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Everything you need to know about dental zirconia

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Abstract

Zirconia has become the most prescribed material for posterior crowns in the US. This material has undergone an evolution in the fabrication process since its introduction as primarily a framework material. Newer forms of zirconia have become more translucent, such that they may be used as anterior crowns. The increased translucency, however, comes with a trade-off in strength. This article will review the generations of zirconia, some of their clinically relevant properties (strength, translucency, degradation), and the process of fabricating these crowns in the dental laboratory.

Educational objectives

At the conclusion of this course, the dental practitioner will be able to:

1. Describe the compositional differences among the various generations of zirconia and how they affect the relevant clinical properties of the material.
2. Describe how the relevant properties of zirconia can be altered by the methods in which zirconia is fabricated by manufacturers and sintered in the dental laboratory.
3. Choose a generation of zirconia based on specific clinical needs.
4. Use high-quality zirconia materials and follow manufacturer's recommendations for milling and sintering.

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A recent study from the National Dental Practice-Based Research Network reported that monolithic zirconia was the most commonly used material for posterior single-unit crowns and that layered zirconia is the second most commonly used material for anterior single-unit crowns.[1] An American Dental Association Clinical Evaluator (ACE) Panel survey reported that 98% of dentist respondents used zirconia for posterior crowns, 78% for posterior bridges, 61% for anterior crowns, and 57% for anterior bridges—not to mention that 12% even used the material for veneers.[2] Zirconia has become ubiquitous in dentistry, and therefore, clinicians should be aware of the different types of zirconia, some of their relevant properties, and problems that can arise with zirconia restorations before they even arrive in the dental clinic.

The popularity of zirconia originated sometime after 2008. Christensen reported that the largest US dental laboratory used all-ceramic materials to produce 24% of their fixed dental restorations in 2008 and 78% of their fixed restorations in 2013.[3] This trend might be explained by several factors, such as increasing prices of noble metals and ever-increasing demands for esthetic restorations. Perhaps the largest contributor to this trend, however, was the introduction of monolithic zirconia in 2009.[4] Prior to the use of monolithic zirconia, laboratories used framework zirconia that needed to be veneered with porcelain to achieve adequate optical translucency to be used in the mouth. Layered zirconia was plagued by chipping of the layering porcelain, likely due to porcelain with incorrect coefficient of thermal expansion, incorrect cooling protocols in the dental laboratory, and nonanatomical framework designs.[5,6] The zirconia introduced in 2009 was more translucent than framework zirconia and could therefore be used for monolithic full-contour restorations.[4]

Despite improved translucency of monolithic zirconia, it still lacked the esthetic qualities of lithium disilicate, the other major high-strength dental ceramic. In 2015, however, a new generation of zirconia was introduced with further improved translucency.[4] This generation of zirconia was informally referred to as anterior zirconia or translucent zirconia because it was recommended for anterior restorations. Some confusion then existed within dental laboratories because the zirconia introduced in 2009 was more translucent than framework zirconia, and therefore, both the zirconia introduced in 2009 and 2015 could be considered "translucent zirconia." However, it is critical for clinicians to be aware of which type of zirconia they receive, as the zirconia of 2015 possessed only about 60% of the strength of the original zirconia.[7] The first aim of this article is to review the compositional differences among the various generations of zirconia and how they affect the relevant clinical properties of the material.

Aside from the differences in formulation of zirconia, there are also differences in the ways in which the raw material is manufactured, and the steps taken within the dental laboratory to fabricate zirconia restorations. These differences may affect many of the relevant clinical properties of zirconia restorations, including its toughness, internal fit, translucency, and long-term behavior. The second objective of this article is to describe how the relevant properties of zirconia can be altered by the methods in which it is fabricated by manufacturers and sintered in the dental laboratory.

Generations of dental zirconia

Zirconia is a polycrystalline material, meaning the zirconium and oxygen atoms from which it is derived are arranged in ordered crystal structures. When observing the microstructure of zirconia, individual crystalline arrangements following the same orientation are referred to as grains, which are separated by grain boundaries (figure 1). Zirconia is a polymorphic material, meaning its constituent atoms may take on different crystallographic arrangements. In pure zirconia, there are three main crystal arrangements that can form depending on the temperature at which the material exists. The cubic arrangement is formed from the material's melting point until 2,370 degrees C. The tetragonal arrangement will then form down to a temperature of 1,170 degrees C. And below that temperature (including room temperature), the material is stable in its monoclinic form. As all clinical dental applications of zirconia will occur around 37 degrees C, the use of pure zirconia would result in a material composed entirely of monoclinic zirconia.

Monoclinic zirconia, however, is not the most favorable crystalline arrangement of zirconia. Therefore, additives are added to zirconia in order to stabilize the more favorable tetragonal or cubic phases of zirconia at room temperature. The stabilizer used most commonly in dental zirconia is yttria. When added at 3 mol%, yttria can almost completely stabilize the tetragonal form of zirconia at oral temperature. When added at 8 mol%, yttria can almost completely stabilize the cubic phase of zirconia.

The original formulation of zirconia used as the framework for dental crowns and fixed partial dentures contained 3 mol% yttria to stabilize the tetragonal phase of zirconia. In addition, 0.25% alumina was added to the material to help further stabilize the tetragonal phase. This framework zirconia can be considered the first generation of zirconia. The addition of the alumina stabilizer, however, was a source of opacity since alumina has a different index of refraction than zirconia. The monolithic zirconia introduced in 2009 improved translucency by reducing the alumina content from 0.25% to 0.05%, while keeping the yttria content at 3 mol%. This is known as the second generation of zirconia. The further increase in translucency of zirconia occurred in 2015 when the amount of yttria was increased to 5 mol%. At this concentration of yttria,

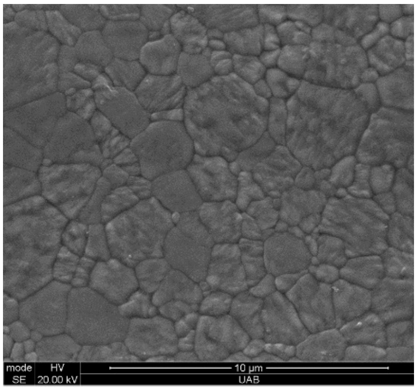

FIGURE 1: Microstructure of zirconia showing grains separated by grain boundaries

about 50% of the cubic phase and 50% tetragonal phase are stabilized. The increased translucency of this third generation of zirconia comes from the increased cubic phase. A later modification of the formulation of zirconia occurred by adding 4 mol% yttria to the zirconia to stabilize about 25% of the cubic phase. Some may refer to these 4 mol%-containing zirconia materials as the fourth generation.[8]

The various formulations of zirconia are mostly affected by the ratio of tetragonal:cubic phase, which is controlled by yttria concentration. A shorthand for referring to different types of zirconia is to call them 3Y, 4Y, and 5Y to represent 3 mol%-, 4 mol%-, and 5 mol%-containing zirconia respectively. These compositional differences affect three major clinically relevant properties of zirconia: its toughness, opacity, and resistance to low-temperature degradation. Each of these properties will be discussed.

Zirconia, like other ceramics, is brittle and fails through crack propagation. The ability to resist crack propagation is known as a material's fracture toughness. The reason that the tetragonal phase of zirconia is desirable is that it imparts toughness to zirconia through a process known as transformation toughening. Transformation toughening takes advantage of 3%–4% volumetric expansion that occurs when zirconia in its tetragonal phase transforms to its monoclinic phase.[9] The volumetric expansion is a result of the atomic arrangement in the monoclinic phase being less dense than in the tetragonal phase. The tetragonal to monoclinic transformation occurs when a stress is applied, such as a crack. The expansion associated with the transformation compresses the forming crack and stops its propagation. The cubic phase of zirconia is unable to undergo transformation toughening.

A recent study examined the ability of 3Y, 4Y, and 5Y zirconia to undergo transformation toughening. 3Y was capable of transformation toughening. 4Y (containing 75% tetragonal zirconia) underwent some transformation toughening. 5Y (containing 50% tetragonal zirconia) underwent almost no transformation toughening.[10] Therefore, clinicians should reserve the use of 4Y and 5Y zirconia for times when the esthetic needs of the material are required.

Broadly, ceramics may be classified as glass, which has a random orientation of constituent atoms, or crystals, with an ordered arrangement of atoms. Atoms may be packed more densely into an ordered crystalline arrangement, and therefore, crystals are considered to be opaquer because light has to bypass more atoms than it would in a more loosely packed glass. But common knowledge reveals that there are some crystals that are nearly translucent. These crystals have their atoms arranged in such a manner as to avoid interaction with the wavelength of visible light. For example, cubic zirconia has an isotropic arrangement of its atoms that allows light to pass through the material equally in all directions.[8] Tetragonal zirconia, on the other hand, is arranged in an optically anisotropic crystalline structure (called birefringence), which means light will pass through these crystals only in certain directions. As light attempts to pass through grains of tetragonal zirconia oriented in different directions, the light will be partially or completely scattered when reaching a grain boundary.[11] Since 4Y and 5Y zirconia contain cubic zirconia, these types of zirconia are more translucent than 3Y zirconia. A recent study reported that 4Y is 13% more translucent than 3Y, and 5Y is 33% more translucent than 3Y zirconia.[10]

Tetragonal zirconia can also spontaneously transform into monoclinic zirconia in the presence of humidity at oral temperatures in a process known as low-temperature degradation (LTD). The mechanism by which this occurs has been credited to water interacting with Zr-O bonds, Y_2O stabilizers, or oxygen vacancies, all of which could destabilize the tetragonal zirconia.[12] LTD is an undesirable outcome as the 3%–4% volumetric expansion associated with tetragonal-monoclinic transformation occurring in neighboring grains causes microcracking within the zirconia. The negative effects of LTD may be simulated in an accelerated rate in the laboratory by placing zirconia in an autoclave. Zirconia with laboratory-accelerated LTD has demonstrated significantly lower mechanical properties.[13] The clinically important question is whether LTD will occur at a rate fast enough in which it will negatively affect the properties of a zirconia restoration during its clinical lifetime. Most studies on LTD have placed zirconia in an autoclave and reported the negative effects from simulated accelerated LTD.[13] Very few studies have been conducted in which dental zirconia was stored in oral conditions for extended periods of time to examine the real-time progression of LTD.

In one study, 3Y zirconia was stored in water for one year, and transformation occurred to a depth of 0.5 microns within the surface. The authors speculated that at this rate it would take 20–30 years for cracking to form that could contribute to fracture of a zirconia restoration.[14] Since cubic zirconia does not transform to monoclinic zirconia, it does not undergo LTD. A recent study reported that a 5Y-containing zirconia that underwent accelerated autoclave aging suffered

TABLE 1: Generations of dental zirconia

	Generation 1	Generation 2	Generation 3	*Generation 3
Yttria (mol%)	3	3	5	4
Yttria (wt%)	5.2	5.2	8.8	7.1
Alumina (wt%)	0.25	0.05	0.05	0.05
% cubic phase	0	0	25	50
Examples	Prettau Zirconia	BruxZir, Lava Plus, Katana HT, ZirCAD LT	ZirCAD MT, Katana STML	BruxZir Anterior, Lava Esthetic, Latana UTML, Prettau Anterior

* Sometimes referred to as Generation 4

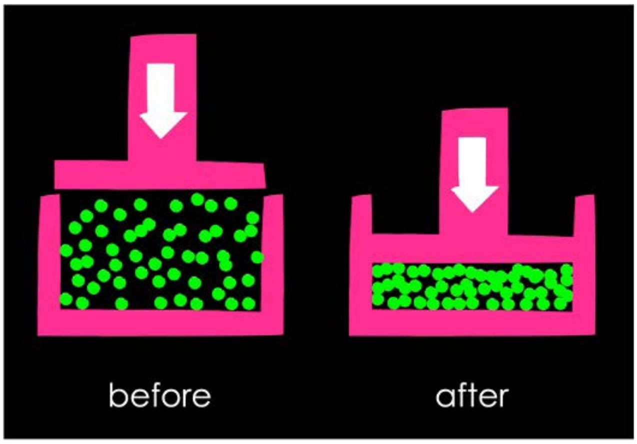

FIGURE 2: Uniaxial pressing of zirconia powder

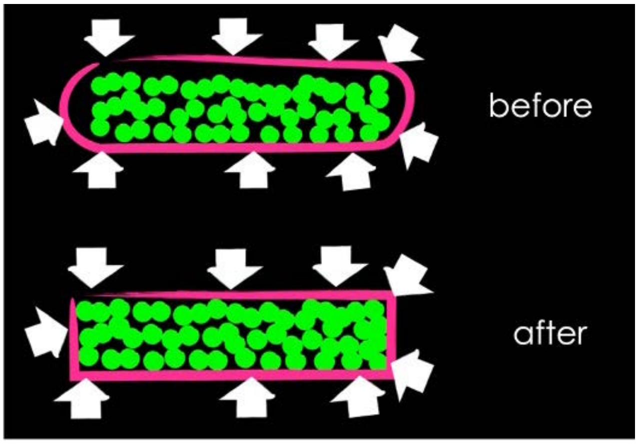

FIGURE 3: Isostatic pressing of zirconia powder

FIGURE 4: Presintered zirconia disk

less LTD than a reference 3Y zirconia; however, both the 3Y and 5Y zirconia materials experienced a reduction in strength from accelerated aging.[15]

Despite the very different properties reported for 3Y, 4Y, and 5Y zirconia, there is no standardization within the industry for labeling various formulations/generations of zirconia. Clinicians must research the brand of zirconia used by their laboratories to ensure that they are receiving the desired clinical properties of their material. A summary of the different generations of zirconia is presented in Table 1.

Fabrication of zirconia disks

Currently, the only major fabrication technique for dental zirconia restorations is to mill them from a presintered disk. These presintered disks have a chalklike consistency, and they are formed by pressing microscopic powders into a disk-shaped mold. Many different manufacturers fabricate presintered zirconia disks, and the fabrication process of these disks can affect the ultimate properties of a zirconia restoration. A summary of the fabrication process of a zirconia disk will be described in order to better understand pitfalls that may be encountered with the raw material.

Some manufacturers may produce their own zirconia powder, or they may obtain it from a manufacturer. Perhaps the most common zirconia powder manufacturer used for research purposes and some commercial zirconia brands is Tosoh (tosoh.com). The most obvious difference between different powders will be the amount of yttria content, as this will determine the amount of cubic phase within the material (for example, 3Y, 4Y, and 5Y). The method by which the yttria content is achieved within the disk can have a significant effect on its properties.

A recent study examined 5Y zirconia fabricated from either 5Y zirconia powders or a combination of 3Y and 8Y zirconia powders. The study reported that zirconia formed from mixing 3Y and 8Y resulted in a heterogeneous microstructure with patches of cubic zirconia grains surrounded by patches of tetragonal grains. As a result, the zirconia material demonstrated a combination of the worst characteristics of either phase—it had lower strength, less translucency, and more LTD than the zirconia fabricated from 5Y powder.[16]

Binder is another component of zirconia that can affect its properties. Binder is added to the zirconia powder to help keep the particles of zirconia bound together in the presintered disk so that it does not chip when the restoration is being milled. Binder can also help to lubricate the particles of zirconia when they are being condensed into a mold.[17]

The process of compacting power into a mold is called pressing. Uniaxial pressing of zirconia implies that the powders are pressed into the mold from the top (figure 2). A study has determined that the firmness of the pressing tool can affect the amount of porosities formed between compacted powders.[18] Additionally, uniaxial pressing leads to powders that are more compact at the top surface near the pressing tool and less compact at the bottom of the mold. As a result, there was more shrinkage of the zirconia at the bottom of the disk than the top of the disk when sintered in a furnace.[19] Ultimately, this may lead to deformation of a zirconia restoration during the sintering process. Another method of pressing is isostatic pressing, in which a uniaxially pressed disk is then bagged and placed into a fluid that applies pressure from all directions (figure 3). The proposed advantage of isostatic pressing is a more even compaction of powder.

Once the powders are compacted into a disk (figure 4), it is in its green state. Zirconia may be directly milled in its green state or it may be partially sintered and then milled. The disadvantage of green-state milling is that the particles of zirconia are being held together only by its binder. If too much pressure is applied to the zirconia by the milling tool, the restoration may chip. If the zirconia is partially sintered prior to milling, it will be less likely to chip during milling. But zirconia that is partially sintered during milling has been shown to be less able to heal porosities or cracks created during milling when it is fully sintered.[18]

Pigments are another component of zirconia powders. These pigments can be composed of oxides of iron, cobalt, copper, magnesium, tin, zinc, aluminum, and titanium. The pigments decrease translucency of zirconia, because they have a different index of refraction than zirconia, and they also cause a slight increase in the grain size of zirconia.[20] There is contradictory evidence whether incorporation of pigments negatively affects the strength of zirconia.[21,22] There are multilayered zirconia disks that contain a gradient of pigments included from the top (incisal) to the bottom (cervical) part of the disk. Although no difference in strength was measured among different layers of the disk, the interface between the layers was shown to have a 30% lower strength than the bulk material.[23]

Aside from coloring zirconia with oxide pigments, chloride solutions may be infiltrated into the presintered zirconia to impart changes in color. A study reported that coloring 3Y zirconia with up to 5 wt% cerium acetate solution or up to 1 wt% bismuth chloride solution was able to impart a cream and orange color respectively. At higher concentrations, these solutions increased porosity in the sintered zirconia and caused a reduction in strength.[24]

Sintering of dental zirconia in the dental laboratory

Once the zirconia restoration has been milled out of presintered or partially sintered zirconia, it will be sintered in a furnace. Sintering is the process of heating the restoration to cause the individual powders to coalesce and form a solid material (figure 5). During this process, the zirconia restoration will shrink around 20% (figure 6). The exact amount of shrinkage of the zirconia is specific for each zirconia disk and is compensated for in the design of the restoration prior to milling. The shrinkage of zirconia during sintering is nearly the same in all directions, but not exactly.[25] The shrinkage can also be affected by the thickness of zirconia, with thicker areas shrinking more. For example, the cement gap and marginal opening on abutments of a zirconia bridge were shown to be slightly larger on the side of the abutment near the pontic due to increased shrinkage of the thick pontic.[26]

The temperature at which zirconia is sintered and the time for which it is sintered will affect grain size and corresponding properties of the material. Increasing sintering temperature and sintering time both will increase grain size.[27] There is a complex relationship between grain size and strength, translucency, and LTD. If grain size is smaller than the wavelength of light (380–700 nm), then zirconia should be more translucent due to wavelengths of light not interfering with its microstructure.[11,28] In fact, nanograined zirconia (less than 100 nm) is speculated to be the next evolution in zirconia; however, condensing nanograined zirconia without agglomeration and porosity is a barrier.[29] On the other hand, light is scattered at grain boundaries, so larger grains can also be more translucent as they will create a lower density of grain boundaries.[27,30]

Grain size can also affect the ability of tetragonal zirconia to transform. A study has reported that tetragonal grains may start to undergo transformation at a size of 0.3 microns; as they grow larger, there is an increased chance for transformation.[12] If tetragonal grains cannot transform, this will limit transformation toughening. If tetragonal zirconia can transform too easily, this will encourage LTD. Varying sintering conditions will also have different effects on 3Y, 4Y, and 5Y zirconia as tetragonal grain growth likely has a bigger effect on properties than cubic grain growth.

Finally, speed-sintering programs in induction furnaces are available that can reduce sintering time from hours to minutes. Certain zirconia brands are optimized for speed sintering and can tolerate this accelerated sintering program without sacrificing optical or mechanical properties. Other brands that are not optimized

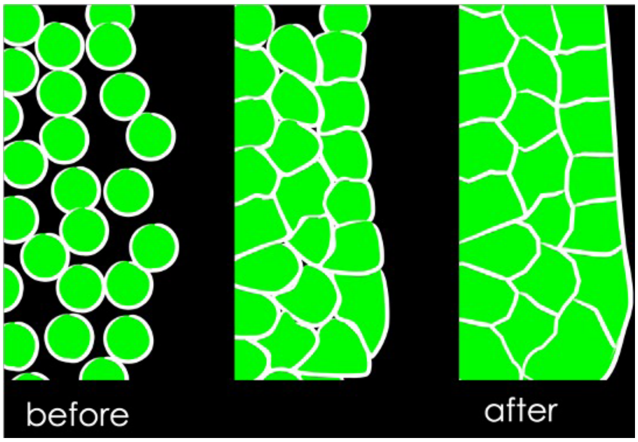

FIGURE 5: Sintering of zirconia powder

FIGURE 6: Zirconia restoration prior to sintering (above) and after sintering (below)

for speed sintering can undergo extensive grain growth and sintering porosities that reduce strength and translucency.[31]

Summary

The different generations of zirconia vary on the ratio of tetragonal:cubic phase present within the material as determined by the percentage of yttria added. Zirconia restorations can also be affected by powder compaction (homogeneity and pore incorporation), milling defects, grain size, uneven sintering, and sintering porosities. All of these changes in the microstructure affect translucency, transformation toughness, and LTD. Clinicians and laboratories should choose a generation of zirconia based on clinical needs, use high-quality materials, and follow manufacturer's recommendations for milling and sintering.

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QUESTIONS

1. What is the most commonly used material for posterior single-unit crowns according to the 2016 National Dental Practice-Based Research Network?
   - A. Zirconia
   - B. Lithium disilicate
   - C. Porcelain-fused-to-metal
   - D. Feldspathic porcelain

2. What percentage of dentists used zirconia for posterior crowns based on a 2020 ADA Clinical Evaluator Panel survey?
   - A. 98%
   - B. 70%
   - C. 30%
   - D. 10%

3. What are some contributing factors to the increase in ceramic restorations around 2008?
   - A. Increasing cost of metal
   - B. Ever-increasing esthetic concerns
   - C. Introduction of full-contour zirconia
   - D. All of the above

4. Which was a reason that layered zirconia experienced chipping?
   - A. Patients started bruxing more in the 2000s.
   - B. Porcelain for zirconia is weaker than porcelain for metal.
   - C. Zirconia is a heat conductor, so it overheated the veneering porcelain.
   - D. The coefficient of thermal expansion of the original veneering porcelain on zirconia was not matched to zirconia.

5. Which is a constituent atom of zirconia?
   - A. Oxygen
   - B. Carbon
   - C. Silicon
   - D. Hydrogen

6. Which is not a crystalline arrangement of zirconia?
   - A. Cubic
   - B. Tetragonal
   - C. Octagonal
   - D. Monoclinic

7. Which arrangement of pure zirconia is stable at room temperature?
   - A. Cubic
   - B. Tetragonal
   - C. Octagonal
   - D. Monoclinic

8. What is used at 3 mol% to stabilize tetragonal zirconia at room temperature?
   - A. Yttria
   - B. Hafnium
   - C. Cerium
   - D. Oxygen

9. How was translucency improved in the second generation of zirconia?
   - A. Removing alumina
   - B. Adding yttria
   - C. Increasing grain size
   - D. Removing oxygen

10. About how much cubic zirconia is stabilized with the addition of 5 mol% yttria?
    - A. 10%
    - B. 25%
    - C. 50%
    - D. 100%

11. What is fracture toughness?
    - A. Resistance to permanent deformation
    - B. A measure of flexibility
    - C. Ability to resist crack propagation
    - D. Another term for ultimate yield strength

12. Why does some zirconia demonstrate a higher fracture toughness than other ceramics?
    - A. Transformation toughening, which occurs through tetragonal-monoclinic transformation
    - B. Stronger crystalline structure than other ceramics
    - C. Larger microstructure than other ceramics
    - D. The stability of the tetragonal phase

13. Which type of zirconia is the most capable of undergoing transformation toughening?
    - A. 3Y
    - B. 4Y
    - C. 5Y
    - D. 8Y

14. Which phase of zirconia is optically isotropic?
    - A. Cubic
    - B. Tetragonal
    - C. Octagonal
    - D. Monoclinic

15. What is low-temperature degradation?
    - A. Weakening of grain boundaries when zirconia is placed in cold temperatures
    - B. Overcrystallization of zirconia from temperatures below freezing
    - C. Spontaneous transformation of zirconia from tetragonal to monoclinic phase at oral temperature and humidity
    - D. Cracking of zirconia derived from temperatures below freezing

16. What would be a disadvantage of placing zirconia in an autoclave?
    - A. It would overheat.
    - B. It would accelerate the process of low-temperature degradation.
    - C. It would cause it to change color.
    - D. It is an insufficient method of sterilization.

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QUESTIONS

17. Which generation of zirconia contains 3 mol% yttria and 0.25% alumina?
    - A. First
    - B. Second
    - C. Third
    - D. Fourth

18. What is the disadvantage of forming 5Y zirconia from 8Y and 3Y powders?
    - A. The microstructure of tetragonal and cubic grains is heterogeneous.
    - B. There is sintering porosity.
    - C. There is uneven compaction of particles.
    - D. The green state disk is too brittle.

19. What is added to zirconia powder in order to stabilize the powder in the presintered disk?
    - A. Surfactant
    - B. Binder
    - C. Adhesive
    - D. Silica coating

20. What is the disadvantage of uniaxial pressing of zirconia powder?
    - A. Deformation of the powder particles
    - B. Discoloring of powder from residue in the pressing machine
    - C. Insufficient force to adequately press powder
    - D. Uneven compaction of powder at the top and bottom of the mold

21. What is the state of the zirconia disk after pressing but prior to sintering?
    - A. Blue
    - B. Green
    - C. Red
    - D. Yellow

22. Which of the following is not a pigment added to zirconia?
    - A. Iron
    - B. Tin
    - C. Zinc
    - D. Hydrogen

23. What is the disadvantage of adding too much of the cerium acetate- or bismuth chloride-based color infiltrating liquids?
    - A. They will increase grain size.
    - B. They will decrease grain size.
    - C. They will destabilize the tetragonal phase.
    - D. They can create porosity.

24. What is the process of sintering?
    - A. The formation of crystals within the glass phase of zirconia
    - B. The melting of solid zirconia into a liquid
    - C. The coalescence of individual zirconia powders into a solid
    - D. The heating of zirconia to change its phase composition

25. About how much do zirconia restorations shrink during sintering?
    - A. 1%
    - B. 5%
    - C. 10%
    - D. 20%

26. Which will increase grain size of zirconia?
    - A. Increasing sintering temperature
    - B. Decreasing sintering time
    - C. Both A and B
    - D. Neither A nor B

27. What would be an advantage of nano-sized grains of zirconia?
    - A. Increased translucency
    - B. Increased fracture toughness
    - C. Decreased porosity
    - D. Decreased time needed for sintering

28. Why could increasing grain size improve translucency?
    - A. It allows more cubic zirconia to form.
    - B. It decreases the width of grain boundaries.
    - C. It decreases the density of grain boundaries within a material.
    - D. It helps to align the grains.

29. What has been reported as the threshold of grain size at which grains begin to transform?
    - A. 0.1 micron
    - B. 0.3 micron
    - C. 1 micron
    - D. 3 microns

30. What is a proven disadvantage of speed sintering certain zirconia that has not been optimized for these sintering conditions?
    - A. Sintering porosities
    - B. Uneven shrinkage
    - C. Grain instability
    - D. Lack of grain growth

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ANSWER SHEET

Everything you need to know about dental zirconia

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4. How would you rate the objectives and educational methods?	5	4	3	2	1	0
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