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ZIRCONIA BIOCERAMICS AS ALL-CERAMICS CROWNS MATERIAL: A REVIEW

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Abstract. Zirconia (ZrO_2), known as a kind of bioceramics widely applied in prosthodontics, is considered as a promising alternative to conventional bioceramics owing to its desirable mechanical strength, toughness, wear resistance, corrosion resistance, biocompatibility etc. However, the development of zirconia is hindered due to its instability in long-term clinical observations such as the cracking (chipping) of veneering porcelain and deterioration of mechanical properties of zirconia dental crowns under intraoral condition. The aim of this study is to review the development and actuality of ZrO_2 in prosthodontics. In addition, stability problems in commercial zirconia crowns are discussed in detail and the potential solution has been proposed. Furthermore, the authors' ongoing works and perspective has also been put forward.

1. INTRODUCTION

Nowadays, metal-ceramic restorations have been widely applied in prosthodontics. However, the colors of most metal crowns often lead to the catastrophic esthetic outcomes. In addition, noble metal crown is expensive for clinical popularization, while non noble metals have problems of corrosion and biological safety. Furthermore, the obviously different properties of metal and porcelain can lead to undesirable interface adhesion between crowns and porcelains, which may affect the long-term clinical results of metal-ceramic restorations. As a promising solution, all-ceramic crown possess remarkable esthetics characteristic, biological compatibility and potential superior adhesion between crowns and porcelains, becoming a hot issue in dental clinics [1-3]. Alumina bioceramic [4,5] used to prepare all-ceramic crowns, while it failed in the preparation of post crown and implanting abutment due to its poor bending strength and wear resistance. Furthermore, high cost and poor toughness of all ceramic crowns cannot be ignored in clinical popularization.

Zirconia (ZrO_2), a well-known structural and biomedical ceramic, has received extensive attention in the past decades owing to its excellent biocompatibility, aesthetics and heat conductivities. Furthermore, as an alternative to alumina, ZrO_2-based restoration has a superior mechanical properties (fracture toughness, strength and hardness) comparable to that of the metallic-based ones [6-8], which is feasible to prepare all ceramic crowns (Fig. 1), bridges and implants [9], becoming a hot issue in stomatology [10-15].

At ambient pressure, different ZrO_2 polymorphs, i.e., the monoclinic (m), tetragonal (T) and cubic (c) fluorite structures can be formed depending on the temperature (Fig. 2). Phase transformations of ZrO_2 accompanied with volume change tend to take place under different conditions. As a result, pure ZrO_2 tends to fracture even at room temperature, known as low temperature degradation (LTD) or aging, which

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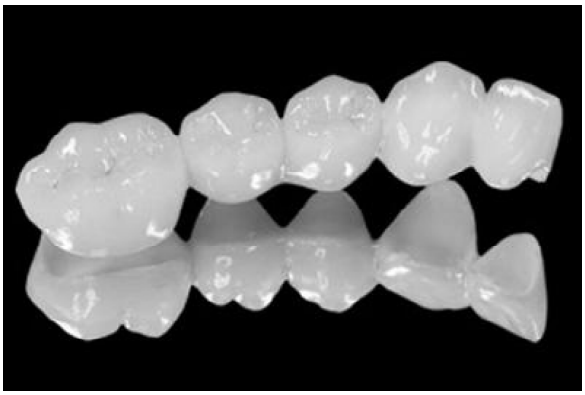

Fig. 1. ZrO_2 crown for dental application.

deteriorates the mechanical properties of ZrO_2 and makes it unsuitable for clinical applications. As a solution, ZrO_2-based composites can enhance the toughness of ceramics system by controlling the phase transformation of ZrO_2. There are three types of transformation-toughened ZrO_2 composites: 1. Zirconia toughened ceramics such as ZrO_2-Al_2O_3 (ZTA). In such system, ZrO_2 particles are dispersed in another matrix such as alumina; 2. Tetragonal zirconia polycrystals such as Y_2O_3-ZrO_2 (Y-TZP). Second phase (Y_2O_3) adopted as a stabilizer is dispersed in ZrO_2 matrix, which can retain the tetragonal structure of ZrO_2 at room temperature by controlling the phase transformation. In this case, the external strain can be neutralized by phase transformation toughening (PPT) of ZrO_2 based ceramic from tetragonal phase to monoclinic phase. As a result, the bending strength and fracture toughness can be enhanced remarkably; 3. Partial stabilized zirconia such as Mg-ZrO_2 (Mg-PSZ), where Mg can be adopted as stabilizing agent to obtain the partial stabilized ZrO_2 polycrystals.

To date, extensive investigations have been performed on the above-mentioned transformation-toughened ZrO_2 composites [16-23], and the clinical observations of zirconia-based materials in prosthodontics are also well documented. However, many clinical failures of ZrO_2 dental crowns can be found in long-term clinical observations such as the cracking (chipping) of veneering porcelain and deterioration of mechanical properties under intraoral condition. Therefore, in this paper, the clinical failure and current status of ZrO_2-based all ceramic crowns are summarized, and the progresses and perspective of solutions including our ongoing works are proposed.

2. EXISTING CHALLENGES

Up to day, many manufacturers such as Vita Zahanfabirk, Sirona, and Ivoclar Vivadent have realized the mass production Y-TZP bulks (grain size: 200-500 nm) to prepare dental crowns (bending strength $\geq$ 900 MPa, fracture toughness $\geq$ 5 MPa·$m^{1/2}$). However, clinical failures such as chipping or cracking of veneer porcelain and LTD of Y-TZP, especially in moisture, are also observed in long-term clinical observation [20,24-26]. The reasons can be attributed to the followings:

1. The sintering temperature range of clinical-demanded ZrO_2 based ceramics is broad (1300-1500 °C), which lead to the obvious difference in grain sizes of samples (Fig. 3). There are few systematic investigations concerning the influence of sintering conditions on the grain size, orientation, and stability of ZrO_2 crystal, increasing the uncertainty in long-term clinical observations; Besides, the influence of size effect especially in the nanometer scale on the phase stability of ZrO_2 have yet to be systematically clarified. Furthermore, the potential bioeffects brought by nanotechnology are still uncertain.

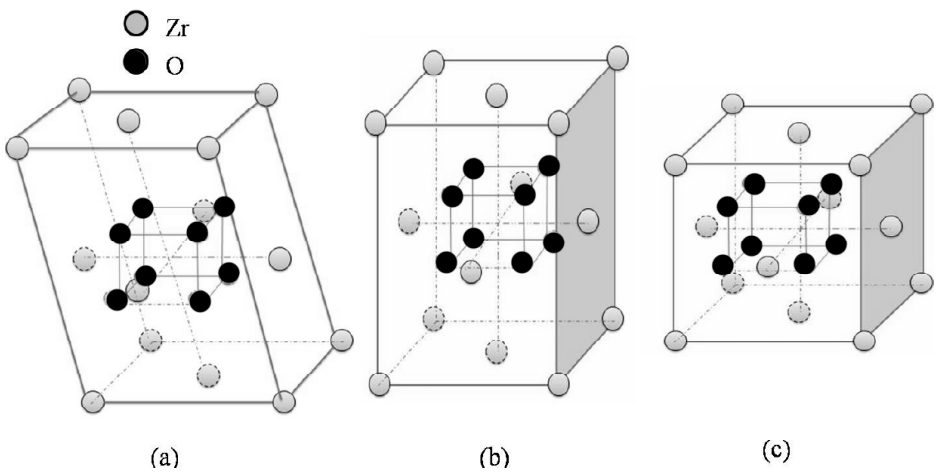

Fig. 2. Types of polymorphs of zirconia: (a) monoclinic phase; (b) tetragonal phase; (c) cubic phase.

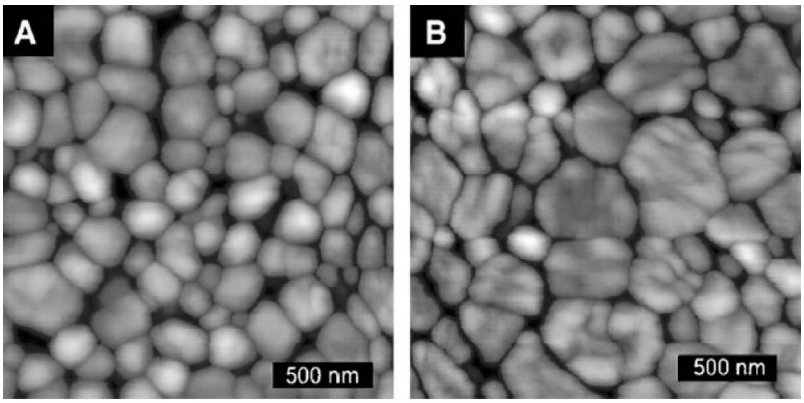

Fig. 3. Atomic force micrographs of 3Y-TZP sintered at 1300 °C (A) and 1450 °C (B) [20], reprinted with permission from I. Denry, J.R. Kelly, Dental Materials, Volume 24, 299-307 (2008)], (c) (2008) Elsevier.

2. It is necessary to veneer high-translucent dental porcelains on the surface of CAD/CAM derived Y-TZP crown to enhance the bending strength and esthetics of crown. Accordingly, the porcelain chipping or cracking tends to take place if the wettability of Y-TZP crown to veneer porcelain coating is unsuitable, or the difference in coefficient of thermal expansion is large. As there is no standard surface treatment for Y-TZP crown, and the systematic fundamental investigations on the interface between porcelain and core have yet to investigate, which increase the occurrences of the clinical failures.

3. RESEARCH PROGRESS

In order to investigate the long-term stability and safety of Y-TZP crowns systematically, numerous experiments have been performed to investigate the influence of heat treatment and surface modification on mechanical and biological properties of ZrO_2 [28-37]. In addition, based on the well-known phase transformation toughening mechanism, some interesting and novel theoretical investigations are also carried out to further study the phase transformation and crack propagation of ZrO_2 [38-42].

3.1. Preparation process investigation

Nowadays, ZrO_2 powder has been prepared by various methods such as gas phase method, solid phase method and liquid phase method [43-49]. In gas phase method, powder can be obtained through the aggregations of precursor vapor and in solid phase process, powder can be prepared through mechanical comminuting or solid-phase reaction. While in liquid phase process, crystals or precipitates can be derived through the reactions taken place in the solution, and final products can be obtained through dehydration or thermal decomposition of the precursor. Among the methods mentioned-above, the liquid method has been widely adopted to prepare ZrO_2-based ceramics because of its simplicity and low cost. The liquid methods include precipitation method, microemulsion method, hydrothermal method and sol-gel method, etc. For precipitation and microemulsion methods, reaction conditions must be rigorously controlled, which increase the complexity of the experiment. Therefore, hydrothermal method and sol-gel method are preferential to prepare ZrO_2-based powder.

For hydrothermal method, reacting solution is sealed in a high pressure reaction kettle and the grain size of samples could be controlled in several nanometers owing to the relative low reaction temperature. In this way, it is feasible to systematically clarify the influence of nanometer-size effect on phase stability and mechanical stability of $ZrO-_2$ crowns. However, for Y-TZP ceramics, the distribution uniformity of second phase (Y^{3+}) in ZrO_2 matrix is uncontrollable due to the different precipitation consequence of matrix and second phase in hydrothermal method, which may play an important role in the phase stability of Y-TZP for dental applications [20].

For sol-gel method, molecular homogeneity within the elementary mixing scale of ingredient can be achieved, which can be applied to improve the distribution of second phase in ZrO_2 matrix. Among the sol-gel methods, the conventional alkoxide reactor is expensive to clinical popularization. As an alternative, some relatively inexpensive raw materials are dissolved in organic solvent, and ZrO_2 powder can also be obtained through drying, dehydration and calcinations process. However, the process is complicated, and the conditions for gel

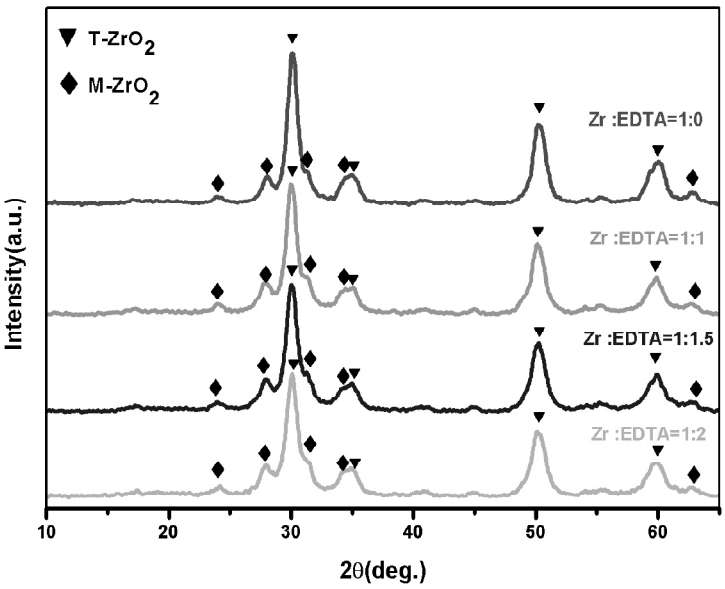

Fig. 4. XRD patterns of ZrO_2 powders derived by different addition of EDTA.

formation should be rigorously controlled. Besides, agglomeration phenomena and second phase segregation (uneven distribution of Y^{3+} in matrix) can also be observed in traditional sol-gel method, which can influence the mechanical properties and stability of Y-TZP ceramics. Therefore, formation of colloid and bridging stability of gel skeleton should be investigated systematically to improve the phase purity of ZrO_2 and distribution uniformity of second phase.

In fact, we have investigated the bridging mechanism of gel skeleton under various conditions for some ceramics such as CeO_2 and Bi-Sr-Ca-Cu-O (BSCCO) ceramics in detail [50-52]. It is found that the association mode of bridging bonds could determine the degree of chemical segregation, which can influence the ingredient distribution and phase purity of ceramics. The novel secondary gel technique can improve the bridging stabilities of the precursor gel skeleton, which can decrease the chemical segregation. Accordingly, the technique can also be applied to improve the distribution uniformity of second phase in Y-TZP, which provides a promising way to overcome the obstacles in the Y-TZP all ceramic crowns. However, it should be noted that, grain size of particle derived from sol-gel method is from tens to hundreds nanometers, which can hardly reduced owing to the relative high calcinations temperature. Kelly et al. found that TZP with different amounts of second phase have different critical grain size, above which the TZP is less stable and more susceptible to spontaneous phase transformation from monoclinic structure to tetragonal structure [20,23]. However, the relative investigation is unsystematic especially for TZP with grain size of several nanometers to tens of nanometers.

In the meanwhile, influence of nanometer-size effect and distribution of second phase on the phase stability of ZrO_2 is also an interesting issue. Since hydrothermal method can control the grain size of several nanometers, and sol-gel method can improve the distribution uniformity of second phase, some novel and interesting outcomes may be found if the two methods can be integrated. To date, we have prepared ZrO_2 powders via the combined complex-hydrothermal methods. Fig. 4 is our unpublished investigation, which shows the XRD patterns of stabilizer-free ZrO_2 powders derived from different addition of EDTA. Then, the grain size of ZrO_2 powders can be calculated according to Scherrer formula.

$$D_{khl} = K\lambda / (\beta \cos\theta),$$

where $K = 0.89$, β is FWHM of diffraction peak, λ is wave length of X-ray and θ is the diffraction angle

The grain size of ZrO_2 powder for all samples is smaller than 10 nm. Furthermore, pure tetragonal structure of ZrO_2 can be obtained at room temperature without the addition of second phase. The relative work on doping of secondary phase in ZrO_2 matrix via this method is in progress.

3.2. Theory investigation

Few exciting theoretical progress have been reported since the famous phase transformation toughening

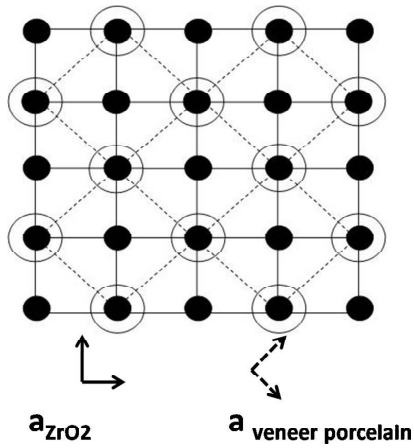

Fig. 5. Schematic diagram for magnetic field orientation of crystals.

theory of ZrO_2-based ceramics. To make it worse, most manufactures only concern on the short term mechanical properties and stability of ZrO_2-based ceramics available for dentistry, while the motivation on theory investigation is insufficient, which may affect the long term clinical effect of zirconia-based all ceramic crowns. Although the pinning role of second phase on grain boundaries of matrix and the phase transformation toughening theory under external force have been investigated, the relative investigations are insufficient [20]. The influence of crystal size on mechanical properties of crown is still controversial on the critical size to retain the tetragonal stable phase [20,23]. Therefore, role of second phase and the size effect of ZrO_2 crystal on martensite phase transformation temperature and energy, especially nanometer-size effect triggered mechanical property and biostability are still unknown; besides, grain boundary diffusion, crystal nucleation and growth, lattice mismatch between veneer porcelain and crown have yet to be further studied. As well known, temperature and duration have a remarkable influence on grain boundary migration, crystal growth and phase stability, which can thereby dramatically influence the phase structure and properties of crowns; Furthermore, according to lattice matching theory, large lattice mismatch will lead to large mismatch energy, which is detrimental to the interface of porcelain (e.g., feldspar porcelain) and crown. Since the lattice mismatch between porcelain and Zirconia-based crowns is large (larger than 10%), the combination of interface have yet to be investigated.

Our group has focused on the combination of films and substrate for many years [53-55]. It has been found that the crystal orientation of BSCCO films can be altered through induction of external field such as temperature and magnetic field. As a result, the lattice mismatch between films and substrates can be decreased, as shown in Fig. 5. For temperature field induction, the crystal

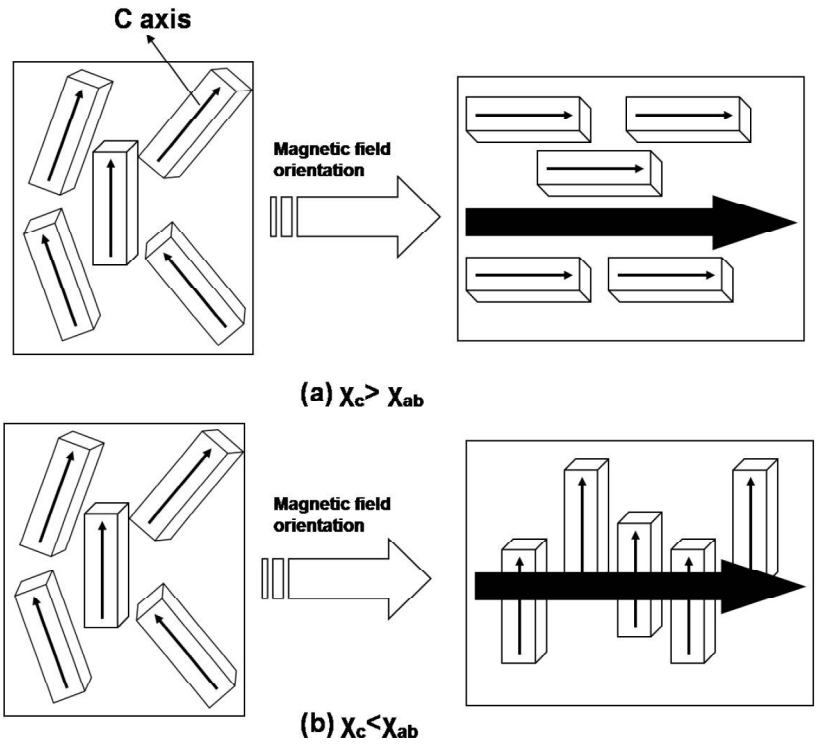

Fig. 6. Schematic lattice matching diagram between ZrO_2 and veneer procelain, in which the $[110]_{ZrO2}$ direction is oriented parallel to $[100]_{veneer\ procelain}$. ●: ZrO_2 lattice, O: Veneer porcelain lattice.

orientation rotation growth mode of film may be attributed to the spontaneous nucleation orientation of films under certain thermodynamic condition to decrease the lattice mismatch energy [55]; while for magnetic field, the crystals with different magnetic susceptibility can be induced to change their original orientation, as shown in Fig. 6. In this way, the orientation of veneer porcelain can be altered to decrease the lattice mismatch between the veneer porcelain and Y-TZP crowns. The relative works are in progress.

4. CONCLUSIONS

Long-term stability of ZrO_2 based TZP crowns, i.e., mechanical and biological properties, is crucial for clinical application. Therefore, special attention should be paid on the crystal growth, role of second phase, size effect of grain and the matching degree between veneer porcelain and crown [56]. At the same time, the cost and the complexity of experiment should also be taken into account. It is believed that under the efforts of both researchers and manufacturers, ZrO_2-based ceramics would take an increasingly important role in the field of prosthodontics in the near future.

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