

FABRICATION AND PROPERTIES OF YTTRIA, CERIA DOPED ZIRCONIA-ALUMINIA CERAMIC COMPOSITES

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At present, zirconia-based ceramics are gaining popularity in dentistry, particularly in fixed prosthodontics. Clinically, it is important that ceramic restorations reproduce the translucency and color of natural teeth. Zirconia based ceramics is a high performance material with excellent biocompatibility and mechanical properties, which suggest its suitability for posterior fixed partial dentures. Y_2O_3 -stabilized tetragonal zirconia polycrystalline (YTZ/ Al_2O_3) and CeO_2 -stabilized tetragonal zirconia polycrystalline (CZA) ceramics with high-performance were prepared for dental application by use the wet chemical route, consolidated by cold isostatic pressing, and two-step sintering method. Physical and mechanical properties test results show that the bending strength, fracture toughness, and the density of full sintered ceramics suggest that the material is relatively suitable for dental restoration.

INTRODUCTION

At present, zirconia-based ceramics are gaining popularity in dentistry, particularly in fixed prosthodontics. Clinically, it is important that ceramic restorations reproduce the translucency and color of natural teeth [1]. At ambient pressure, unalloyed zirconia can assume three crystallographic forms depending on the temperature. At room temperature and upon heating up to 1170 °C, the symmetry is monoclinic ($P21/c$). The structure is tetragonal ($P42/nmc$) between 1170 and 2370 °C and cubic ($Fm\bar{3}m$) above 2370 °C and up to the melting point [2, 3]. The transformation from the tetragonal (t) phase to the monoclinic (m) phase upon cooling is accompanied by a substantial increase in volume (~ 4.5 %), sufficient to lead to catastrophic failure. This transformation is reversible and begins at ~950 °C on cooling. Alloying pure zirconia with stabilizing oxides such as CaO, MgO, Y_2O_3 or CeO_2 allows the retention of the tetragonal structure at room temperature and therefore the control of the stress-induced $t \rightarrow m$ transformation, efficiently arresting crack propagation and leading to high toughness [1, 4, 5].

Zirconia based ceramics is a high performance material with excellent biocompatibility and mechanical properties, which suggest its suitability for posterior fixed partial dentures. Y_2O_3 -stabilized tetragonal zirconia polycrystalline (YTZ/ Al_2O_3) and CeO_2 -stabilized tetragonal zirconia polycrystalline (CZA) ceramics with high-performance were prepared for dental application by use the wet chemical route, consolidated by cold isostatic pressing, and two-step sintering method. Physical and mechanical properties test results show that the bending strength, fracture toughness, and the density of full sintered ceramics suggest that the material is relatively suitable for dental restoration.

EXPERIMENTAL PROCEDURE

Aqueous solutions of $Al(NO_3)_3 \cdot 9H_2O$, $ZrO(NO_3)_2 \cdot 4H_2O$, $Y(NO_3)_3 \cdot 6H_2O$ and $(NH_4)_2Ce(NO_3)_6$ were used as the starting materials. The mixed hydrogel was obtained by adding 1:1 NH_3 solution to the mixed aqueous solution maintained at 25 °C with continuous

stirring. The viscosity of the batch gradually increased and finally set to gel at pH 8.7. The gels were then aged at room temperature for 48 h. After aging, the gel was repeatedly washed with boiled distilled water to remove extraneous impurities and filtered. The filtered cake was dried at 40 °C for 48 h. The synthesized specimens were characterized for specific average surface area (BET) TriStar II 3020, DTA/TG (SDT Q600) and TEM (JEM 2010). The dried gel was calcined in a muffle furnace at 700 °C for 4 h in air. Samples were cold isostatic pressed at 300 MPa for 3 minutes. Subsequently two-step sintering methods were adapted for the samples. In the first step, a slow thermal debinding profile with a very slow heating rate (1 K min^{-1} to 600 °C held for 2 hours; and 5 K min^{-1} to 1100 °C held for 2 hours and 5 K min^{-1} to room temperature) was carried out in Nabertherm Furnace in an atmosphere environment. In the second step, the samples were sintered in air at 1350 °C for 2 hours, followed by 5 K min^{-1} cooling down to room temperature. Sinterability was evaluated through the shrinkage, density value. The percent shrinkage measures the dimensional change of a sintered body from a green body, as indicated by the fractional shrinkage, $\Delta L/L_0$ in length. Specimens were characterized by XRD (Rigaku Ultima IV), AFM (Ntegra Aura), SEM (Quanta 200 3D). Mechanical properties (microhardness and fracture toughness) were measured using INSTRON Vickers microhardness-tester 402MVD and fracture toughness tester INSTRON 5882.

RESULTS AND DISCUSSION

The synthesized powder was characterized for specific average surface area and TEM was used for the determination of exact particle size. Most of the particles are spherical and in the range of 12...20 nm (Fig. 1).

The specific surface area of the final powders is determined by the BET surface area analysis and is calculated as 79 m^2/g . The DTA/TG result indicates three-stage decomposition for pseudoboehmite and single stage decomposition for amorphous $Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$.

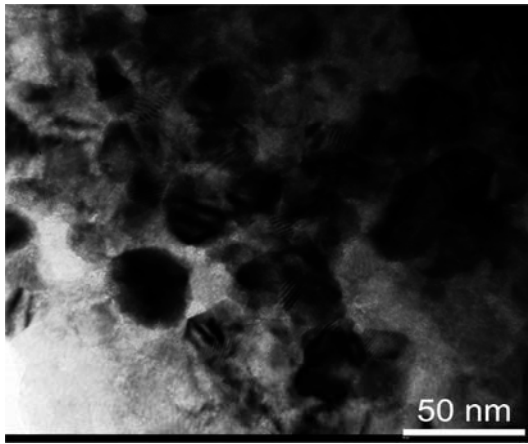


Fig. 1. TEM image of the $10\%Al_2O_3-90\%Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$

$10\%Al_2O_3-90\%Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$ powder was compacted by cold isostatic pressing of green compacts at 300 MPa and calcined. Densification studies are carried out in both the muffle furnace as well as a dilatometer in atmospheric conditions.

The sintering was carried out without any isothermal treatment with heating rate of 5 K/min. The small initial shrinkage curve up to 100 °C of the compacts during sintering is responsible for the expulsion of the residual water from the sample (Fig. 2). The densification starts at around 940 °C. Beyond 1145 °C, the slope has been changed due to completion of $\alpha-Al_2O_3$. Pores are also eliminated with an achievement of 65 % of the theoretical density of that particular composition.

The present results exhibit the sintering without sintering additive and isothermal treatment is mainly attributed to high surface area of starting powders.

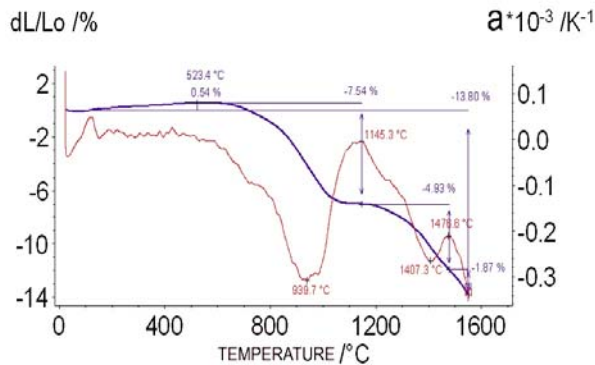


Fig. 2. Sintering of a green body $10\%Al_2O_3-90\%Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$

Microstructure of $10\%Al_2O_3-90\%Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$ studied by Atomic Force Microscopy (AFM) and scanning electron microscopy (SEM) reveals that particles are present as either intergranular or intragranular in the ZrO_2 matrix. The average grain size of alumina is about 500 nm – 1.5 μ m and fairly homogeneous in the entire matrix. Zirconia particles are smaller in size (90...300 nm) and are isolated at grain boundaries between larger alumina grains. The microstructure of $10\%Al_2O_3-90\%Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$ is shown in Fig. 3, in which the zirconia grains appear brighter compared to the darker alumina grains.

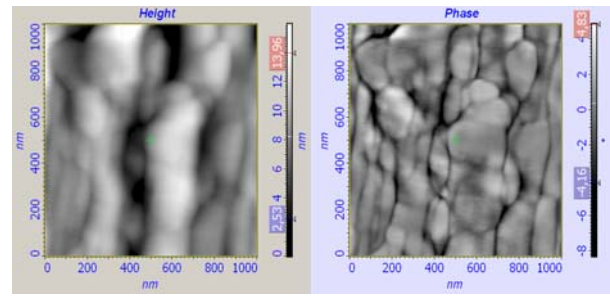


Fig. 3. Microstructure of $10\%Al_2O_3-90\%Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$

However, the amount of porosity is greater than that of sintered Y-TZP and comprises between 8 and 11 % [6]. This partially explains the generally lower mechanical properties of ceria-zirconia ceramics when compared to 3Y-TZP dental ceramics [7]. It should be pointed out, however, that Ce-Y-TZP ceramics usually exhibit better thermal stability and resistance to low temperature degradation than Y-TZP under similar thermo-cycling or aging conditions [8, 9]. It was confirmed that the Ce-Y-TZP ceramic was constituted of two crystalline phases, a rhombohedral alumina matrix (Fig. 4), so-called α -alumina (R-3c, hexagonal ICDD (PDF2008) and cubic zirconia (Fm-3m ICDD (PDF2008)).

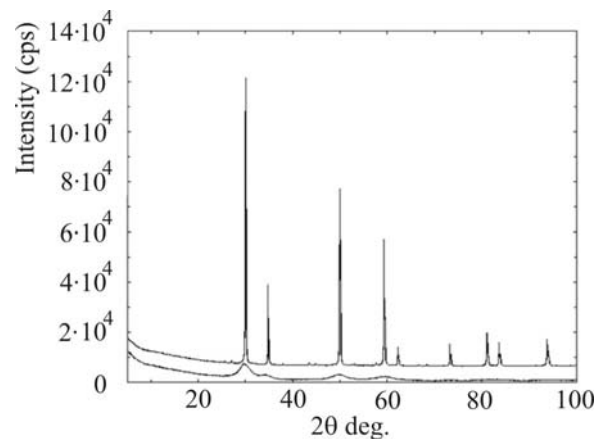


Fig. 4. XRD pattern of $10\% Al_2O_3-90\% Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$ sintered body sintered at 1350 °C for 2h

The X-ray mapping (EPMA analysis) of polished and thermally etched surface showing the presence of different elements (Al, Zr, Ce, Y) within the matrix is illustrated in Fig. 5. The EPMA analysis shows an almost uniform distribution of $Y_2O_3-CeO_2-ZrO_2$ and alumina.

This homogeneous distribution assists to enhancement of the thermo-mechanical properties. The principal merit of the microstructure observed in the $10\%Al_2O_3-90\% Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$ composites obtained by the chemical wet route is the adequate relative grain size ratio and phase distribution between the both phases, allowing zirconia particles to be present mostly at grain boundaries.

The mechanical properties of zirconia are the highest ever reported for any dental ceramic. This may allow the realization of posterior fixed partial dentures and permit a substantial reduction in core thickness. These capabilities are highly attractive in prosthetic dentistry, where strength and esthetics are paramount.

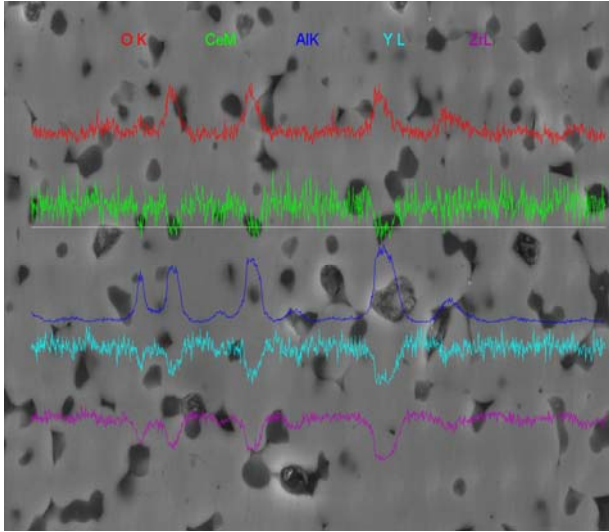


Fig. 5. X-ray mapping (EPMA analysis) of polished and thermally etched surface
10%Al₂O₃-90%Ce_{0.1}Y_{0.1}Zr_{0.8}O₂

However, due to the metastability of tetragonal zirconia, stress-generating surface treatments such as grinding or sandblasting are liable to trigger the $t \rightarrow m$ transformation with the associated volume increase leading to the formation of surface compressive stresses, thereby increasing the flexural strength but also altering the phase integrity of the material and increasing the susceptibility to aging [6]. The low temperature degradation (LTD) of zirconia is a well-documented phenomenon, exacerbated notably by the presence of water [10]. The consequences of this aging process are multiple and include surface degradation with grain pullout and microcracking as well as strength degradation.

Hardness was determined by the Vickers hardness test. Vickers hardness values were calculated using Eq. (1) where «P» was the applied load (N) and «d» was the average of the diagonal length (m) and the angle between the opposite faces of the indenter (136°)

$$H_v = \frac{\alpha P}{d^2}. \quad (1)$$

Elastic modulus was determined by the resonance vibration method. Flexural strength was measured by a three-point bending test at room temperature. The tensile surfaces of the specimens were polished with a diamond liquid suspension. The span length and the cross-head speed were 30 mm and 0.5 mm/min, respectively. The fracture toughness was estimated by the indentation-fracture method with the use of the following equation of Marshall and Evans [11]:

$$K_{1C} = 0.036 E^{0.4} P^{0.6} \alpha^{-0.7} \left(\frac{c}{\alpha} \right)^{-1.5}, \quad (2)$$

where E is the elastic modulus, P is the applied load, a is the half length of the Vickers impression, and c is the half length of the median crack.

The mechanical properties of the 10%Al₂O₃-90%Ce_{0.1}Y_{0.1}Zr_{0.8}O₂ nanocomposite and Y-TZP are listed in Table. The fracture toughness of the Ce-Y-TZP/Al₂O₃ was much higher than that Y-TZP, whereas the toughness values measured by the indentation-

fracture method might be overestimated because of the rising R-curve behavior of Ce-Y-TZP/Al₂O₃.

The alumina grains prevent nucleation of zirconia monoclinic phase and prevent transformation propagation to neighboring zirconia grains, and due to the mismatch in the elastic module between alumina and zirconia, the transformation of bulk grains becomes severely restricted. On the other hand, surface grains can accommodate such strain in a vertical direction, which may lead to grain pop-out and detachment.

Mechanical properties of the 10%Al₂O₃-90%Ce_{0.1}Y_{0.1}Zr_{0.8}O₂ and Y-TZP

Properties	Composites	
	10%Al ₂ O ₃ -90%Ce _{0.1} Y _{0.1} Zr _{0.8} O ₂	Y _{0.55} Zr _{0.93} O ₂
Flexural strength	507 ± 65 MPa	1003 ± 132 MPa
Vickers hardness H_v	6 GPa	13.5 GPa
Fracture toughness K_{1C}	8.2±0.2 MPa·m ^{1/2}	6.0 ± 0.2 MPa·m ^{1/2}
Elastic modulus E	87 GPa	200 GPa
Thermal expansion coefficient α	10.1 μm/°C	10.4 μm/°C

CONCLUSION

This technique of preparation provides a straightforward method for the preparation of Y₂O₃-CeO₂-doped ZrO₂-Al₂O₃ nanocrystalline homogeneous solid solutions at low temperatures and for shorter annealing times, reducing segregation of the components. The mechanical properties of obtained ceramic strongly depend on its grain size. Above a critical grain size, YTZ/Al₂O₃ is less stable and more susceptible to spontaneous $t \rightarrow m$ transformation whereas smaller grain sizes (< 1 μm) are associated with a lower transformation rate [12]. Moreover, below a certain grain size (~ 0.2 μm), the transformation is not possible, leading to reduced fracture toughness. Consequently, the sintering conditions have a strong impact on both stability and mechanical properties of the final product as they dictate the grain. Higher sintering temperatures and longer sintering times lead to larger grain sizes. High fracture toughness of 90%Ce_{0.1}Y_{0.1}Zr_{0.8}O₂ is attributed to the presence of a coupled mechanism of stress-induced transformation toughening and transformation-induced microcrack toughening, and high flexural strength of the ceramics is a coupled result of small-size flaw and high fracture toughness.

These results further indicate that the product can be used as a promising new ceramic material to fabricate dental base crowns and bridges. Composite (CZA) not only exhibited higher strength, but might also have higher fracture toughness when compared with YTZ/Al₂O₃.

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REFERENCES

1. R.C. Garvie, R.H. Hannink, R.T. Pascoe. Ceramic steel // *Nature*. 1975, v. 258, p.703–704.
2. E.C. Subbarao. Zirconia-an overview // *Heuer AH, Hobbs LW / editors. Science and technology of zirconia*. Columbus, OH: The American Ceramic Society; 1981, p. 1–24.
3. E. Kisi, C. Howard. Crystal structures of zirconia phases and their interrelation // *Key Eng Mater*. 1998, v.153/154, p.1–35.
4. R.C. Garvie, P.S. Nicholson. Phase analysis in zirconia systems // *J. Am Ceram Soc*. 1972, v. 55, p. 303–305.
5. A.H. Heuer, F.F. Lange, M.V. Swain, A.G. Evans *Transformation toughening: an overview* // *J. Am Ceram. Soc*. 1986, v.69, p. i–iv.
6. M. Guazzato, M. Albakry, M.V. Swain, S.P. Ringer. Microstructure of alumina- and alumina/zirconia-glass infiltrated dental ceramics // *Bioceramics*. 2003, v.15, p. 879-882.
7. M. Guazzato, M. Albakry, S.P. Ringer, M.V. Swain. Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics // *Dent Mater*. 2004, v. 20, p. 449-456.
8. K. Tsukuma. Mechanical properties and thermal stability of CeO₂ containing tetragonal zirconia polycrystals // *Am Ceram Soc Bull*. 1986, v.65, p.1386-1389.
9. K. Tsukuma, M. Shimada. Strength, fracture toughness and Vickers hardness of CeO₂-stabilized tetragonal ZrO₂ polycrystals (Ce-TZP) // *J. Mater. Sci*. 1985, v.20, p.1178-1184.
10. T. Sato, S. Ohtaki, M. Shimada. Transformation of yttria partially stabilized zirconia by low-temperature annealing in air // *J. Mater. Sci*. 1985, v.20, p.1466-1470.
11. C.B. Ponton, R.D. Rawlings. Vickers indentation fracture toughness test. Part 1—review of literature and formulation of standardized indentation toughness equations // *Mater. Sci. Technol*. 1989, v.5, p.865-872.
12. B.A. Cottom, M.J. Mayo. Fracture toughness of nanocrystalline ZrO₂-3mol% Y₂O₃ determined by Vickers indentation // *Scripta Mater*. 1996, v.34, p. 809.

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СОЗДАНИЕ И СВОЙСТВА ЛЕГИРОВАННЫХ ИТТРИЕМ И ЦЕРИЕМ ЦИРКОНИЙ-АЛЮМИНИЕВЫХ КЕРАМИЧЕСКИХ КОМПОЗИТОВ

Р.А. Любушкин, О.Н. Иванов, В.Р. Чуев, А.А. Бузов

В настоящее время керамика на основе диоксида циркония приобретает большую популярность в стоматологическом протезировании ввиду исключительных механических и косметических (прозрачность и цвет естественных зубов) свойств, биоинертности. Композиционная керамика $Y_{0,1}Zr_{0,9}O_2/Al_2O_3-CeO_2$ была синтезирована обратным соосаждением из водных растворов, компактирована методом холодного изостатического прессования и спечена пошагово на воздухе. Охарактеризованы свойства исходного порошка методами БЭТ, просвечивающей микроскопии и дифференциальной сканирующей калориметрии. Изучена микроструктура, фазовый состав, микротвердость и прочность на сжатие консолидированного $Y_{0,1}Zr_{0,9}O_2/Al_2O_3-CeO_2$.

СТВОРЕННЯ ТА ВЛАСТИВОСТІ ЛЕГОВАНИХ ІТРИЄМ І ЦЕРИЄМ ЦИРКОНІЙ-АЛЮМІНІЄВИХ КЕРАМІЧНИХ КОМПОЗИТИВ

Р.А. Любушкін, О.М. Іванов, В.Р. Чуєв, А.А. Бузов

В даний час кераміка на основі діоксиду цирконію набуває великої популярності в стоматологічному протезуванні зважаючи на виняткові механічні та косметичні (прозорість і колір природних зубів) властивості, біоінертність. Композиційна кераміка $Y_{0,1}Zr_{0,9}O_2/Al_2O_3-CeO_2$ була синтезована зворотним співосадженням з водних розчинів і компактуванням методом холодного ізостатичного пресування та поетапного спікання на повітрі. Охарактеризовано властивості вихідного порошку методами БЕТ, просвічуючої микроскопії і диференціальної скануючої калориметрії. Вивчено микроструктуру, фазовий склад, микротвердість і міцність на стискання консолидovanого $Y_{0,1}Zr_{0,9}O_2/Al_2O_3-CeO_2$.