRCONIA CERAMICS

Background

Zirconia ceramics were introduced in dentistry more than a decade ago (Denry and Kelly, 2008; Kelly and Denry, 2008). Clinical studies have demonstrated their excellent performance despite early issues involving chipping of veneering porcelain (Sailer *et al.*, 2006, 2007). Zirconia ceramics owe both clinical popularity and success to their outstanding mechanical properties and ease of machining in the green stage *via* computer-aided design and computer-aided manufacturing (CAD-CAM) technology. Zirconia is monoclinic at room temperature and becomes tetragonal above 1,170°C. The third most common phase is cubic, above 2,370°C (Subbarao, 1981). The reversible tetragonal-to-monoclinic (*t-m*) phase transformation is accompanied by an increase in volume upon cooling. This transformation can be prevented by stabilizing tetragonal zirconia at room temperature *via* alloying with various oxides. Zirconia ceramics for dental applications are commonly stabilized with 3 mol% yttria. Stabilized tetragonal zirconias exhibit excellent mechanical properties imparted by the stress-induced *t-m* transformation, which is accompanied by a 4.5% volume increase (Garvie and Nicholson, 1972; Garvie *et al.*, 1975). This unique behavior leads to development of a transformation zone, shielding the propagating crack tip and inhibiting further crack propagation, successfully enhancing toughness. Zirconia ceramics exhibit the highest flexural strength and fracture toughness of all dental ceramics currently available.

Early issues with chipping of veneering porcelain appear to have been successfully addressed with adoption of slower heating and cooling rates reflected in laboratory practices and manufacturer recommendations, in addition to a compelling scientific explanation regarding temperature rate sensitivity (Benetti *et al.*, 2014). However, other than one presentation (at a General Session of the International Association for Dental Research [IADR]) evaluating 702 zirconia/porcelain units for up to five years, with porcelain failures no more prevalent than those for metal-ceramic systems (Nathanson *et al.*, 2010), nothing clinical appears to have been published. In the opinion

of the authors, most of the clinical trials reporting porcelain problems likely include a majority of prostheses predating the now-widespread practice of slow cooling.

It can be argued that the perception of porcelain issues likely contributed to the development of full-contour zirconias. With the elimination of veneering porcelain, only internal coloration and stains remain to achieve adequate esthetics. However, the use of full-contour zirconias in dental applications, which include single- and multi-unit restorations, full-arch implant-supported prostheses, abutments, implants, and orthodontic brackets, raises a set of unique challenges stemming from shade production, tribological behavior, and long-term chemical stability. Intricate complexities in mechanical and chemical behavior of partially stabilized zirconia have not yet been fully explored. However, it is well-established that every step of the fabrication process of zirconia ceramics has to be carefully controlled to achieve expected mechanical and chemical properties. This includes blank fabrication, green machining, sintering process, and surface treatments, whether chemical, thermal, or mechanical.

Blank Fabrication

Blank fabrication is the first step of the fabrication process, in which powder chemical purity, granule characteristics, type of pressing, and pre-sintering treatment all play a critical role in final properties. One study (Stoto *et al.*, 1991) compared two 3Y-TZP powders of nearly identical chemical composition, except for the amount of residual impurities (820 ppm *vs.* 360 ppm). It was shown that a glassy phase forming a continuous layer (1.5 to 2 nm) at grain boundaries and multiple junctions was present in the material containing the largest amount of impurities, together with a greater grain size. The conclusion that larger amounts of impurities favor yttrium transport, leading to cubic phase formation, has serious implications for the stability of 3Y-TZP: cubic grains are enriched in yttrium, leaving surrounding tetragonal grains depleted, less stable, and more susceptible to transformation (Chevalier *et al.*, 2004).

Powder granulometry and compaction mode also play a key role in determining the final microstructure. 3Y-TZP powders typically start with a crystallite size of 30-40 nm, from which spray-dried agglomerates (diameter, 20-80 μm) are then produced. These agglomerates have been shown to induce a coarse pseudo-grain structure, more likely to occur when blanks are uniaxially pressed. This is due to the fact that the degree of compaction obtained with uniaxial pressing is not as intense or homogeneous as that obtained with isostatic pressing. The presence of micropores at pseudo-grain boundaries could potentially decrease resistance to low-temperature degradation (LTD) by facilitating diffusion of water species (Swain, 2014). The pre-sintering conditions of blanks directly influence machinability in the green stage, final sharpness, and accuracy from the sizes and shapes of chippings (Filser *et al.*, 2003).

Sintering Process

Sintering conditions are influential in determining the final properties of 3Y-TZP by acting on chemical species distribution and microstructure. Sintering temperature and duration determine grain size, amount of cubic phase, and yttrium segregation, which in turn dictate metastability, mechanical properties, and resistance to LTD. It is well-established that grain size in 3Y-TZP ceramics increases as the sintering temperature increases from about 0.3 μm after sintering at 1,350°C for 2 hr up to >2.0 μm after sintering at 1,650°C for the same duration (Fig. 1). Larger grains are more susceptible to transformation. A larger grain size is therefore beneficial to mechanical properties but decreases the resistance to LTD. Considering that sintering temperatures of dental 3Y-TZPs vary from 1,350°C to 1,600°C, it is clear that these materials will behave very differently, depending on sintering conditions and final grain size. The sintering temperature will also determine the amount of cubic phase and yttrium distribution (Matsui *et al.*, 2003), which have been shown to directly influence resistance to LTD (Chevalier *et al.*, 2004).

Although, to the authors' knowledge, no clinical evidence of LTD has yet been reported for dental zirconias, the combination of lower-grade powders, high sintering temperatures, and direct exposure to oral fluids has the potential to trigger this slow but autocatalytic phenomenon (Keuper *et al.*, 2013). Indeed, looking back at the performance of zirconia femoral heads in orthopedics, the lack of consistency throughout clinical studies is worth noticing, with some excellent *in vivo* performance reports mixed with some clearly alarming reports (Clarke *et al.*, 2003), independently of process-related series of failures reported in 2001. This clearly indicates that *in vivo* use of zirconia should, at the very least, be carefully monitored over time, and failures analyzed.

Tooth Color Reproduction

Precise tooth color reproduction presents one of the most significant clinical challenges associated with full-contour zirconia. Whether monolithic zirconia can ever match the esthetics of veneered all-ceramics is questionable, and today's clinicians are left with a subjective decision often involving the position of the dentition in question and whether the entire esthetic zone is being restored (*e.g.*, complete implant-supported denture). From a materials viewpoint, a traditional ceramic-engineering approach would be to add coloring oxides to zirconia powders prior to pressing the blanks. Another possibility is color-doping of powder granules by co-precipitation, leading to homogeneous color distribution; but many shades are needed, making both of these approaches financially challenging. A popular means of coloring zirconia restorations is by infiltration of various metal salts at low concentrations (Suttor *et al.*, 2004). However, the infiltration technique has some drawbacks, such as a non-uniform color due to the possible presence of porosity gradients (Shah *et al.*, 2008). Issues related to limited diffusion depth of coloring solutions have also been reported, leading to lighter areas after grinding adjustments (Oh *et al.*, 2012). Finally, the sintering temperature should be carefully controlled, since it may influence oxidation state and therefore color. Esthetics-matching with monolithic zirconia also relies on achieving an acceptable degree of translucency. Mean grain size influences translucency through the number of grain boundaries, with
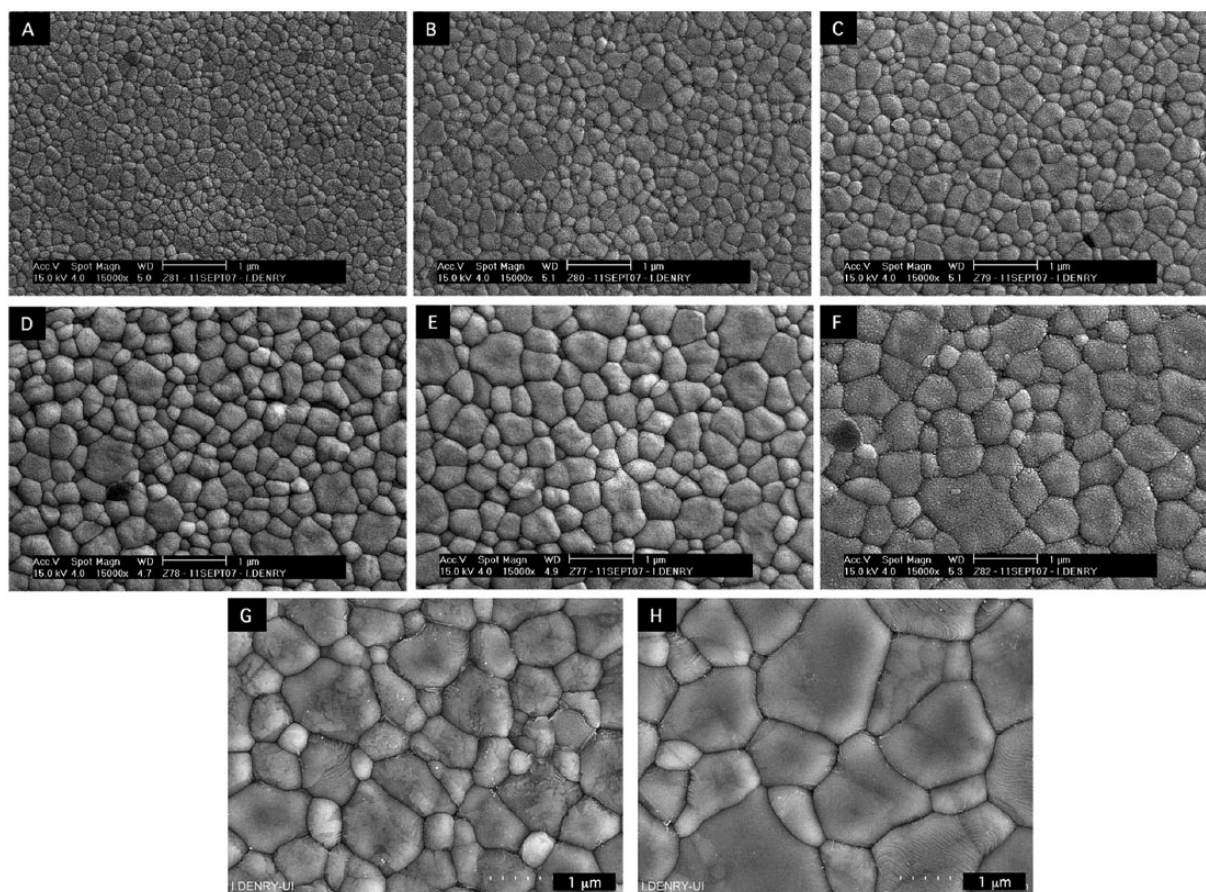
Figure 1. Scanning electron micrographs showing the effect of sintering temperature on grain size in 3Y-TZP sintered for 2 hr. **(A)** 1,300°C; **(B)** 1,350°C; **(C)** 1,400°C; **(D)** 1,450°C; **(E)** 1,500°C; **(F)** 1,550°C; **(G)** 1,600°C; and **(H)** 1,650°C.

smaller grain sizes leading to decreased translucency due to the larger number of grain boundaries. For reasons explained earlier and including greater metastability, increasing the sintering temperature to obtain a more translucent ceramic by increasing grain size is not desirable.

Final Surface State and Tribological Behavior

The quality of the final surface state in monolithic zirconia restorations is particularly important, since it will condition both metastability and tribological behavior. It is well-established that grinding or sandblasting lead to surface phase transformation to monoclinic, and the associated development of compressive stresses. Meanwhile, chair-side polishing to a mirror finish successfully eliminates the thin layer of monoclinic phase and compressive stresses but may not fully remove deep defects created by grinding, due to grain pullout and formation of microcraters. In addition, *via* the surface stress state, polishing increases the sensitivity to LTD by enhancing monoclinic phase nucleation around residual scratches (Deville *et al.*, 2006). Heat treatment following grinding, sandblasting, or aging was shown to reverse the transformation and eliminate compressive stresses, or surface roughening in the case of LTD (Deville *et al.*, 2006; Denry *et al.*, 2010). Indeed, a few manufacturers recommend a

"regeneration firing" (1,000°C/15 min) to reverse the transformation (*m-t*). Heat treatments as low as 650°C for 1 min were shown to reverse the transformation successfully (Denry *et al.*, 2010). Other work revealed a significant reduction in grain size from 0.38 to 0.15 micrometers after diamond grinding and annealing at 1,200°C (Kao *et al.*, 2000). Grain refinement occurred by recrystallization, made possible from the strain energy associated with plastic deformation during grinding. This also points out the complex nature of metastable zirconia ceramics.

Although wear protocols vary widely, there seems to be a consensus on the fact that glazed zirconia is more abrasive than polished or as-sintered zirconia (Figueiredo-Pina *et al.*, 2013; Janyavula *et al.*, 2013; Kontos *et al.*, 2013). It is estimated that the glaze layer is only between 30 and 50 μm thick and worn in 6 mo *in vivo* against enamel. The surface state under the glaze layer will therefore determine further wear characteristics (Etman, 2009). One study reported 100% enamel cracks in natural teeth in contact with zirconia, possibly due to fatigue mechanisms (Stawarczyk *et al.*, 2013). It is worth noticing that extensive formation of monoclinic phase and associated compressive stresses decreases the wear resistance of 3Y-TZP. This was attributed to microcracking, larger grain size, and weakness of the *m*-phase (Conoci *et al.*, 1999). Concurrently, wear of
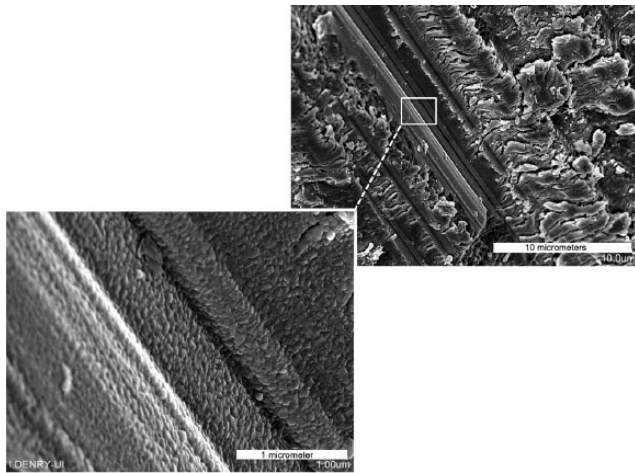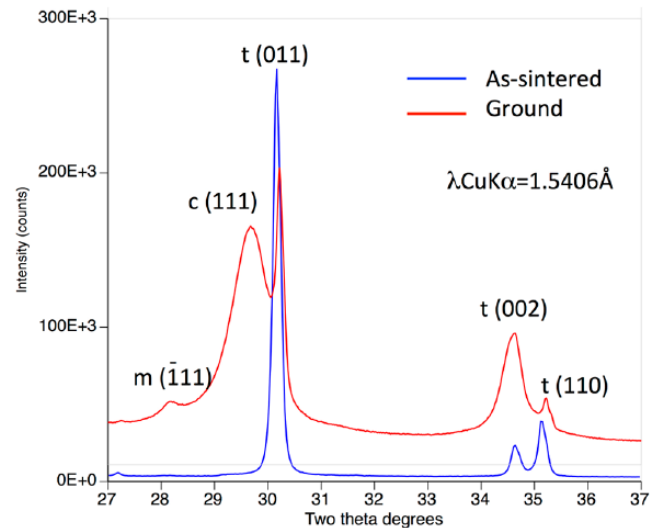
Figure 2. Scanning electron micrographs of as-received machined dental implant abutment surfaces. Extensive microcracking can be seen, as well as some grain refinement within deep machining grooves.

Figure 3. X-ray diffraction pattern of 3Y-TZP dental implant abutment as-received (blue) and after rough grinding (red).

3Y-TZP in self-mated conditions was shown to increase with increasing grain size (Gahr *et al.*, 1993). This ensures that when monolithic zirconia is used, surfaces should be carefully polished if grinding adjustments are necessary, since rougher surfaces lead to increased wear of antagonist enamel (Mitov *et al.*, 2012).

Tribology is a "black art". In the opinion of the authors, wear suitability will likely be settled not by *in vitro* analyses but by clinical measures and observations. In our experience, many clinicians we know who place monolithic zirconia have yet to observe untoward findings. Yet the definitive answer awaits quantitative clinical assessment.

Dental Implant Abutments (the importance of processing/property relationships and design)

Zirconia is also used in the manufacture of implant abutments. While full-contour zirconia has been clinically successful in single- or multi-unit cemented restorations, there have been reports of implant abutment failures (both *in vivo* and *in vitro*) related to processing and design problems with custom CAD/CAM abutments (Aboushelib and Salameh, 2009; Sailer *et al.*, 2009). Abutment surfaces are likely to play a key role in long-term clinical performance, with significant differences between machined and as-heat-treated surfaces. Machined surfaces exhibit extensive microcracking as well as some grain refinement within deep machining grooves (Fig. 2). Some products may also exhibit surface defects such as pore clusters, together with various amounts of cubic grains, easily identified from their large size (Denry, 2013). The presence of significant amounts of cubic phase at abutment surfaces is not desirable, since it indicates inhomogeneities in yttrium distribution (Chevalier *et al*., 1999; Chevalier, 2006). The quality of surface finish and the associated stress-state is unequivocally a key issue when considering clinical applications of monolithic zirconia. In addition to the formation of the monoclinic phase, grinding of 3Y-TZP leads to the formation of a rhombohedral or pseudo-

cubic phase, characterized by x-ray diffraction (XRD) as a significant shoulder to the left of the main reflection *(011)* of the tetragonal phase (Hasegawa, 1983; Hasegawa *et al.*, 1985; Kitano *et al*., 1988; Kondoh, 2004). Grinding also triggers ferroelastic domain switching, expressed by XRD as a reversal of intensities of the *t(002)* and *t(110)* tetragonal reflections (Fig. 3). Ferroelastic domain switching has been identified as an important additional toughening mechanism for zirconia and is not reversed by annealing (Virkar and Matsumoto, 1986; Chevalier *et al*., 2009). Evidence of microstructural domain reorientation (switching) in 3Y-TZP is shown in Fig. 4. Of clinical concern, abutment failure without screw fracture can lead to the production of sufficient titanium debris to cause gingival tattooing (Taylor *et al.*, 2014).

In summary, full-contour zirconias represent a class of emerging ceramics that show excellent promise in terms of mechanical properties. Hopefully, future research in the refinement of these materials for dental applications can benefit from the wealth of information and literature already available from other applications of these ceramics. Emphasis should be placed on proper control of the final surface-state to ensure reliability and long-term performance.

ZIRCONIA-CONTAINING LITHIUM SILICATE CERAMICS (ZLS)

Lithium silicate-based glass-ceramics were recently introduced as machinable materials (Celtra™, Dentsply; Suprinity®, Vita) for CAD-CAM techniques, with claimed mechanical properties comparable with those of lithium disilicate glass-ceramics (L2S). The technology relies on the addition of 10 wt% zirconium oxide to lithium silicate glass compositions. Zirconia acts as nucleating agent but remains in solution in the glassy matrix, with two main consequences: A dual microstructure consisting of very fine lithium metasilicate (Li_2SiO_3) and lithium disilicate ($Li_2Si_2O_5$) crystals is obtained (Fig. 5), with a glassy matrix containing zirconium oxide in solution (Kruger *et al.*, 2013).
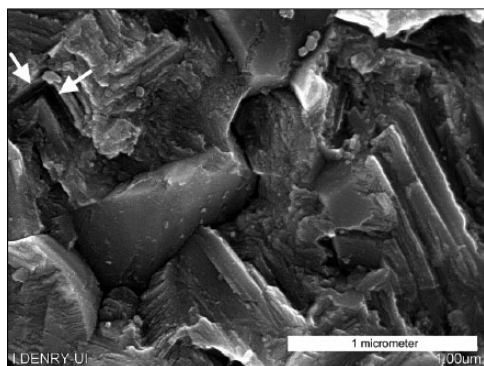
Figure 4. Scanning electron micrograph of a 3Y-TZP fractured surface. Arrows indicate evidence of domain reorientation, characteristic of ferroelastic domain switching.

Figure 5. Scanning electron micrograph showing the microstructure of the lithium silicate glass-ceramic Suprinity (Vita), exhibiting platelet-shaped crystals.

The microstructure is achieved in two stages. The glass-ceramic in the first pre-crystallized stage contains only lithium metasilicate crystals and is easy to machine. The final crystallization stage, leading to the dual lithium silicate microstructure, is obtained after a short heat treatment at 840°C for 8 min. The main difference between ZLS and L2S glass-ceramics in their final stage of crystallization resides in the nature of the crystalline phases: lithium metasilicate plus lithium disilicate for ZLS and lithium disilicate only for L2S.

The development of zirconia-containing lithium silicate glass-ceramics illustrates the ongoing quest for ceramic materials that offer adequate translucency combined with superior mechanical properties. These stable ceramics may offer a better reliability than zirconia ceramics but may not represent the endpoint for this quest.

INTERPENETRATING PHASE COMPOSITES

Indeed, the development of a new class of interpenetrating phase composites (IPC) further illustrates this ongoing quest. IPCs are characterized by two phases that are each intact three-dimensionally (intertwined) throughout the fully dense material. Such composites are formed by infiltration of a porous structure (first phase) with a liquid to form the second interpenetrating phase. Melt-infiltration of glasses followed by solidification and monomer infiltration followed by thermoset polymerization are common fabrication methods (Wegner and Gibson, 2001). IPCs are often tougher and stronger and display a higher damage tolerance (R-curve behavior) than either pure phase.

Due to esthetic needs, only ceramic-glass and ceramic-polymer IPCs have been developed for dentistry. The first (In-Ceram® Alumina, Vita) is based on alumina (68%) infiltrated with a lanthanum-containing glass (Guazzato *et al.*, 2004). Fabrication of porous alumina is achieved by initial sintering characterized by surface diffusion without shrinkage. In-Ceram® Alumina was the first fully-dense net-shape ceramic available for dental restorations and performed very well (91.5-100% success) in at least eight clinical trials lasting between five and seven years (Della Bona and Kelly, 2008). It is still available, mainly for CAD/CAM, but has never been highly marketed.
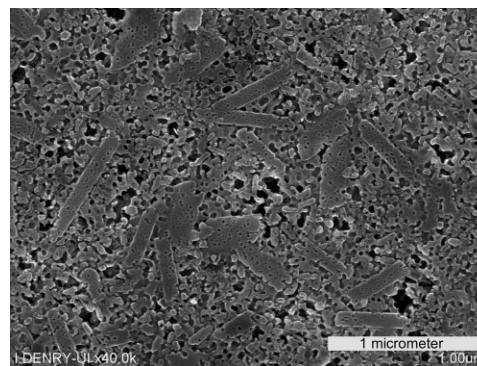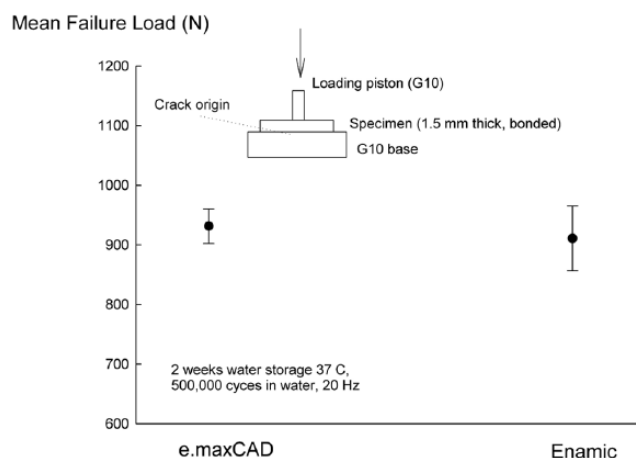
Figure 6. Mean failure loads for IPS e.max CAD (Ivoclar Vivadent, Schaan, Liechtenstein) and Enamic® (Vita) in sinusoidal loading of adhesively bonded specimens *per* Kelly *et al.* (2010). Analysis of such data suggests identical clinical performance against bulk fracture by radial cracking.

In 2013, the second IPC for dental restorations was introduced (Enamic®, Vita). This IPC is based on initial sintering of porcelain powder to approximately 70% of full density, followed by infiltration with dental monomers (He and Swain, 2011). While the porous ceramic network has a strength of 135 MPa and the polymer below 30 MPa, the infiltrated IPC has a strength of 160 MPa (Coldea *et al.*, 2013b). As would be expected, many bulk and elastic properties are intermediate between those of particle-filled resins and those of ceramics. While not as strong as CAD/CAM ceramics, this IPC has an elastic modulus of approximately 38 GPa, slightly higher than that of dentin (Della Bona *et al.*, 2014), so that for any given load the interfacial stress causing bulk fracture by radial cracking is lower. In fatigue testing (500,000 cycles, water), Enamic® performed as well as lithium disilicate [Fig. 6; testing performed as *per* Kelly *et al.* (2010)]. Recent study showed that this IPC has three additional advantages over CAD/CAM and pressable ceramics: (1) reasonable brittleness index; (2) lower hardness; and (3) creep response similar to that of enamel (lower contact stress development and good stress redistribution) (He and

Swain, 2011). Both this IPC and In-Ceram Alumina were found to be more damage-tolerant than other CAD/CAM and pressed materials (Coldea *et al.*, 2013a). Damage tolerance during machining is also better than for other CAD/CAM ceramics and one particle-filled polymer block (as measured by brittleness index), as was shown to correlate linearly with less marginal chipping (Tsitrou *et al.*, 2007; He and Swain, 2011).

It is likely that IPC materials will continue to be explored. There would appear to be much engineering latitude, given all the variables available for manipulation: choice of each phase, initial particle size and shape of the first phase, coupling or not between phases, and toughness of infiltration phase. Enamic® appears to be performing very well in a clinical study nearing its 24-month completion (personal communication, Dr. Petra Guess, University of Freiburg, Germany). If this continues, as for the alumina-glass IPC, and early commercial success continues, this class of material will likely be added to in the future.

In parallel with materials development, refinement of processing techniques has actively taken place to reduce energy costs (microwave sintering), adapt to nanoscale particle sizes (spark plasma sintering), or permit the realization of intricate shapes (additive manufacturing). These emerging techniques certainly have the potential to be used for dental applications in the future.

MICROWAVE SINTERING

On the electromagnetic spectrum, microwave radiation falls just above radio waves and just below visible light, with wavelengths between 1 mm and 1 m corresponding to frequencies of about 1 to 300 GHz. Regarding microwave-material interactions, three basic conditions exist. Materials having very low loss-tangents allow microwave radiation to pass through with little or no absorption. Materials having very high loss-tangents (*e.g.*, metals) reflect this radiation and are considered to be opaque. Materials that efficiently absorb microwaves have intermediate loss-tangents. Loss-tangents of ceramic powders are a strong function of temperature, often increasing linearly. Thus, powders that do not absorb at room temperature can be efficient absorbers at 500°C to 600°C. Direct dielectric heating can become very efficient, as high as 80% to 90%, in dramatic contrast to conventional heating (Katz, 1992).

Sintering consists of at least two heat-activated processes, densification and grain growth. Densification involves atomic diffusion (surface and lattice) in polycrystalline ceramics and viscous flow in glassy materials. Grain growth involves grain boundary diffusion and is usually thought to be deleterious, especially if leading to the emergence of non-uniform grains, *i.e., via* Ostwald ripening. Microwave energy not only provides volume heating *vs.* surface heating, but also lowers the activation energy for atomic diffusion, reducing sintering times by up to 10 times. It provides for sintering at lower temperatures and avoids the prolonged heating that would encourage grain growth (Oghbaei and Mirzaee, 2010). These processes have been collectively termed the "microwave effect." Therefore, in many cases, microwave sintering leads to materials having a more uniform grain size and higher density. In one dental porcelain, microwave sintering led to higher density and flexural strength than seen with conventional sintering (Menezes *et al.*, 2007).

Many problems must be dealt with in microwave sintering. First, the least expensive and most widely available microwave applicators are low-frequency (2.45 GHz) and do not couple power efficiently to many ceramics at room temperature, making initial heating difficult. Second, thermal instabilities may arise, leading to catastrophic overheating. Third, volumetric heating can produce severe temperature gradients, leading to non-uniform microstructures and properties and localized cracking (Menezes *et al.*, 2007). Researchers have addressed these problems by developing hybrid techniques—for example, combining microwave and infrared heating or using microwave-absorbing materials (susceptors, *e.g.*, SiC) to provide initial heating up to temperatures where most ceramic powders do become absorbers of microwave radiation.

Currently, the dental literature on microwave sintering seems limited to work with zirconia (Almazdi *et al.*, 2012; Kim *et al.*, 2013; Marinis *et al.*, 2013). It appears that microwave sintering does not alter fracture toughness and permits the use of higher heating rates, leading to increased productivity and reduced energy costs (Almazdi *et al.*, 2012; Marinis *et al.*, 2013). Zirconias processed by microwave sintering can have smaller grain sizes and increased translucency compared with those from conventional firing (Kim *et al.*, 2013).

SPARK PLASMA SINTERING (KINETIC ENGINEERING)

Precise control of sintering kinetics is becoming of special interest in the development of nano-ceramics and multifunctional composite-ceramics where "kinetic windows" can be very narrow for the retention of fine grain microstructures and the prevention of unwanted side reactions (Shen and Nygren, 2005). As with microwave sintering, the main aim of spark plasma sintering is to enhance surface diffusion (leading to densification) while limiting grain boundary diffusion leading to coarsening and side reactions. Grain boundary diffusion is activated at higher temperatures than surface diffusion. Precursor powders are loaded into an electrically conductive die that provides uniaxial pressure as well during sintering. Strong direct current (DC) is applied through the die, and possibly the powders, providing heat from the outside as well as the inside. Under such conditions, rapid consolidation is driven at relatively low temperatures, enhancing mass transport in a relatively short time period (Shen and Nygren, 2005). Although implied by the commonly used term, it appears that a plasma is not created.

Since this process requires that sintering be done within the confines of a die, complex shapes such as those required for dental restorations are not possible. Therefore, the emphasis is on developing special microstructures, such as carbon nano-tube-reinforced hydroxyapatite (Kim *et al.*, 2014). Apatite powders can be sintered to high density in approximately 5 min at < 300°C to retain non-stoichiometric compositions and preserve surface hydration (Grossin *et al.*, 2010). This process has also been applied to calcium phosphate ceramics and glass compositions (Champion, 2013; López-Esteban *et al.*, 2014; Porwal *et al.*, 2014).

ADDITIVE MANUFACTURING (ROBOCASTING, 3D PRINTING, SELECTIVE LASER SINTERING)

Solid freeform fabrication of complex ceramic parts is mainly being explored by slurry additive manufacturing ("robocasting"), which consists of extrusion of continuous filaments or rods to additively build complex porous scaffolds, mainly for bone tissue engineering. While slurry additive manufacturing has been investigated for fabrication of zirconia/alumina prostheses cores, the process is still too crude where fine control over final dimensions is required (Silva *et al.*, 2011). More commonly, various combinations of bioactive calcium phosphate ceramic powders are processed into scaffolds for orthopedic applications (Miranda *et al.*, 2006).

Such additive manufacturing is essentially a complex example of ceramics powder processing in which water-based "inks" are developed with specific properties. First, these inks must have well-controlled viscoelastic properties such that they can flow through a deposition nozzle and then "set" to facilitate both shape retention and bridging of small gaps (*i.e.*, be pseudoplastic). Second, they need to contain high volume fractions of colloidal particles to reduce drying shrinkage and resist compressive stresses from capillary tension (Smay *et al.*, 2002). These inks are often specific to the powders being processed, depending on particle size and distribution, and zeta potentials. Although computers control build-up of the assemblies, all steps of colloidal processing of ceramics are utilized: (1) powder synthesis, (2) powder dispersion (or suspension), (3) powder consolidation, (4) removal of solvent and organic processing components, and (5) densification (Lewis, 2000). While one of the benefits of robocasting is the ability to fabricate complex shapes, limitations for broad dental use include low packing density and a lack of uniformity of the greenwares fabricated, which limits control over final dimensional tolerances.

Ink production for robocasting involves controlling colloidal stability, *i.e.*, control over interparticle potential energy—both attractive and repulsive using organic additives (and inorganic) for pH adjustments. For an excellent example of robocasting ink development, see Smay *et al.* (2002).

One modification of this method, using an inkjet printer, has been explored to fabricate crude prostheses, but the total process remains cumbersome, and significant defect introduction has been reported (Ebert *et al.*, 2009). Layer-by-layer greenware build-up of a bioactive ceramic was demonstrated where part definition occurs by laser sintering of a binder included in the ceramic powder bed (Goodridge *et al.*, 2006). In the opinion of the authors, other than for porous scaffold fabrication, ceramic additive manufacturing remains exploratory.

CONCLUDING REMARKS

The evolution of dental ceramics over the past 30 years has been most interesting from a biomedical engineering point of view. Introduction of zirconia ceramics has opened a wide range of all-ceramic applications unthinkable 30 years ago. The consensus, however, is on caution in selecting highest product quality and strict respect of manufacturers' recommendations, with special attention on sintering temperature. Interpenetrating phase composites show great promise as excellent attempts at reproducing tooth structure. Remarkable progress has been made in ceramic processing and development over the past few years. It is likely that further breakthroughs will occur in the near future.

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