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One-step preparation of CaO-doped partially stabilized zirconia from fused zirconia

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Abstract:

Partially stabilized zirconia (PSZ) replaces the widespread applications of full stabilized zirconia (FSZ) on ceramics materials and refractories materials, attributed to its excellent properties including small coefficient of thermal expansion, low thermal conductivity and good thermal shock resistance. In this work, CaO-doped partially stabilized zirconia

(CaO-PSZ) was optimizedly prepared from fused zirconia through conventional roasting. Meanwhile, the effects of roasting temperature and duration time on stability properties were explored to determine the stability parameters of the prepared CaO-PSZ. Results indicated that the zirconia stability rate synchronously improved with the decrease of roasting temperature and duration time, which was attributed to that the martensitic transformation of fused zirconia with volume change plays a toughening effect, further rendering the change of zirconia stability properties. XRD patterns verified the martensitic transformation, representing by cubic ZrO_2 phase (c- ZrO_2) in raw fused zirconia was partially transformed into monoclinic ZrO_2 phase (m- ZrO_2) at 1450 °C for 4 h. Moreover, the phase transition law of fused zirconia was revealed through SEM and EDAX characterization for the raw fused zirconia and the prepared CaO-PSZ. SEM patterns showed acicular patterns of grains and round fine particles clustered at grain boundaries, indicating that CaO stabilizer precipitated on grain boundaries and rendered the crystal structure enhanced, which the result was consistent with EDAX analysis. This work can lay a significant foundation for applications of microwave heating on the preparation of partially stabilized zirconia (PSZ) from fused zirconia.

Keywords: partially stabilized zirconia; fused zirconia; stability properties; phase structure

1 Introduction

Zirconia (ZrO_2) as important ceramic coating material, endows excellent physical properties such as high-temperature resistance, wear resistance and corrosion resistance, rendering it widely applied as refractory materials and ceramic pigments [1, 2]; additionally,

it has received greatly increasing interest in the high-tech fields of bio-ceramics, electronic ceramics, functional ceramics and structural ceramics, etc., [3-6]. However, during the heating and cooling process, undoped pure zirconia with polymorphism is accompanied by volume expansion, and this volume expansion exceeds the elastic limit of zirconia [7]. In addition, the small thermal conductivity and large thermal expansion coefficient of undoped pure zirconia render it with poor mechanical, electrical and thermal shock resistance properties, further causing its applications in the manufacture of large and shaped products being blocked [8]. Hence, before developing the further deeper and broader utilization of zirconia material, undoped pure zirconia firstly needs to be treated with the stabilized process. Pure zirconia cannot maintain cubic phase (c-ZrO₂) and tetragonal phase (t-ZrO₂) at room temperature, and can only exist in a monoclinic phase (m-ZrO₂); and a reversible martensitic transformation occurs between the three crystal forms of zirconia with temperature change, representing by the conversion of tetragonal phase (t-ZrO₂) to monoclinic phase (m-ZrO₂) occurred at 1000 °C, with a corresponding reverse phase transition occurring at 1170 °C, and the conversion of tetragonal phase (t-ZrO₂) to cubic phase (c-ZrO₂) occurs at 2370 °C [9,10]. During the transformation of tetragonal phase (t-ZrO₂) to monoclinic phase (m-ZrO₂), many microcracks smaller than the critical dimension are formed around the converted particles, due to volume change. These microcracks are non-expanding under load, therefore without degrading the strength of the material. When the large cracks expand under load to encounter these cracks, a new phase change will be induced, and the extended crack will be diverted to absorb energy, thereby achieving a toughening effect [9, 10]. Meanwhile, Garvie et al. [11] reported the fine precipitates of monoclinic zirconia in a cubic stable matrix greatly improved

the toughness and strength of the material. Therefore, the toughening effect of zirconia ceramics material can be achieved through the stabilized process by controlling the heating temperature and duration time.

The stabilized process for zirconia materials refers to that the high temperature phase of zirconia, the tetragonal (t-ZrO₂) or cubic (c-ZrO₂) crystal structure is irreversibly transformed through chemical doping or physical methods into different steady-state forms of zirconia materials, which are stable at room temperature, usually by controlling the amount and type of added stabilizer or the grain size [12, 13]. Generally, the stable zirconia materials are classified into three types identified by the microstructure: full stabilized zirconia (FSZ), partially stabilized zirconia (PSZ), tetragonal zirconia polycrystalline (TZP) [14]. Moreover, partially stabilized zirconia (PSZ) endows more excellent mechanical properties than full stabilized zirconia (FSZ), including high melting point, low thermal conductivity, good thermal stability, low temperature creep, and good thermal shock resistance, which is mainly prepared by full stabilized zirconia (FSZ) doping with various stabilizing oxides, accompanied with a martensitic transformation, The stabilizing oxides are mainly the alkaline earth metal oxides or rare earth metal oxides, having a lower valence than tetravalent, including CaO [15, 16], MgO [17], CeO₂ [18], UO₂ [19], and Y₂O₃ [20], etc. Moreover, the difference between the cation radius of these oxides and the Zr⁴⁺ ion radius was less than 12% [21]; hence, the solubility properties of these oxides in zirconia are very high. After high-temperature treatment, these low-valence cations will replace the position of Zr⁴⁺; meanwhile, oxygen vacancies are introduced in the lattice to maintain the local electrical neutrality of zirconia material [22], and the oxidation is distributed inside of zirconia material,

vacancies around Zr^{4+} reduce the repulsive force between local oxygen and oxygen, causing large distortion of the coordination layer, thereby forming a stable solid solution, with a lattice-type structure representing by a mixed phase of tetragonal phase (t- ZrO_2) and cubic phase (c- ZrO_2), rendering the zirconia material can maintain the metastable state at room temperature by preventing eutectoid decomposition with rapid cooling [23, 24].

In this work, optimization preparation of CaO-doped partially stabilized zirconia (CaO-PSZ) was investigated, with fused zirconia as raw material treated by conventional roasting. Meanwhile, the effects of roasting temperature and duration time on stability properties of CaO-doped partially stabilized zirconia (CaO-PSZ) were explored. Moreover, the phase transition mechanism of fused zirconia was revealed through characterization of phase transformation and physical structure, with the raw fused zirconia and the CaO-doped partially stabilized zirconia (CaO-PSZ) samples characterized by XRD, SEM, and EDAX.

2 Materials and methods

2.1 Materials

The fused zirconia raw material was the full stabilized zirconia (FSZ), prepared by the electrofusion method and received from a factory in Yingkou City, Liaoning Province, P.R. China. The chemical compositions of fused zirconia raw material were provided by Kunming Metallurgical Research Institute (Kunming City, Yunnan Province, P.R. China), and the analytical results were shown in Table 1. It was characterized by the full stabilized zirconia (FSZ) was doped with Cao stabilizer with high zirconia content (95.1%) and other minor elements such as Al_2O_3 , TiO_2 and Fe_2O_3 , with the 3.8% of CaO stabilizer content. Moreover,

based on Table 1, it can be considered that the solid solution was composed as 0.08 CaO·0.92ZrO₂, referring to that the solid solution was composed of 8 (M)% of CaO content

The XRD pattern of fused zirconia raw material was illustrated in Fig.1. As shown in Fig.1, the diffraction peak of calcium oxide (CaO) did not appear, therefore, it can be confirmed that the calcium oxide (CaO) was completely dissolved in the full stabilized zirconia (FSZ) to form a solid solution. Moreover, in accordance with the standard PDF cards of the three crystals of zirconia (see Supplementary data), including monoclinic phase zirconia (m-ZrO₂, JCPDS: 37-1484), cubic phase zirconia (c-ZrO₂, JCPDS: 49-1642), and tetragonal phase zirconia (t-ZrO₂, JCPDS: 42-1164), it can be concluded that the fused zirconia was a solid solution formed by adding Cao stabilizer, which was a complete cubic phase zirconia (c-ZrO₂) with the fluorite structure, without any monoclinic phase zirconia (m-ZrO₂) and tetragonal phase zirconia (t-ZrO₂) detected.

2.2 Characterization

X-ray diffraction (D/Max 2500, Rigaku, Japan) was applied to comparatively analyze the crystal structures of the raw material and the prepared CaO-PSZ, with the XRD patterns recorded at a scanning rate of 3 °/min with 2-theta regime from 10 ° to 100 ° using CuKα Radiation ($\lambda=1.54056 \text{ \AA}$), and with the anode current and voltage operated at 20 mA and 35 KV, respectively. Scanning electron microscopy (XL30ESEM-TMP, Philips, Holland) was applied to characterize the microstructure morphologies of the raw material and the prepared CaO-PSZ. Meanwhile, energy dispersion scanner spectrometer (EDAX) attached to the SEM apparatus was utilized to determine elemental compositions of the prepared CaO-PSZ.

2.3 Procedure

The fused zirconia raw materials were ground by a test sample crusher (TJ-1003), and then screened to 10~20 mm, followed by the ground samples were dried at 120 °C for 2 h in a digital blast drying oven (GZX-9030MBE). After drying, the samples with 200.0 g mass were introduced into a ceramic crucible and roasted by an electric resistance furnace (SGM3817B), without protective gas injected into furnace. Followed by the fused zirconia material was roasted at different temperatures with a temperature rise rate of 4 °C/min, including 1000 °C, 1100 °C, 1200 °C, 1300 °C, 1400 °C and 1450 °C, and treated with different duration time ranged from 0 h to 6 h, with 1 h as a variable node. After attaining the specific roasting temperature and duration time, the roasted samples were removed and cooled to 950 °C with the control cooling rate of 4 °C/min and through quenching treatment, with the CaO-doped partially stabilized zirconia (CaO-PSZ) prepared. Finally, the stability properties, phase compositions, microstructure morphology, and elemental compositions of the prepared partially stabilized zirconia (PSZ) samples were calculated and determined.

2.4 Determination of zirconia stability properties

The stability properties of zirconia ceramic material are generally measured by the stability rate, and the stability rate is defined as the quotient value of the sum of the X-ray diffraction peak intensities of the cubic phase zirconia (c-ZrO₂) and the tetragonal phase zirconia (t-ZrO₂) with the sum of the X-ray diffraction peak intensities of the cubic phase (c-ZrO₂), the tetragonal phase (t-ZrO₂), and the monoclinic phase zirconia (m-ZrO₂) [25]. Simply, the stability rate of zirconia materials is defined as the following equation [26],

$$\text{Stability rate} = \frac{\text{Intensity of } 29.92^\circ}{\text{Intensity of } 28.06^\circ + \text{Intensity of } 31.24^\circ + \text{Intensity of } 29.92^\circ} \times 100\% \quad (1)$$

Where Intensity of 29.92° indicates the peak intensity of cubic-phase zirconia (c-ZrO₂); Intensity of 28.06° and Intensity of 31.24° represent the peak intensities of monoclinic zirconia (m-ZrO₂). Moreover, these peaks are theoretically unchanged; therefore, the stability rate of the zirconia ceramic material can be calculated based on the XRD analysis by the K-value semi-quantitative method.

3 Results and discussion

3.1 Stability properties analysis

The stability properties of partially stabilized zirconia (PSZ) material are influenced by many factors, including roasting temperature, and duration time, etc. Therefore, influence of roasting temperature and duration time on the stability properties and phase composition of partially stabilized zirconia (PSZ) was studied, further to determine the optimum roasting preparation parameters for the CaO-doped partially stabilized zirconia (CaO-PSZ) from fused zirconia.

3.1.1 Effect of roasting temperature on stability rate

Effects of roasting temperatures on stability properties and phase compositions of the prepared CaO-doped partially stabilized zirconia (CaO-PSZ) were investigated by fused zirconia material roasted at 1000 °C, 1100 °C, 1200 °C, 1300 °C, 1400 °C, 1450 °C, respectively, and the relationship of stability properties and phase structure change with temperature was illustrated in Fig. 2 and Fig. 3, respectively.

Fig. 2 displayed the effects of roasting temperature on the stability rate of the prepared

CaO-doped partially stabilized zirconia (CaO-PSZ), with the results calculated by Eq. (1). As illustrated in Fig. 2, the zirconia stability rate gradually decreased with the increase of temperature, with 100% at 950 °C dropped to 98.6% at 1050 °C, to 95.6% at 1250 °C and 75.2% at 1450 °C; and the higher the temperature, the more obvious the decline of zirconia stability rate, indicating that the higher temperature was favorable for the phase transition of zirconia and rendered bigger influence on the zirconia stability rate. Moreover, referring to the definition of Eq. (1), it can be concluded that there must occur the phase transition of fused zirconia, with the reversible martensitic transformation occurring in zirconia material with temperature change. The conversion of tetragonal phase ($t\text{-ZrO}_2$) to monoclinic phase ($m\text{-ZrO}_2$) occurs at 1000 °C with a corresponding reverse phase transition occurring at 1170 °C [25, 26], and the roasting temperatures in the work were controlled at the regimes of 1000 °C to 1450 °C; therefore, it can be speculated that at the chosen temperature regime, the conversion of cubic phase ($c\text{-ZrO}_2$) to tetragonal phase ($t\text{-ZrO}_2$) and the conversion of tetragonal phase ($t\text{-ZrO}_2$) to monoclinic phase ($m\text{-ZrO}_2$) occurred, causing that the cubic phase ($c\text{-ZrO}_2$) was partially converted into monoclinic phase ($m\text{-ZrO}_2$), further rendering the decrease of stability properties. Additionally, the stability rate was 100% at 950 °C, indicating that there was no monoclinic phase zirconia ($m\text{-ZrO}_2$) produced, which was ascribed to that the temperature at 950 °C was lower than the conversion temperature of tetragonal phase ($t\text{-ZrO}_2$) to monoclinic phase ($m\text{-ZrO}_2$) at 1000 °C.

Fig. 3 presented the phase compositions of zirconia material roasted at different roasting temperatures, and it was observed from Fig. 3 that with roasting temperature increasing, the intensity of cubic phase zirconia ($c\text{-ZrO}_2$) diffraction peak at 29.92° gradually decreased, and

the intensities of monoclinic phase zirconia ($m\text{-ZrO}_2$) diffraction peaks at 28.06° and 31.24° gradually increased, indicating the decrease of cubic phase ($c\text{-ZrO}_2$) and the increase of monoclinic phase ($m\text{-ZrO}_2$) in the prepared CaO-doped partially stabilized zirconia (CaO-PSZ), further to cause the phenomenon that the stability properties decreased with temperature increasing. The findings were consistent with the results obtained in Fig. 2, which was ascribed to that the reversible martensitic transformation of fused zirconia and the cubic phase ($c\text{-ZrO}_2$) was partially converted into monoclinic phase ($m\text{-ZrO}_2$) with temperature change. Meanwhile, at a roasting temperature of 950°C , only cubic phase zirconia ($c\text{-ZrO}_2$) was detected without monoclinic phase zirconia ($m\text{-ZrO}_2$) observed, which was attributed to that the temperature at 950°C was lower than the conversion temperature of tetragonal phase ($t\text{-ZrO}_2$) to monoclinic phase ($m\text{-ZrO}_2$) at 1000°C , therefore without monoclinic phase zirconia ($m\text{-ZrO}_2$) formed. Moreover, the stability rate can be speculated to be 100% referred to Eq. (1), which was consistent with the results shown in Fig. 2. Moreover, compared with the raw zirconia material (Fig. 1), it was concluded the after roasting, the new phase, monoclinic phase zirconia ($m\text{-ZrO}_2$) appeared, and its peak intensities increased with temperature increasing, which was attributed to the phase transformation between cubic phase zirconia ($c\text{-ZrO}_2$) and monoclinic phase zirconia ($m\text{-ZrO}_2$).

3.1.2 Effect of duration time on stability rate

Effects of duration times on stability properties and crystal structures of the prepared CaO-doped partially stabilized zirconia (CaO-PSZ) were explored by controlling fused zirconia material roasted at 1450°C and treated with different duration times, including 0 h, 1 h, 2 h, 3 h, 4 h, 5 h and 6 h, and the calculated and characterization results were plotted in Fig.

4 and Fig. 5, respectively.

Effects of duration times on zirconia stability rate were determined, and the calculated results were plotted in Fig. 4. As seen from Fig. 4, at the roasting temperature of 1450 °C, the zirconia stability rate decreased with duration time prolonging, representing by 95.8% at 0 h dropped to 78.8% at 3 h and 73.5% at 6 h. The phenomenon observed from Fig. 4 indicated that prolonging duration time contributed to the conversion of cubic phase zirconia (c-ZrO₂) to monoclinic phase zirconia (m-ZrO₂). With duration time prolonging, the higher content of monoclinic phase zirconia (m-ZrO₂) was formed by the martensitic transformation to cubic phase zirconia (c-ZrO₂). Hence, the stability rate of the prepared CaO-doped partially stabilized zirconia (CaO-PSZ) decreased with duration time prolonging. Moreover, in the initial stage of heat preservation, the zirconia stability rate sharply decreased with duration time; while the duration time prolonged to 4 h, the zirconia stability rate generally showed a slower decreasing trend with duration time, and gradually tended to be balanced. Therefore, it can be concluded that the influence law of duration time on zirconia stability properties can be summarized as that at a fixed roasting temperature, the phase transition gradually increased with the prolong of duration time, rendering the gradual decrease of stability rate and the equilibrium reached at 4 h.

Fig. 5 illustrated the crystal structures of zirconia material roasted at 1450 °C with different duration times. As observed from Fig. 5, without holding treatment (the duration time of 0 h), the intensity of cubic phase zirconia (c-ZrO₂) diffraction peak at 29.92° was very strong, while the intensity of monoclinic phase zirconia (m-ZrO₂) at 28.06° and 31.24° was very weak. However, after 1 h of insulation treatment, the intensity of cubic phase zirconia

(c-ZrO₂) diffraction peak at 29.92° was weakened; conversely, the intensity of monoclinic phase zirconia (m-ZrO₂) at 28.06° and 31.24° was enhanced; meanwhile, the intensity of monoclinic phase zirconia (m-ZrO₂) at 28.06° and 31.24° enhanced with duration time prolonging, indicating that prolonging duration time improved the phase transformation process of cubic phase zirconia (c-ZrO₂) into monoclinic phase zirconia (m-ZrO₂). Similarly, the findings obtained from XRD patterns (Fig. 5) were consistent with the stability properties analysis.

3.2 Phase structure characterization analysis

The phase transformation of zirconia material causes the change of stability properties. Therefore, to better reveal the phase transition mechanism of fused zirconia, the phase transformation and physical structure of the raw fused zirconia and the prepared CaO-doped partially stabilized zirconia (CaO-PSZ) sample were characterized by XRD, SEM, and EDAX, respectively, prepared at the optimal roasting temperature of 1450 °C and duration time of 4 h; and the characterization results were presented in Fig. 6, Fig. 7, and Fig. 8, respectively.

3.2.1 Characterization by XRD

Fig. 6 displayed the phase composition change of fused zirconia before and after roasting. Compared with the XRD patterns of raw zirconia and the prepared CaO-doped partially stabilized zirconia (CaO-PSZ), the distinct diffraction peaks of monoclinic phase zirconia (m-ZrO₂) appeared at 28.06° and 31.24°, and the intensity of cubic phase zirconia (c-ZrO₂) diffraction peak at 29.92° reduced sharply, which was similarly ascribed to the martensitic transformation of fused zirconia, and the cubic phase (c-ZrO₂) was partially converted into monoclinic phase (m-ZrO₂) with temperature change.

Moreover, the thermal shock stability of partially stabilized zirconia (CaO-PSZ) is related to the content of the three crystal phase, wherein the relationship between the thermal shock stability and monoclinic phase content in zirconia material was detailed in Supplementary data. With the increase of monoclinic phase content, the thermal shock stability of partially stabilized zirconia (CaO-PSZ) is obviously improved; however, when the monoclinic phase zirconia ($m\text{-ZrO}_2$) content is larger than the certain value at 30%, its thermal stability is significantly reduced. Therefore, the index for the best thermal shock resistance for the partially stabilized zirconia (PSZ) is obtained with the monoclinic zirconia content at about 30%, and with only monoclinic phase zirconia ($m\text{-ZrO}_2$) and cubic phase zirconia ($c\text{-ZrO}_2$) in the partially stabilized zirconia (PSZ). Therefore, combined with the XRD pattern and the thermal shock stability (see Supplementary data), it can be concluded that the partially stabilized zirconia (PSZ) prepared from fused zirconia had better thermal shock stability than fused zirconia.

3.2.2 Characterization by SEM

Fig. 7 presented the microscopic appearance change of fused zirconia before and after roasting. Wherein Fig. 7(a), (b) and (c) presented the SEM patterns of the raw fused zirconia material, Fig. 7(d), (e) and (f) presented the SEM patterns of CaO-doped partially stabilized zirconia (CaO-PSZ) prepared at the optimum process conditions.

Compared with Fig. 7(a) and Fig. 7(d), it was observed from Fig. 7(a) that the raw fused zirconia sample was grayish black, which was mainly attributed to that the formation environment of the fused zirconia sample was deficient in oxygen, and oxygen in the crystal lattice escaped, causing oxygen vacancies in the crystal, further rendering the fused zirconia

material represented this color [21, 25]. While for the roasted fused zirconia material, the color changed from grayish black to yellow, and the color for the inside and outside of the roasted sample was the same, which indicated that during the conventional roasting process, there maintained a certain partial pressure of oxygen in the furnace; meanwhile, the gray-black fused zirconia fully contacted with air during roasting process, and part of the existing oxygen vacancies were filled by oxygen diffusion mechanism [13, 27]. Moreover, it was obviously observed from Fig. 7(b) and Fig. 7(c) that there were regular crystal boundaries, with the angles for the boundary intersection points almost balanced at 120° , indicating that the raw fused zirconia material was mainly cubic phase zirconia (c-ZrO₂), which the result corresponded with the XRD analysis for the raw zirconia material, as shown in Fig. 1. And for the CaO-doped partially stabilized zirconia (PSZ) roasted at 1450 °C for 4 h, as displayed in Fig. 7(e) and Fig. 7(f), numerous acicular patterns of grains and round fine particles gathered at the crystal boundary, indicating the CaO stabilizer precipitated in the fused zirconia material during the roasting process. Meanwhile, after roasting treatment, no cracks appeared on the sample surface, with only small pores existing, indicating the prepared CaO-doped partially stabilized zirconia (PSZ) met the basic requirements of high-performance products.

3.2.3 Characterization by EDAX

Fig. 8 illustrated the SEM pattern and EDAX spectra of zirconia material roasted at 1450 °C for 4 h, wherein Fig. 8(a) presented the SEM pattern and Fig. 8(b), (c), (d) and (e) displayed the EDAX spectra of spot 1, spot 2, spot 3, and spot 4, respectively, as marked in Fig. 8(a). As observed from Fig. 8, spot 1 and spot 2 were located at acicular pattern crystal

grains; hence, there was little difference for the elemental compositions. Wherein spot 1 was characterized with the 1.19% of CaO content and 83.94% of ZrO_2 content, and spot 2 was determined with the 1.19% of CaO content and 84.81% of ZrO_2 content. However, the CaO contents at spot 3 and spot 4 were much higher than that at spot 2, with 3.49% at spot 3 and 3.26% at spot 4, respectively; meanwhile, the ZrO_2 contents at spot 3 and spot 4 were lower than that at spot 2, with 83.79% at spot 3 and 80.21% at spot 4, respectively, which clearly indicated that the CaO stabilizer was precipitated at the grain boundary of the prepared partially stabilized zirconia (PSZ) during roasting process, representing the formation of CaO-doped partially stabilized zirconia (CaO-PSZ).

4 Conclusions

In this work, CaO-doped partially stabilized zirconia (CaO-PSZ) was optimizedly prepared from fused zirconia by conventional roasting. Results indicated roasting temperature and duration time showed the same influence trend for zirconia stability properties, representing by the stability rate conversely declined. XRD patterns revealed the phase transition mechanism of fused zirconia during roasting process, and the CaO-doped partially stabilized zirconia (CaO-PSZ) with mixed cubic ZrO_2 phase (c- ZrO_2) and monoclinic ZrO_2 phase (m- ZrO_2) was obtained after fused zirconia roasted at 1450 °C for 4 h, which was ascribed to the reversible martensitic transformation of fused zirconia with temperature change. SEM and EDAX analysis simultaneously indicated CaO stabilizer precipitated at the grain boundary, with acicular patterns of grains and round fine particles gathered at the crystal boundary. The work confirms effective preparation for CaO-doped partially stabilized

zirconia (CaO-PSZ) from fused zirconia, furthermore demanding further studies to explore the economic feasibility for commercial adoption.

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Appendix A. Supplementary data

Supplementary data to this work can be found in e-version of this paper online.

References

1. W.P. Halperin, Quantum size effects in metal particles, *Rev. Mod. Phys.* 58(3) (1986) 533-606. <https://doi.org/10.1103/RevModPhys.58.533>.
2. K. Kato, Tribology of advanced ceramics and hard coatings, *Key. Eng. Mat.* 264-268 (2004) 449-452. <https://doi.org/10.4028/www.scientific.net/KEM.264-268.449>.
3. P.M. Ajayan, T. Ichihashi, S. Iijima, Distribution of pentagons and shapes in carbon nano-tubes and nano-particles, *Chem. Phys. Lett.* 202(5) (1993) 384-388. [https://doi.org/10.1016/0009-2614\(93\)90057-8](https://doi.org/10.1016/0009-2614(93)90057-8).
4. S. Nath, N. Sinha, B. Basu, Microstructure, mechanical and tribological properties of microwave sintered calcia-doped zirconia for biomedical applications, *Ceram. Int.* 34(6) (2008) 1509-1520. <https://doi.org/10.1016/j.ceramint.2007.04.021>.
5. A.P. Singh, N. Kaur, A. Kumar, K.L. Singh, Preparation of fully cubic calcium-stabilized zirconia with 10 mol% calcium oxide dopant concentration by

- microwave processing, *J. Am. Ceram. Soc.* 90(3) (2007) 789-796.
<https://doi.org/10.1111/j.1551-2916.2006.01379.x>.
6. R.S. Lima, A. Kucuk, C.C. Berndt, Evaluation of microhardness and elastic modulus of thermally sprayed nanostructured zirconia coatings, *Surf. Coat. Tech.* 135(2) (2001) 166-172. [https://doi.org/10.1016/S0257-8972\(00\)00997-X](https://doi.org/10.1016/S0257-8972(00)00997-X).
 7. P.E. Reyes-Morel, I.W. Chen, Transformation plasticity of CeO₂-stabilized tetragonal zirconia polycrystals: I, stress assistance and autocatalysis, *J. Am. Ceram. Soc.* 71(5) (2010) 343-353. <https://doi.org/10.1111/j.1151-2916.1988.tb05052.x>.
 8. L.L. Fehrenbacher, L.A. Jacobson, Metallographic observation of the monoclinic-tetragonal phase transformation in ZrO₂, *J. Am. Ceram. Soc.* 2010, 48(3) (2010) 157-161. <https://doi.org/10.1111/j.1151-2916.1965.tb16054.x>.
 9. M.H. Bocanegra-Bernal, S.D. De La Torre, Phase transitions in zirconium dioxide and related materials for high performance engineering ceramics, *J. Mater. Sci.* 37(23) (2002) 4947-4971. <https://doi.org/10.1023/a:1021099308957>.
 10. R.H.J. Hannink, P.M. Kelly, B.C. Muddle, Transformation toughening in zirconia-containing ceramics, *J. Am. Ceram. Soc.* 83(3) (2002) 461-487.
<https://doi.org/10.1111/j.1151-2916.2000.tb01221.x>.
 11. R.G. Garvie, R.H. Hannink, R.T. Pascoe, Ceramic steel, *Nature.* 258(1975) 703-704.
<https://doi.org/10.1038/258703a0>.
 12. B.T. Lin, M.D. Jean, J.H. Chou, Using response surface methodology for optimizing deposited partially stabilized zirconia in plasma spraying, *Appl. Surf. Sci.* 253 (2007) 3254-3262. <https://doi.org/10.1016/j.apsusc.2006.07.021>.
 13. A. Bogicevic, C. Wolverton, G.M. Crosbie, E. Stechelet, Defect ordering in aliovalently doped cubic zirconia from first principles, *Phys. Rev. B.* 2001, 64(1) (2001) 167-173.
<https://doi.org/10.1103/PhysRevB.64.014106>.

14. S.H. Guo, G. Chen, J.H. Peng, J. Chen, J.L. Mao, D.B. Li, L.J. Liu, Preparation of partially stabilized zirconia from fused zirconia using roasting, *J. Alloy. Compd.* 506 (1) (2010) L5-L7. <https://doi.org/10.1016/j.jallcom.2010.06.156>.
15. R.C. Garvie, G.H.J. Hannink, C. Urbani, Fracture mechanics study of a transformation toughened zirconia alloy in the CaO-ZrO₂ system, *Ceram. Int.* 6(1) (1985) 19-24. [https://doi.org/10.1016/0390-5519\(80\)90028-9](https://doi.org/10.1016/0390-5519(80)90028-9).
16. R.C. Garvie, Structure and thermomechanical properties of partially stabilized zirconia in the CaO-ZrO₂ system, *J. Am. Ceram. Soc.* 55 (2010) 152-157. https://doi.org/10.1007/978-94-009-0741-6_15.
17. M.J. Readey, R.R. Lee, J.W. Halloran, A. Heueret, Processing and sintering of ultrafine MgO - ZrO₂ and (MgO, Y₂O₃) - ZrO₂ powders, *J. Am. Ceram. Soc.* 2010, 73(6) (2010) 1499-1503. <https://doi.org/10.1111/j.1151-2916.1990.tb09786.x>.
18. E. Tani, M. Yoshimura, S. Somiya, Revised phase diagram of the system ZrO₂ - CeO₂ below 1400 °C, *J. Am. Ceram. Soc.* 66(7) (2010) 506-510. <https://doi.org/10.1111/j.1151-2916.1983.tb10591.x>.
19. I. Cohen, B.E. Schaner, A metallographic and X-ray study of the UO₂-ZrO₂ system, *J. Nucl. Mater.* 9(1) (1963) 18-52. [https://doi.org/10.1016/0022-3115\(63\)90166-1](https://doi.org/10.1016/0022-3115(63)90166-1).
20. K. Chihwei, Y. Shen, F. Yen, H. Cheng, I. Hung, S. Wen, M. Wang, M. Stack, Phase transformation behavior of 3mol% yttria partially-stabilized ZrO₂ (3Y-PSZ) precursor powder by an isothermal method, *Ceram. Int.* 40 (2014) 3243-3251. <https://doi.org/10.1016/j.ceramint.2013.09.112>.
21. S. Fabris, A.T. Paxton, M.W. Finnis, A stabilization mechanism of zirconia based on oxygen vacancies only. *Acta. Mater.* 50(20) (2002) 5171-5178. [https://doi.org/10.1016/S1359-6454\(02\)00385-3](https://doi.org/10.1016/S1359-6454(02)00385-3).

22. A. Bogicevic, C. Wolverton, G.M. Crosbie, E.B. Stechel, Defect ordering in aliovalently doped cubic zirconia from first principles. *Phys. Rev. B.* 64(1) (2001) 014106.
<https://doi.org/10.1103/PhysRevB.64.014106>.
23. H. Wang, M.H. Wang, W.Y. Zhang, N. Zhao, W. Wei, Y.H. Sun, Synthesis of dimethyl carbonate from propylene carbonate and methanol using CaO-ZrO₂ solid solutions as highly stable catalysts, *Catal. Today.* 115(1) (2006) 107-110.
<https://doi.org/10.1016/j.cattod.2006.02.031>.
24. H. Wang, M.H. Wang, N. Zhao, W. Wei, Y. Sun, CaO-ZrO₂ solid solution: a highly stable catalyst for the synthesis of dimethyl carbonate from propylene carbonate and methanol, *Catal. Lett.* 105(3-4) (2005) 253-257.
<https://doi.org/10.1007/s10562-005-8699-0>.
25. Y. Murase, E. Kato, K. Daimon, Stability of ZrO₂ phases in ultrafine ZrO₂-Al₂O₃ mixtures, *J. Am. Ceram. Soc.* 69(2) (1986) 83-87.
<https://doi.org/10.1111/j.1151-2916.1986.tb04706.x>.
26. M.Y. Zhang, L. Gao, J.X. Kang, J. Pu, J.H. Peng, M. Omran, G. Chen, Stability optimisation of CaO-doped partially stabilised zirconia by microwave sintering, *Ceram. Int.* <https://doi.org/10.1016/j.ceramint.2019.08.024>.
27. X.Y. Lu, K.M. Liang, S.R. Gu, H.S. Fang, Y.K. Zheng, P. Liu, Influence of oxygen vacancy on phase structure and transformation of zirconia, *J. Chin. Ceram. Soc.* 6 (1996) 670-674. <https://doi.org/10.14062/j.issn.0454-5648.1996.06.011>.

Table captions

Table 1 Chemical compositions of fused zirconia raw material

Figure captions

Fig. 1 XRD pattern of fused zirconia raw material

Fig. 2 Effects of roasting temperatures on zirconia stability rate

Fig. 3 XRD patterns of zirconia material roasted at different roasting temperatures

Fig. 4 Effects of duration times on zirconia stability rate

Fig. 5 XRD patterns of zirconia material roasted at 1450 °C with different duration times

Fig. 6 XRD pattern of zirconia material roasted at 1450 °C for 4 h

Fig. 7 SEM patterns of zirconia material before and after roasting treatment; (a) raw material;

(b) 200 ×; (c) 1000 ×; (d) roasted sample; (e) 2000 ×; (f) 2000 ×

Fig. 8 SEM pattern and EDAX spectra of zirconia material roasted at 1450 °C for 4 h, (a)

SEM pattern; (b) EDAX of spot 1; (c) EDAX of spot 2; (d) EDAX of spot 3; (e) EDAX of spot 4

Table 1 Chemical compositions of fused zirconia raw material

Compositions	ZrO ₂	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃
Mass/W%	95.1	3.8	0.4	0.3	0.3	0.1

Fig. 1 XRD pattern of fused zirconia raw material.

Fig. 2 Effects of roasting temperatures on zirconia stability rate.

Fig. 3 XRD patterns of zirconia material roasted at different roasting temperatures.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: