# Low-temperature Degradation of Zirconia-based All-ceramic Crowns Materials: A Mini Review and Outlook

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Zirconia-based bioceramics have been widely applied in the field of prosthodontics owing to its desirable mechanical performance, biocompatibility and aesthetics. However, the low-temperature degradation (LTD) of tetragonal zirconia ($ZrO_2$) under intraoral condition can lead to the deterioration of mechanical properties of $ZrO_2$ dental crowns, which contribute to many clinical failures in long-term observations. The long-term tetragonal phase stability and mechanical properties of yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) are influenced by grain size of $ZrO_2$ crystals, distribution and properties of stabilizers, the humid environment, etc. However, it is still difficult to control the abovementioned factors at the same time. This review summarizes the major advances in researches dealing with LTD and clarifies the obstacles to stabilization of the tetragonal $ZrO_2$. Furthermore, the suggestions on improving the LTD resistance of tetragonal $ZrO_2$ are proposed, which is the catalyst to promote the long-term stability of $ZrO_2$-based all-ceramic crowns.

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## 1. Introduction

Zirconia-based bioceramic has attracted significant attention as a desirable all-ceramic crown material due to its excellent mechanical properties (hardness, fracture toughness and strength), biocompatibility and aesthetics, etc., which are more auspicious relative to other bioceramics, e.g., alumina[1–23]. Especially, yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) can further enhance the bending strength and fracture toughness of crowns remarkably by neutralizing the external strain through phase transformation toughening (PPT) of zirconia ($ZrO_2$) from tetragonal phase to monoclinic phase[24–26]. As a result, Y-TZP has been widely applied in the field of prosthodontics.

To date, many manufacturers, e.g., Vita Zahanfabirk, Ivoclar Vivadent and 3M ESPE, have devised various techniques such as In-Ceram and CAD/CAM to prepare Y-TZP bulks in mass production for dental crowns (bending strength ≥900 MPa, fracture toughness ≥5 MPa m$^{1/2}$)[27]. However, the long-term tetragonal phase stability of Y-TZP deteriorates under intraoral condition due to the low-temperature degradation (LTD) of tetragonal zirconia ($ZrO_2$), which contributes to many clinical failures of Y-TZP dental crowns[27–31].

Therefore, it is of great importance to improve the LTD (also referred as aging) resistance of tetragonal $ZrO_2$ for long-term stability of $ZrO_2$-based all-ceramic crowns.

## 2. Research Advances

Although the specific mechanism of LTD is still controversial, there are several reasonable speculated explanations on LTD phenomenon of Y-TZP, including[32]: (1) $Y_2O_3$ stabilizer in the neighboring tetragonal $ZrO_2$ grains is depleted through the reaction of the stabilizer with water, resulting in the tetragonal-to-monoclinic (t-m) transformation of zirconia; (2) Zr—O bond is attacked and broken by water vapor, and stress is accumulated due to the movement of —OH, leading to the lattice defects acting as nucleation sites for t-m phase transformation; (3) $O^{2-}$ originated from water will fill oxygen vacancies of matrix, resulting in the t-m phase transformation. Overall, the following view has reached consensus: Y-TZP is prone to generate t-m phase transformation in the presence of water, and the transformation initially originates from the surface of the sample and then penetrate underneath, resulting in LTD of Y-TZP and cracks in the crown. To enhance the LTD resistance of TZP, numerous studies have been carried out experimentally and theoretically[33–38]. In particular, the grain size of TZP, and types and contents of stabilizers are considered as two major factors to influence the tetragonal phase stability and aging performance of the sample.
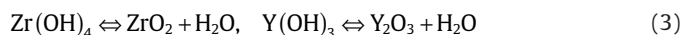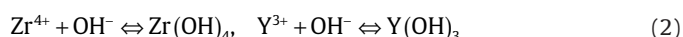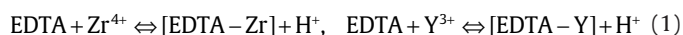
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## 2.1. Influence of grain size and yttria stabilizer on LTD resistance

From the thermodynamic perspective, the driving force of phase transformation can be reduced by decreasing the grain size of TZP, which is favorable for the stabilization of the tetragonal phase and LTD resistance; while from kinetic perspective, more grain boundaries acting as nucleation sites for t-m phase transformation will be generated[32]. Therefore, grain size will significantly affect the tetragonal phase stability and aging performance of the sample. A number of reports suggest that the critical grain size (GS) of stabilized tetragonal phase for pure $ZrO_2$ powder is 5-10 nm at room temperature, under which the tetragonal phase is thermodynamically stable and would have good LTD resistance[27,33]. While for Y-TZP system, the critical GS is closely related with the amount of $Y^{3+}$, yet it is still controversial in the detailed critical GS even for the same amount of $Y^{3+}$[27,29,34]. Denry and Kelly indicated that such controversy may be due to the different distribution $Y^{3+}$ in the matrix, which will affect the t-m phase transformation of $ZrO_2$ grains[27]. However, to the best of our knowledge, there are virtually few undisputed systematical studies involving the relation between $Y^{3+}$ distribution and GS of $ZrO_2$ to stabilize the tetragonal phase, which is definitely unfavorable to investigate the stabilization of tetragonal Y-TZP and its LTD resistance theoretically and experimentally. The critical GS of powder sample is quite different from that of solid sample, and the distribution of $Y^{3+}$ in the matrix may also influence GS.

In fact, it is particularly difficult to rigorously control the GS of $ZrO_2$ and distribution of $Y^{3+}$ at the same time through conventional methods[38]. Till now, the liquid method, such as sol-gel method and hydrothermal method are the most popular methods to prepare Y-TZP due to their simplicity and low cost, yet both methods have their restrictions. For sol-gel method, although the homogenous distribution of $Y^{3+}$ in $ZrO_2$ matrix can be achieved, it is very difficult to control the GS of samples especially to several or dozens of nanometers. While for hydrothermal method, the GS of samples can be controlled to as low as several nanometers owing to the relatively low reaction temperature, but the distribution of $Y^{3+}$ in $ZrO_2$ matrix is uncontrollable due to the different precipitation consequence of $ZrO_2$ and $Y_2O_3$ during the hydrothermal process. Therefore, it is of great importance to overcome such restrictions to further enhance the LTD resistance of Y-TZP for dental applications.

Our group has been working on dental materials[38–41], and we devised a novel "complexing-hydrothermal" method to prepare $ZrO_2$-based materials by integrating complexing sol-gel method and hydrothermal method. The flowchart of the so-called "complexing-hydrothermal" is shown in Fig. 1. Zirconium nitrate and/or yttrium nitrate were used as reactants and ethylenediaminetetraacetic acid (EDTA) as chelating agent to prepare the EDTA–zirconium and EDTA–yttrium monomer complexes. With different time of gelation process, the mixed solution was adopted as the precursor of hydrothermal reaction. After the hydrothermal reaction, the pure $ZrO_2$ powders, whose GS is lower than 10 nm, and Y-TZP powders, whose GS is lower than 15 nm, were obtained by washing and drying the precursor powder. In addition, the stability of tetragonal phase could be enhanced even if no $Y^{3+}$ stabilizer was added, which was favorable to enhance the LTD resistance of samples. The reactions related to the "complexing-hydrothermal" process are as follows:

$$EDTA + Zr^{4+} \Leftrightarrow [EDTA - Zr] + H^+, \quad EDTA + Y^{3+} \Leftrightarrow [EDTA - Y] + H^+ \quad (1)$$

$$Zr^{4+} + OH^- \Leftrightarrow Zr(OH)_4, \quad Y^{3+} + OH^- \Leftrightarrow Y(OH)_3 \quad (2)$$

$$Zr(OH)_4 \Leftrightarrow ZrO_2 + H_2O, \quad Y(OH)_3 \Leftrightarrow Y_2O_3 + H_2O \quad (3)$$

where reactions (1) and (2) are the complexation reaction of metal ions and complexing agents, i.e., EDTA and $OH^-$, respectively.
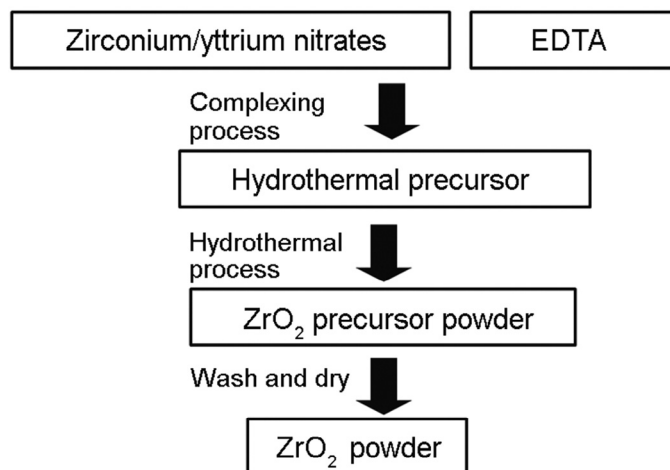


**Fig. 1.** Flowchart of complexing-hydrothermal method to prepare $ZrO_2$-based powder.

Reaction (3) is the hydrothermal reaction of the hydroxide of $Zr^{4+}$ and $Y^{3+}$. Unlike conventional hydrothermal process, whose reaction is just reactions (2) and (3), a strong complexing agent, i.e., EDTA, was adopted to complex both $Zr^{4+}$ and $Y^{3+}$. In this way, the competition of complexation reactions of reactions (1) and (2) can delay the precipitation of $ZrO_2$ and $Y_2O_3$ during the hydrothermal reaction, which can improve the control of GS and distribution of $Y^{3+}$ in $ZrO_2$ matrix. The preliminary energy spectrum analysis also confirmed the speculation, although the ratio of $Zr^{4+}$ and $Y^{3+}$ was still nonstoichiometric. Therefore, further investigations on the competition and balance of different reactions are in need in this promising method to clarify the relation mechanism between GS and distribution of stabilizer in stabilization of tetragonal Y-TZP, and then to improve the LTD resistance of Y-TZP.

## 2.2. Influence of ceria-yttria stabilizers on LTD resistance of TZP

It was reported that the LTD resistance of Ce-TZP was bigger than that of Y-TZP after the International Standard Organization (ISO) aging cycles test in water vapor conducted at 134 °C and $2 \times 10^5$ Pa (2 bar) for 5 h[42]. Unlike the stabilization mechanism of yttria, ceria ($CeO_2$) stabilizes the tetragonal zirconia by generating the $O^{2-}$ vacancies due to the different ionic radius of $Ce^{4+}$ and $Zr^{4+}$. Generally speaking, the amount of $CeO_2$ should be in the range of 8-12 mol% to obtain the stabilized tetragonal zirconia[32]. However, the stabilization mechanism of the concentration of $Ce^{4+}$ on tetragonal zirconia is still unknown. Furthermore, $Ce^{4+}$ can be reduced to $Ce^{3+}$ under the reaction of many factors, e.g., sintering, local stress or glucose in oral cavity. As a result, the phase stabilization ability of $CeO_2$ will deteriorate and the color of Ce-TZP will change, which are unfavorable for Ce-TZP crowns from both mechanical and aesthetic point of views. As an alternative, $CeO_2$ can be applied as a secondary stabilizer of Y-TZP to prepare $Ce^{4+}$ doped Y-TZP, i.e., Ce/Y-TZP, which can improve the LTD resistance of Y-TZP without affecting the mechanical properties and aesthetics obviously. This promising system, however, cannot solve LTD of tetragonal zirconia in the long term.

It is of great importance to restrict the contact and reaction between water molecules and tetragonal zirconia to improve the LTD resistance. From this perspective, it can shield tetragonal zirconia from water effectively if we can coat Y-TZP grains with shell. The choice of shell materials should base on the following: the shell should restrict the penetration of water to affect the stability of tetragonal zirconia; the introduction of shell should not deteriorate