Densification and mechanical behaviour of zirconia containing flyash as dopant

R Singh1,2*, S R Ya’akub1, A D A Hamid1, Z Ibrahim1, and M Y Ali1
1 Mechanical Engineering Programme Area, Faculty of Engineering, Universiti Teknologi Brunei, Tungku Highway, Gadong BE1410, Brunei Darussalam
2 University of Malaya, 50603 Kuala Lumpur, Malaysia

* Email: ramesh.singh@utb.edu.bn

Abstract. The densification and mechanical behaviour of tetragonal zirconia doped with up to 2 wt% flyash as dopant were studied. In this work, the dopant was blended with commercial 3 mol% yttria-stabilised zirconia powders by attrition milling. Sintering was accomplished by firing the green bodies at various temperatures ranging from 1250 ºC to 1500 ºC under atmospheric conditions. Sintered bodies were evaluated for bulk density, phase retention, elastic modulus, Vickers hardness and fracture toughness. An improvement in the zirconia properties in terms of bulk density, Vickers hardness and matrix stiffness were evident at low sintering temperatures for samples containing up to 0.5 wt% flyash. In contrast, the fracture toughness and tetragonal phase stability of the zirconia was not influenced by the dopant and sintering temperature. The addition of 1 wt% and 2 wt% flyash, however, were not effective in enhancing the properties of the sintered zirconia. This study also found that the addition of flyash as dopant was beneficial in suppressing the low-temperature degradation kinetics of tetragonal zirconia in steam environment.

Keywords: flyash-doped zirconia, sintering behaviour, mechanical properties, low-temperature degradation

1. Introduction
Zirconia-based ceramics, in particular when stabilized with 2.5 to 3 mol% yttria, results in the retention of a fully tetragonal structure that exhibits the highest mechanical strength and fracture toughness, suitable for many industrial applications [1-3]. This improvement in the mechanical behaviour can be attributed to a self-healing mechanism subsequently known as transformation toughening. According to this mechanism, the stress induced by a propagating crack will be absorbed by the tetragonal grains and transformed to the monoclinic symmetry with the accompanying volume expansion which occurs ahead of a propagating crack front [2-5]. The efficacy of the transformation toughening, however is dependent on several factors including yttria content and distribution, tetragonal grain size and grain boundary modification due to impurity present during powder manufacturing or added as a sintering additives to lower the densification temperature [6-10].

One of the limitations of tetragonal zirconia is the undesirable phase transformation resulting in formation of micro-cracks and property deterioration when the ceramic is exposed in steam.
environment, a phenomenon known as hydrothermal ageing or low-temperature degradation (LTD) [8, 11-13]. Many researchers have investigated this LTD phenomenon plaguing tetragonal zirconia and the general understanding is that the severity of LTD is predominantly governed by the tetragonal grain size after sintering [14, 15] and so there is a need to limit grain coarsening during powder sintering.

There are many methods that have been proposed to control grain growth but the most cost-effective and yet simple method has been to lower the densification temperature through the use of low-melting dopants or sintering additives. There were many dopants that have been explored by many researchers including that of MnO2, CuO, TiO2, SiO2, Al2O3, GeO2, CeO2, etc. [16-18]. For example, Ramesh et al. [13, 14, 19, 20] have reported that the incorporation of low amounts of CuO and MnO2 were effective in aiding low-temperature sintering, enhancing mechanical properties and suppressing LTD in tetragonal zirconia.

In the present work, the addition of up to 2 wt% flyash as dopant in a commercial 3 mol% yttria-stabilised zirconia was investigated.

2. Methods and Materials
A commercially available 3 mol% yttria-stabilised zirconia manufactured by Kyoritsu, Japan was used in the present work. The flyash dopant, varying up to 2 wt%, obtained from a local power station was refined by ball milling in ethanol for 2 h. The wet slurry was dried in an oven at 60 °C for 24 h and finally sieved to obtain fine powder. The chemical analysis by x-ray florescence performed on the as-refined flyash indicated that the powder comprised 60% silica, 15% alumina and 12% iron oxide as the major impurities. The balance 13% represents some minor impurities such as calcium and magnesium oxides.

In a typical doping, the flyash-doped zirconia (FZ) powders was prepared by blending both powders via attrition milling using ethanol as the mixing medium and zirconia beads (2 mm in diameter) as the milling medium. The rotation speed was kept constant at about 500 rpm. After the milling, the wet slurry was filtered, dried in an oven at 60 °C for 24 h and sieved to obtain fine powder. Two different shape samples were prepared, i.e. rectangular bar for elastic modulus measurement and disc (20 mm diameter) for other tests, by uniaxial compaction at 10 kN to form green samples. Prior to sintering, the samples were subjected to cold isostatic pressing at 200 MPa. Pressureless sintering in air was accomplished using a box furnace. The samples were sintered over the range of 1250 °C to 1500 °C and a holding time of 2 h was used.

The phases present in the powders and sintered samples were determined by x-ray diffraction (XRD) performed under normal atmospheric conditions using Cu-Kα as the radiation source. The tetragonal and monoclinic phases were determined using the method proposed by Toraya et al. [21]. The sintered density of the samples was obtained by water immersion method based on Archimedes’ principle and the relative density was calculated by taking the theoretical density of tetragonal zirconia as 6.1 g/cm³. The Vickers indentation method was used to determine the hardness and fracture toughness of sintered bodies. An indentation load of 10 kg and a loading time of 10 s were employed for all samples. The Niihara et al. [22] equation was used to calculate the fracture toughness of the sample. The sonic resonance technique was used to determine the elastic modulus of the sintered bar samples in accordance to ASTM standard [23]. Finally, the LTD resistance of the FZ samples were evaluated by measuring the monoclinic phase present after exposure in superheated steam at 180°C/10 bar for periods ranging up to 50 h.

3. Results and discussion
The XRD analysis of the zirconia powders indicated that the monoclinic phase content did not change significantly with the introduction of flyash as dopant. In all cases, the monoclinic phase content varied between 17% (undoped) to about 19% (FZ powders). Similarly, the XRD patterns of all sintered samples indicated the retention of a fully tetragonal structure regardless of dopant amounts and sintering temperatures.

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The effect of sintering temperatures on the relative density of the zirconia are shown in Figure 1. In general, a similar density trend was observed for all samples i.e. the density increases rapidly with increasing sintering temperature up to 1350 °C for the FZ samples and 1400 °C for the undoped sample before remaining almost constant (for FZ up to 0.5 wt% and undoped samples) for sintering temperature up to 1500 °C. In contrast, the relative density of the 1 wt% and 2 wt% FZ started to declined when sintered above 1350 °C. Nevertheless, Figure 1 clearly shows the beneficial effect of flyash (up to 0.5 wt%) in promoting densification at low temperatures of 1250 °C, 1300 °C and 1350 °C. For instance, the relative density of the ceramic sintered at 1250 °C improved by about 5% with the additions up to 0.3 wt% flyash. The dopant somehow had negligible effect on the densification for samples sintered above 1350 °C. All the samples with the exception of the 1 wt% and 2 wt% FZ exhibited a relative density of > 99% when sintered > 1350 °C.

The variation in elastic modulus for the undoped and FZ samples with sintering temperature as shown in Figure 2 is in good agreement with the densification trend. Typically, all samples exhibited modulus values above 200 GPa when sintered at and above 1350 °C as depicted in Figure 2. The lower elastic modulus exhibited by the 1 wt% and 2 wt% FZ samples correlated well with the lower relative density of the samples.

In fact, the analysis between the relative density and the elastic modulus of the sintered samples revealed that a linear relationship exists between both properties as shown in Figure 3. It was found that the matrix stiffness of the sintered body increased linearly up to a maximum of about 200 GPa with increasing relative density up to about 98-99% of theoretical density, regardless of dopant amounts. A similar behaviour was also reported for hydroxyapatite bioceramic where the researchers noted that the stiffness of the sintered ceramics was influenced by the bulk density and not significantly affected by grain coarsening [24, 25].
Figure 2. Effect of sintering temperature on the elastic modulus of zirconias.

Figure 3. A linear relationship observed between relative density and elastic modulus of tetragonal zirconia.

The effect of dopant addition and sintering temperature on the Vickers hardness and fracture toughness of zirconia are shown in Figure 4. It has been found that regardless of dopant concentration, the sintering temperature has almost negligible effect on the fracture toughness of the tetragonal
zirconia. However, a slightly lower toughness was noted at all sintering temperatures for the 2 wt% flyash-doped samples. On the contrary, the Vickers hardness was found to vary significantly with increasing temperatures. As can be noted from Figure 4, the hardness increases rapidly from about 9.9 GPa at 1250°C and reached a maximum of about 13.5 GPa at 1350°C before decreasing slightly with increasing temperature to 1500°C.

![Figure 4](image_url)

**Figure 4.** The effect of sintering temperature and flyash doping on the Vickers hardness and fracture toughness of zirconia.

The effect of superheated steam on the tetragonal phase stability of the zirconia as a function of flyash addition for samples sintered at 1350°C is shown in Figure 5. The beneficial effect of flyash in slowing the LTD kinetics in tetragonal zirconia has been revealed, particularly for the 0.5-2 wt% flyash doping. The results showed that the undoped zirconia undergo rapid phase transformation; attained about 65% and 90% monoclinic content after exposure in steam for 1 h and 3 h, respectively. On the other hand, the improved in LTD resistance for the 1 wt% and 2 wt% flyash-doped samples could be attributed to the lower matrix stiffness and lower relative density of the sintered body. It is unclear at this stage of this behaviour and more work is required to elucidate the actual role of the flyash in suppressing the LTD in zirconia.
Figure 5. Monoclinic phase development with ageing time for zirconia exposed in steam environment for samples sintered at 1350 °C.

4. Conclusions
In the present work, the sintering and mechanical behaviour of flyash-doped yttria-stabilised zirconia was investigated. The results showed the addition of flyash up to 0.5 wt% was beneficial in aiding low-temperature sintering (1250-1350 °C), resulting in enhanced relative density, Vickers hardness and elastic modulus. The fracture toughness, however, was not influenced by the sintering temperatures and dopant addition. The addition of higher content of flyash i.e. 1 wt% and 2 wt% was not effective in aiding sintering of zirconia although these samples exhibited improved LTD resistance when compared to other samples when exposed to superheated steam.

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