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Effect of microwave sintering on the properties of copper oxide doped Y-TZP ceramics

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ABSTRACT

The effect of various amounts of copper oxide (CuO) up to 1 wt% on the densification behaviour and mechanical properties of 3 mol% yttria-tetragonal zirconia polycrystal (Y-TZP) were studied by using microwave (MW) sintering method. The MW sintering was performed at temperatures between 1100 °C and 1400 °C, with a heating rate of 30 °C/min. and holding time of 5 min. The beneficial effect of MW in enhancing densification was also compared for the undoped and 0.2 wt% CuO-doped Y-TZP when subjected to conventional sintering (CS) method. The results showed that significant enhancement in the relative density and Vickers hardness were observed for the undoped Y-TZP when MW-sintered between 1100 °C and 1250 °C. It was revealed that the 0.2 wt% CuO-doped Y-TZP and MW sintered at 1250–1300 °C could attain ≥ 99.8% of theoretical density, Vickers hardness of about 14.4 GPa, fracture toughness of 7.8 MPam$^{1/2}$ and exhibited fine equiaxed tetragonal grain size of below 0.25 μm. In contrast, the addition of 1 wt% CuO was detrimental and the samples exhibited about 50% monoclinic phase upon sintering coupled with poor bulk density and mechanical properties. The study also revealed that the addition of 0.2 wt% CuO and subjected to conventional sintering produced similar densification as that obtained for microwave sintering, thus indicating that the dopant played a more significant role than the sintering method.

1. Introduction

Yttria tetragonal zirconia polycrystals or Y-TZPs are well recognized as one of the promising ceramics, owing to its low thermal conductivity, good thermal expansion coefficient and excellent mechanical properties such as a high fracture toughness of 5–8 MPam$^{1/2}$ and Vickers hardness of more than 12 GPa [1,2]. This good mechanical behaviour makes Y-TZP useful for various engineering applications including cutting tools [3], thermal barrier coatings [4] and electrolyte in solid oxide fuel cells [5]. Besides, Y-TZP also have good biocompatibility and aesthetic properties [6], which makes them popular for dental application such as dental prostheses and ceramic crown [7].

Numerous researchers have reported that doping Y-TZP with transition metal oxides such as copper oxide (CuO) and manganese oxide (MnO_2) were beneficial in aiding sintering at lower sintering temperature through a mechanism associated with a liquid phase sintering [8–12]. However, the improved densification was accompanied by grain coarsening when sintered by the conventional sintering (CS) method mainly due to the long holding time during sintering (2 h or longer) [10,13]. In contrast, a fast firing technique based on microwave (MW) sintering has been employed to consolidate the zirconia at a much shorter period, resulting in a highly dense body and fine grain microstructure when compared to the CS method [14,15]. Unlike conventional sintering where the mode of heat transfer is predominantly by conduction, microwave heating uses electromagnetic radiation to induce intermolecular friction to take place within the body

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resulting in volumetric heating of the body [16].

The ability of material to absorb microwave would, however depend on its dielectric properties, i.e. dielectric constant (ε') and dielectric loss (ε''). The ratio of dielectric loss to dielectric constant is defined as permittivity or loss tangent (tan δ). When the tan $\delta \leq 0.01$, microwave can pass through without significant absorption and this material is categorized as microwave transparent [16,17]. The material is defined as microwave absorber when the tan $\delta \geq 0.1$ and will absorb microwave resulting in volumetric heating. Y-TZP ceramic behaves as microwave transparent at a low temperature of 200 °C and changes to microwave absorber at temperature ≥ 600 °C [16]. Therefore, it is common to use a susceptor (i.e. MW absorber) which has a high dielectric loss at low temperatures such as silicon carbide (SiC), placed around the green body. During microwave heating, the SiC will absorb microwave and becomes red hot. The heat generated is transferred, mainly through conduction to the Y-TZP sample. Once the body temperature reached about 600 °C, the zirconia couples MW and the temperature will start to increase rapidly.

Based on the literature, CuO possessed better dielectric properties than zirconia and it is anticipated that CuO would be able to couple microwave faster than zirconia [16]. Thus, it is envisaged that the incorporation of CuO as dopant in Y-TZPs could improve the dielectric properties of the ceramic and promote sintering. Therefore, the main aim of this work was to investigate the effect of microwave sintering at various temperatures on the densification and properties of CuO-doped Y-TZP.

2. Materials and methods

The as-received 3 mol% Y-TZP powder (Kyoritsu Corp. Japan) was employed in this research as the main powder. Varying amounts of high purity copper oxide manufactured by Sigma-Aldrich, USA (0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 1 wt%) were investigated. Mixing was accomplished by attrition milling (Union Process, USA) at a speed of 500 rpm for 30 min. Zirconia balls with diameter of 3 mm were used as the milling media while ethanol as the mixing medium. The slurries were then oven dried at 60 °C overnight. The dried cake was crushed and sieved to obtain the CuO-doped Y-TZP powders. Discs samples, each weighing 2.5 g were uniaxially pressed at 3 MPa and followed by cold isostatic pressing at 200 MPa for 1 min.

Microwave sintering of the green samples was performed at 2.45 GHz using a 6 kW multi-mode microwave furnace. The heating rate was kept at 30 °C/min with a holding time of 5 min before cooling to room temperature. The samples were sintered at various temperatures i.e. 1100 °C, 1200 °C, 1250 °C, 1300 °C and 1400 °C. These samples were arranged with two discs samples stacked up, placed at the center of the enclosed alumina fiberboard box and flanked with silicon carbide as the susceptor. For comparison purpose, selective samples were conventional sintered in a box furnace at the same temperatures using a ramp rate of 10 °C/min for 5 min.

Phase identification by X-ray diffraction (XRD) (EMPYREAN, PANalytical, Netherlands) was carried out at room temperature using Cu-K as the radiation source, operating at 35 kV/15 mA, at a step scan of 0.02° and a scan speed of 0.5°/min. over the 2θ range of 27–36° which covers the monoclinic (m) and tetragonal/cubic (t + c) related {111} peaks. The fraction of monoclinic phase in the as-sintered body was evaluated using the relationship developed by Toraya et al. [18]. The bulk density of sintered samples was determined using water immersion method based on Archimedes principle. Relative density was calculated by taking the theoretical density of Y-TZP as 6.09 g/cm^3. The sintered discs were ground successively using silicon carbide papers of grades 120 (coarse), 240, 600, 800 and 1200 (fine). The ground samples were then polished using 6 μm and 1 μm diamond paste to obtain an optical reflective surface. The fracture toughness (K_{Ic}) and hardness of the polished samples were measured using the Vickers indention method (Mitutoyo AVK-C2, USA). In all cases, the indention load was kept constant at 98.1 N with loading time of 10 s the values of K_{Ic} was computed using the equation derived by Shetty and Wright [19]. Six measurements were recorded on each sample and the average value taken.

Microstructure characterization was carried out using a Field Emission Scanning Electron Microscope (FESEM, Philips). Prior to imaging, the samples were thermally etched at a temperature of 50 °C below the sintering temperature for 30 min. The grain size of the sintered samples was measured by the line intercept method [20].

Table 1
XRD analysis of the MW-sintered samples showing the amount of tetragonal phase present. The monoclinic phase content is given in parenthesis if present.

CuO content (wt%)	Sintering Temperature (°C)				
	1100	1200	1250	1300	1400
0 (undoped)	100	100	100	100	100
0.05	100	100	100	100	100
0.1	100	100	100	100	100
0.2	100	100	100	100	100
0.3	100	100	100	100	100
0.4	100	100	100	100	100
0.5	79.8 (21.2)	100	100	100	100
1	49.3 (50.7)	48.1 (51.9)	51.8 (48.2)	51.6 (48.4)	64.8 (35.2)

3. Results and discussion

3.1. Tetragonal phase stability and densification

The tetragonal and monoclinic phase content of the MW-sintered samples as determined from the XRD analysis are given in Table 1. The results showed that the addition of CuO up to 0.4 wt% did not disrupt the tetragonal phase regardless of sintering temperature. However, for the 0.5 wt% CuO doping, about 21.2% monoclinic phase was measured for sample sintered at 1100 °C but not at higher temperatures. The addition of 1 wt% CuO was found to be detrimental to the tetragonal phase stability of the zirconia and all samples underwent the phase transformation upon cooling from sintering.

It is unclear at this stage on the monoclinic phase development observed for the 0.5 wt% CuO-doped Y-TZP when MW-sintered at 1100 °C and not at higher temperatures. In order to exclude the effect of microwave on the phase transformation during sintering, some of the 0.5 wt% CuO-doped green samples were sintered at various temperatures by the conventional sintering method. The comparison of the XRD traces for both sintering methods performed at 1100 °C is shown in Fig. 1. Surprisingly, a similar trend on the monoclinic phase development was also observed for the conventional sintered samples i.e. only monoclinic phase was detected at 1100 °C and not at other sintering temperatures. The measured monoclinic content for the CS sample was about 32.7% compared to 21.2% for the MW-sintered Y-TZP. Hence, these results show that the sintering method was not responsible for the spontaneous phase transformation in these samples but rather it is believed that the destabilization effect of the tetragonal phase could be associated with the interaction between CuO with either yttria or zirconia during sintering.

The effect of CuO and sintering temperatures on the densification of Y-TZP are shown in Fig. 2. The beneficial effect of CuO in aiding densification of Y-TZP has been revealed. In general, the addition of up to 0.4 wt% CuO-doped samples exhibited higher relative density than the undoped ceramic regardless of sintering temperature. The additions of 0.2, 0.3 and 0.4 wt% CuO were beneficial in promoting sintering of Y-TZP when sintered at lower temperatures, below 1300 °C. In contrast, the undoped ceramic exhibited a low relative density of about 77.5% when compared to 95% for the 0.2 wt% CuO-doped Y-TZP when