Original Article

Advanced 3Y-TZP bioceramic doped with Al₂O₃ and MnO₂ particles potentially for biomedical applications: study on mechanical and degradation properties

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ARTICLE INFO

Article history:
Received 22 February 2017
Accepted 25 May 2017
Available online 28 September 2017

Keywords:
Bioceramic
3Y-TZP
Mechanical properties
Degradation
Ringer's solution
Hip implant

ABSTRACT

The effectiveness of Al₂O₃ and MnO₂ in enhancing mechanical properties and retarding degradation of 3 mol% yttria stabilized tetragonal zirconia polycrystalline (3Y-TZP) ceramic samples was evaluated by pressureless sintering at temperatures ranging from 1250 °C to 1550 °C with standard holding time of 2 h. It was observed that the inclusion of Al₂O₃ and MnO₂ into 3Y-TZP was beneficial for the improvement of mechanical properties and ageing resistance. The optimum amounts of dopants were determined to be of 0.6 wt% Al₂O₃ and 0.4 wt% MnO₂. Microstructural investigation revealed that at the same temperature, the tetragonal grain size was not influenced by the increase of dopant levels. With optimum dopants the 3Y-TZP ceramic (density 6.1 g/cm³) samples demonstrated the Vickers hardness of 11.6 GPa, fracture toughness, $K_{IC}$ of 9.8 MPa m$^{1/2}$, flexural strength of 900 MPa and Young's modulus of 210 GPa. Furthermore, the efficacy of the dopants (MnO₂ and Al₂O₃) in retarding low-temperature degradation of 3Y-TZP ceramic during exposure in Ringer's solution at 37 °C was also evaluated. Overall, the degradation rate and weight loss of 0.6 wt% Al₂O₃ and 0.4 wt% MnO₂ ceramic samples were 0.66% in 8 weeks as compared to the undoped samples. The 3Y-TZP bioceramic doped with Al₂O₃ and MnO₂ could be a potential candidate material for biomedical applications (e.g. hip implants) due to its improved mechanical properties and superior ageing resistance.

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https://doi.org/10.1016/j.jmrt.2017.05.015
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1. Introduction

In the present advanced technological era, ceramic materials (e.g. hydroxyapatite, porcelain, zirconia, etc.) hold great potential for biomedical applications (e.g. load-bearing implants, hip implant, dental applications, regeneration of hard tissues, etc.) [1–4]. Excellent combination of mechanical properties (e.g. higher range of compressive strength, wear resistance, fracture resistance) and biocompatibility makes the yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) ceramics a potential candidate for implant devices including orthopaedic prostheses [4–6]. Despite the excellent properties of zirconia ceramic, some compositions, such as 3Y-TZP, present a major drawback in moist atmosphere, since they undergo low-temperature degradation [7–9]. This is an ageing phenomenon that causes loss of strength and generation of micro-cracking in the presence of water. It consists of a slow transformation of metastable t zirconia to the m phase (without any applied stress) in an important temperature range, typically from room temperature up to around 400 °C, thus including the temperature used for steam sterilization (~140 °C) and the human body temperature (37 °C) [7,8]. Although low temperature degradation has been studied for more than 20 years, the precise mechanism by which moisture catalyses the phase transformation is still not fully clarified [7,8]. This phenomenon also restricts its wider applications as biomaterials [8]. The water present in the atmosphere as liquid or vapour plays an important role in the degradation of properties which is triggered by the undesirable transformation of metastable tetragonal phase to stable monoclinic polymorph [9].

The low temperature degradation (LTD) initially occurs at intergranular grains, where water molecules absorb into zirconia grains by filling oxygen vacancies, and later spread over the surface increasing its roughness [10]. Afterwards, LTD proceeds into the bulk material [11] and jeopardizes the strength, fracture toughness, density, etc. of Y-TZP [12–14]. Steam autoclave treatments at increased temperatures (120–140 °C) have been used to effectively induce LTD, since phase transformation of Y-TZP occurs in the presence of water or steam [15–20]. It was also reported that a LTD simulation method using steam autoclave displayed a strain-induced transformation (t to m) [21].

A small amount of sintering additives can promote densification, controlling the microstructure that can halt the progression of the above described degradation phenomenon, thus, helps to improve the mechanical properties of the sintered material [22]. Anastasia et al. [23] reported that combined doping of alumina and silica did not have much effect on mechanical properties of 3Y-TZP but significantly reduced the hydrothermal degradation.

Similar investigations were made on dental ceramics and it was reported that the contribution of co-dopants, especially oxide ceramics in suppressing the hydrothermal degradation phenomenon was quite significant [18,24–29]. The Ce-TZP/Al showed significantly higher mechanical strength than Y-TZP [30–33] and significantly halted the progression of hydrothermal degradation in oral environment [18]. Furthermore, this invention allowed post-sintered machining, which involved robust milling condition. Producing high accuracy part no further treatment is required. In other words, this new system has potential to solve the clinical problems of Y-TZP, because it allows an optimal framework design with supporting form and precise fitting of the framework to the abutment teeth. Few clinical studies of fixed prostheses with Ce-TZP/A frameworks are available to validate these promising laboratory findings. Tekeli et al. [34,35] reported that the addition of yttria, Y₂O₃, can control the retention of the tetragonal phase transformation that occurs in zirconia. Y₂O₃ has the potential to yield an extremely fine grained microstructure known as yttria-tetragonal zirconia polycrystal (Y-TZP). Borik et al. [36] supported this by finding that the increment of Y₂O₃ is able to retain the tetragonal phase; however, a noticeable decrease in fracture toughness is caused due to the decrease in volume fraction of transformed tetragonal phase. Akmar et al. [37] conducted an experiment using various percentages of CeO₂ (0–15 wt%) considerable evidence stating that the grain size and porosity or densities have significant effects on the properties of the material. Ramesh et al. [38] investigated the effect of the addition of manganese oxide, MnO₂ on the mechanical properties and low temperature degradation of Y-TZP ceramics. In this research, small amounts of MnO₂ (0–1.0 wt%) were added to Y-TZP and it was found that the addition of 0.5 wt% MnO₂ significantly improved the mechanical properties of Y-TZP. Similar work conducted by several authors, [39–41] also proved that the optimum dopant percentage used to obtain optimized mechanical properties was 1 wt% and, therefore, having that theory in mind, the current composition of Al₂O₃ and MnO₂ dopants summed up to 1 wt%.

This work aimed at studying the influence of adding small amounts of Al₂O₃ and MnO₂ (up to 1 wt%) to 3Y-TZP ceramic and sintered at different temperatures. The effects of these dopants in enhancing mechanical properties, and retarding the degradation of 3Y-TZP were evaluated against undoped 3Y-TZP samples with varying amounts of Al₂O₃ and MnO₂ dopants.

2. Materials and methods

2.1. Processing/preparation of doped samples

3 mol% yttria-stabilized zirconia (Nanostructured & Amorphous Materials), 99.9% purity, manganese oxide, MnO₂ (Sigma–Aldrich, USA) and aluminium oxide, Al₂O₃ (Sigma–Aldrich, USA) powders were used in this study. Various weight percentages of MnO₂ and Al₂O₃ as seen in Table 1 were mixed with 3Y-TZP by wet milling in ethanol in an ultrasonic machine. Then the mixture was milled for 1 h, after which the slurry was dried at 60 °C in an oven for 24 h. The dried mixture was then sieved through a stainless steel sieve of 212 μm mesh to obtain a ready-to-press Al₂O₃-MnO₂-doped 3Y-TZP powder. The mixed powder was pressed within a hardened steel circular (20 mm diameter) and rectangular (50 mm × 10 mm × 4 mm) mold at a hydraulic pressure of 0.3 MPa. The samples were subsequently subjected to cold isostatic press (CIP) at a pressure of 200 MPa with a holding time of 5 min. The CIP was followed by the consolidation of the samples by ambient pressure sintering performed in air.
using a heating furnace (ModuTemp) at various temperatures ranging from 1250 °C to 1550 °C. For all samples the ramp rate was set at 10 °C/min for both heating and cooling, and holding time was 2 h prior to cooling to ambient temperature. Afterward, all samples were polished using SiC abrasive papers (120, 240, 600, 800 grades) gradually from coarse to fine, followed by a final stage of polishing with a diamond to obtain an optically reflective surface.

### 2.2. Characterizations

The as-sintered 3Y-TZP samples were used to measure density via Archimedes’ method using a standard (Mettler Toledo Balance AG204) densimeter. The distilled water was used as an immersion medium for this density measurement. Fracture toughness (KIC) and Vickers hardness measurements (Future Tech., Japan) were made on polished samples using the Vickers indentation method. The indentation load was kept constant at 98.1 N and a loading time of 10 s was employed. The values of KIC were computed using the equation derived by Niihara et al. [42]. The flexural strength was determined using rectangular bar samples in order to determine flexural stress at maximum flexural load. This flexural test method was similar to the transverse bending test (3-point technique) following the ASTM-C1161-13 standard. The Young’s modulus of the rectangular samples was measured by sonic resonance instrument (Grindosonic; MK5, Belgium). The instrument permits determination of the resonant frequency of a specimen by monitoring and estimating the vibrational harmonics of the sample by using a transducer; tapping was used to induce physical vibrations in the sample. The modulus of elasticity is calculated using the experimentally determined resonant frequencies, according to standard test method.

The phase analysis of 3Y-TZP was carried out using X-ray diffraction (XRD). A diffractometer with Cu-Kα radiation was used to monitor the development of the monoclinic phase resulting from ageing induced phase transformation of various samples. The Cu-Kα radiation used operates at 35 kV/15 mA in step mode with a 0.02° 2 step and a step scan of 0.5 /min over the 2 range 27° to 36°, which covers the (m) and (e) + (e) related (111) peaks.

\[ V_m = \frac{1.311X_m}{1 + 0.311X_m} \]  

where \( V_m \) is the volume fraction of monoclinic zirconia and \( X_m \) is the integrated intensity ratio, defined as

\[ X_m = \frac{i(111)_m + i(111)_m}{i(111)_m + i(111)_m + i(111)_m} \]  

where \( i \) is the peak intensity and the subscripts \( m \) and \( t \) represent the monoclinic and tetragonal phases respectively.

The microstructural characterization was carried out by SEM (scanning electron microscopy) on polished and platinum coated samples. To determine the average grain size, the average grain intercept method is used. This method involves drawing several lines in the SEM image and the number of intersections was counted in accordance to an international standard test method for intercept counting [43]. The average grain size, \( D \) can be determined by a simple equation as below:

\[ \text{Average intercept number between a series of random lines drawn in the micrograph} = \frac{\text{Magnification of the SEM micrograph}}{\text{Distance between two parallel lines}} \]

Using the RSM method as statistical tool, the optimization of input variables (weight percentage of Al2O3, weight percentage of MnO2 and sintering temperature) with respect to densification, hardness, Young's modulus, flexural strength and fracture toughness were conducted. It was identified that the optimized, best performing sample compositions, obtained form this optimization techniques was 0.6 wt% MnO2/0.4 wt% Al2O3 and 0.5 wt% MnO2/0.5 wt% Al2O3 composition. The optimized composition was further used for hydrothermal degradation investigation.

Sintered and polished disc samples were investigated for hydrothermal degradation by immersing them into Ringer's solution at room temperature for a maximum period of 8 weeks. The samples were placed inside a vessel filled with 5 ml of Ringer’s solution, and incubated in a vacuum chamber at 37 °C. The samples were taken out at 5 intervals (i.e. week 1, week 2, week 4, week 6, and week 8) and the ageing-induced phase transformation from tetragonal to monoclinic was observed using SEM. Besides, the effects of ageing on the physical and mechanical properties were also evaluated by comparing the values obtained from aged and regular samples via the difference in weight at the selected time intervals.

### 3. Results and discussion

#### 3.1. Bulk density

The variation of bulk density of 3Y-TZP doped with various amounts of MnO2 and Al2O3 sintered at temperatures from 1250 °C to 1550 °C is presented in Fig. 1. All the 3Y-TZP compositions including the undoped samples demonstrated a common densification trend; a steady fall in density from 1250 °C to 1350 °C before fluctuating, in the range of 5.75–5.98 g/cm³ for temperatures up to 1550 °C. Both 0.6 wt% MnO2/0.4 wt% Al2O3 and 0.5 wt% MnO2/0.5 wt% Al2O3 samples achieved the highest density, 5.99 g/cm³ and 5.95 g/cm³ respectively, approximately 98% of the theoretical density (6.1 g/cm³). The decrease in bulk density above 1450 °C could be attributed to the formation of grain growth.

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**Table 1 - Compositions of based material and dopants powder.**

<table>
<thead>
<tr>
<th>3Y-TZP</th>
<th>Al2O3</th>
<th>MnO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>99 wt%</td>
<td>0.2 wt%</td>
<td>0.8 wt%</td>
</tr>
<tr>
<td>99 wt%</td>
<td>0.3 wt%</td>
<td>0.7 wt%</td>
</tr>
<tr>
<td>99 wt%</td>
<td>0.4 wt%</td>
<td>0.6 wt%</td>
</tr>
<tr>
<td>99 wt%</td>
<td>0.5 wt%</td>
<td>0.5 wt%</td>
</tr>
<tr>
<td>99 wt%</td>
<td>0.6 wt%</td>
<td>0.4 wt%</td>
</tr>
<tr>
<td>99 wt%</td>
<td>0.7 wt%</td>
<td>0.3 wt%</td>
</tr>
<tr>
<td>99 wt%</td>
<td>0.8 wt%</td>
<td>0.2 wt%</td>
</tr>
</tbody>
</table>
This was evident for the 0.6 wt% Al₂O₃/0.4 wt% MnO₂ when an average pore size of 1.2 μm was measured initially at a sintering temperature of 1250 °C and the same sample evidently displayed an increase in pore size to an average value of 1.5 μm when the sample was sintered at a sintering temperature of 1450 °C as depicted in Figs. 2 and 3. This clearly indicates the presence of grain growth in the sample. Inclusions of manganese oxide and aluminum oxide were found to be more effective at lower sintering temperatures of 1250–1350 °C as these samples became denser as compared to the undoped 3Y-TZP samples. These results agreed well with the findings of some other similar works [44–46].

Manganese oxide in the form of MnO₂ has been shown to be effective in promoting densification of Y-TZP. Zhou et al. [47] investigated the sinterability of 8 wt% yttria-stabilized-zirconia (8YSZ) containing different weight ratios of MnO₂ as a sintering aid. The results showed that the addition of MnO₂ was effective in aiding densification and the MnO₂-doped samples produced better results than undoped samples.

### 3.2. Vickers hardness and fracture toughness

The effects of MnO₂ and Al₂O₃ additions on the Vickers hardness of 3Y-TZP sintered from 1250 °C to 1550 °C are demonstrated in Fig. 4. The Vickers hardness values of 3Y-TZP with various amounts of MnO₂ and Al₂O₃ varied in a similar manner to that of bulk density varied with sintering temperature. The results depicted that the addition of these dopants was more effective in improving the hardness of zirconia sintered at lower temperatures (below 1350 °C). The hardness value of the undoped 3Y-TZP was found to be the lowest (8.5 GPa) at sintering temperature of 1250 °C and increased rapidly to 11.2 GPa at 1400 °C before reaching a maximum of 11.6 GPa at 1450 °C. The hardness of the samples, however, decreased slightly down to 10.9 GPa with further increase of sintering temperature at to 1450 °C. Hardness is strongly dependent on bulk density, and since the bulk density showed a decrease above 1450 °C, there was a decrease for the hardness as well. Besides that, can be associated with the reduction of tetragonal phase content and an increase in the
cubic phase formation in the zirconia matrix with increasing temperature. This result was in agreement with the work of Ramesh et al. [38].

A similar trend was observed for the fracture toughness with respect to sintering temperature as shown in Fig. 5. Additions of up to 0.3 wt% Al₂O₃/0.7 wt% MnO₂ had negligible effect on the fracture toughness of 3Y-TZP for the entire sintering temperatures investigated. The fracture toughness of all these samples was found to fluctuate between 4 MPa m¹/² and 4.5 MPa m¹/². The fact that the fracture toughness did not change significantly indicated that the additions of MnO₂ and Al₂O₃ below 0.3 wt% did not affect the resistance of 3Y-TZP to propagate crack. Besides that, Al₂O₃ and MnO₂ additions of 0.4 wt% Al₂O₃/0.6 wt% MnO₂ and 0.8 wt% Al₂O₃/0.2 wt% MnO₂ also showed similar trend at sintering temperatures up to 1550 °C. At sintering temperature above 1350 °C, the fracture toughness (Kₑ) of all doped Y-TZP samples started to increase with increasing temperature. This observation was more pronounced for the 0.5 wt% Al₂O₃/0.5 wt% MnO₂-doped 3Y-TZP and 0.6 wt% Al₂O₃/0.4 wt% MnO₂-doped 3Y-TZP, which exhibited a significant increase in Kₑ from 6.8 MPa m¹/² at 1350 °C to 8.5 MPa m¹/² at 1450 °C and 5.9 MPa m¹/² at 1350 °C to 9.8 MPa m¹/² at 1450 °C. Similar results were observed by Borik et al. [36] and Akmar et al. [37], whom suggested that when increasing sintering temperature, the presence of Al₂O₃ and MnO₂ may have caused yttria segregation in the Y-TZP matrix, leading to exaggerated grain growth and the formation of cubic phase zirconia. These grains would readily undergo transformation toughening upon indentation resulting in relatively high values of fracture toughness. Besides that, in other studies, it was also observed that the properties of ceramic materials were influenced by the processing parameters [48].

3.3. Flexural strength and Young's modulus

The influence of MnO₂ and Al₂O₃ additions and sintering temperature on the flexural strength and Young's Modulus of 3Y-TZP are presented in Figs. 6 and 7. In general, additions of up to 0.3 wt% Al₂O₃ and 0.7 wt% MnO₂ have reduced effect on the flexural strength of 3Y-TZP for the entire sintering temperature investigated. The flexural strength of these samples was seen to initially fluctuate between 350 MPa and 550 MPa at lower sintering temperature (1250–1350 °C). However, sintering above 1350 °C, the strength of all doped 3Y-TZP samples started to increase with increasing temperature. This observation was more pronounced for samples containing 0.5 wt% Al₂O₃/0.5 wt% MnO₂ and 0.6 wt% Al₂O₃/0.4 wt% MnO₂. These two compositions were seen to be the best among all the
results produced were higher. Both compositions exhibited a similar trend; a significant increase in strength followed by a decrease as the temperature increases. In particular, the sample consisting 0.6 wt% Al₂O₃/0.4 wt% MnO₂ recorded highest value of strength, increasing from ∼700 MPa to ∼900 MPa between 1350 °C and 1450 °C. This result far exceeds the theoretical value of flexural strength obtained (500–600 MPa) for undoped 3Y-TZP between 1350 °C and 1450 °C. Similar results were reported by Luthardt et al. [49] who prefabricated advanced ceramics, yttria stabilized tetragonal zirconia polycrystals (Y-TZP) in contrast to conventional dental ceramics Y-TZF composed of many very small particles (tetragonal crystallites metastable at room temperature, 0.5 mm) without any glassy phase at the crystallite border and distinguished by a crack initiation mechanism. Due to these properties, as sintered Y-TZP showed a mean flexural strength of 900–1000 MPa.

The variation in Young’s modulus of pure and doped 3Y-TZP sintered in the range of 1250–1550 °C is seen in Fig. 7. The addition of Al₂O₃ and MnO₂ was beneficial in enhancing the elastic modulus of 3Y-TZP, particularly at low sintering temperatures of 1250 °C and 1300 °C when compared to the undoped 3Y-TZP. Besides that, the figure also shows that an E value of above 200 GPa could be achieved with the additions of 0.4 wt% MnO₂/0.6 wt% Al₂O₃ up till 0.6 wt% MnO₂/0.4 wt% Al₂O₃ when sintered at 1250 °C as compared to 179 GPa for the undoped 3Y-TZP. An observation that could be made from the figure is that as sintering temperature increased above 1300 °C, all samples including undoped portrayed a similar increasing trend up till 1450 °C. However, as the sintering proceeded above 1450 °C, all samples exhibited a decrease in E value. This behaviour was in agreement with the decrease in bulk density, and can be attributed to the grain growth that occurs with increasing sintering temperature and was in good agreement to Ramesh et al. [38].

### 3.4. Microstructural evolution and grain size

In order to investigate the mechanism of strengthening and toughening with the addition of Al₂O₃ and MnO₂, scanning electron microscopy (SEM) and X-ray diffraction were undertaken on 3Y-TZP ceramics compositions to ascertain the location of the Al₂O₃ and MnO₂ grains within the ZrO₂ based structure. The two best compositions (i.e. 0.5 wt% Al₂O₃/0.5 wt% MnO₂ as depicted in Fig. 8 and 0.6 wt% Al₂O₃/0.4 wt% MnO₂ as depicted in Fig. 9) were selected based on the best mechanical properties and both materials exhibited a regular fine-grained structure. Using the grain intercept technique, a total of 5 grains were measured with a standard deviation of ±0.01 nm and an average grain size of approximately 445.02 nm for the 0.5 wt% Al₂O₃/0.5 wt% MnO₂
Fig. 8 – The grain size of the sample containing 0.5 wt% Al\textsubscript{2}O\textsubscript{3}/0.5 wt% MnO\textsubscript{2} doped 3Y-TZP.

Fig. 9 – The grain size of the sample containing 0.6 wt% Al\textsubscript{2}O\textsubscript{3}/0.4 wt% MnO\textsubscript{2} doped 3Y-TZP.

Table 2 – The phase content (%) of 3Y-TZP in 0.5 wt% Al\textsubscript{2}O\textsubscript{3}/0.5 wt% MnO\textsubscript{2} doped samples.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Percentage of phase</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium yttrium oxide, (Zr0.96Y0.04)O1.984</td>
<td>88.0%</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Baddeleyite, syn, ZrO\textsubscript{2}</td>
<td>2.5%</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Tazheranite, syn, ZrO\textsubscript{2}</td>
<td>9.5%</td>
<td>Cubic</td>
</tr>
</tbody>
</table>

Table 3 – The phase content (%) of 3Y-TZP in 0.6 wt% Al\textsubscript{2}O\textsubscript{3}/0.4 wt% MnO\textsubscript{2} doped samples.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Percentage of phase</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium yttrium oxide, (Zr0.96Y0.04)O1.984</td>
<td>66.3%</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Zirconium yttrium oxide, ([ZrO\textsubscript{2}]0.91(Y\textsubscript{2}O\textsubscript{3})0.09)O0.917</td>
<td>20.2%</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Baddeleyite, syn, ZrO\textsubscript{2}</td>
<td>13.5%</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>

merge into one whole grain. Most importantly, the average grain size of both the specimens was below the theoretical value/critical grain size value of Y-TZP of 500 nm, which is a great achievement in this current work. This is probably due to the important role that Al\textsubscript{2}O\textsubscript{3} and MnO\textsubscript{2} dopant had contributed to this work. However, and EDX analysis of both 0.5 wt% Al\textsubscript{2}O\textsubscript{3}/0.5 wt% MnO\textsubscript{2} specimen and 0.6 wt% Al\textsubscript{2}O\textsubscript{3}/0.4 wt% MnO\textsubscript{2} specimen could not detect the presence of Al\textsubscript{2}O\textsubscript{3} and MnO\textsubscript{2} dopant due to the very minute percentage (1%) present in the sample.

The average strength of the 0.5 wt% Al\textsubscript{2}O\textsubscript{3}/0.5 wt% MnO\textsubscript{2} specimen was 650 MPa, while the average strength for 0.6 wt% Al\textsubscript{2}O\textsubscript{3}/0.4 wt% MnO\textsubscript{2} was 850 MPa. The strength values were considerably higher compared to the strength of the control group respectively (i.e. 600 MPa).

The XRD analysis of the 0.5 wt% Al\textsubscript{2}O\textsubscript{3}/0.5 wt% MnO\textsubscript{2} doped 3Y-TZP samples exhibited 88% tetragonal (t), 9.5% cubic (c) and 2.5% monoclinic (m) phase content. On the other hand, the XRD analysis of the 0.6 wt% Al\textsubscript{2}O\textsubscript{3}/0.4 wt% MnO\textsubscript{2} exhibited 86.5% tetragonal (t) and 13.5% monoclinic (m) phase content. The (m) phase content in the 0.5 wt% Al\textsubscript{2}O\textsubscript{3}/0.5 wt% MnO\textsubscript{2} had a lower monoclinic content of 2.5% as compared to 0.6 wt% Al\textsubscript{2}O\textsubscript{3}/0.4 wt% MnO\textsubscript{2}, which had 13.5% monoclinic content, as shown in Tables 2 and 3.

3.5. Ageing behaviour of 3Y-TZP

One of the major limitations of 3Y-TZP ceramics as engineering materials is the undesirable surface phase transformation from the (t) to (m) symmetry accompanied by property degradation during exposure to low temperature water or aqueous solutions. Samples were prepared using two different dopant compositions such as 0.5 wt% Al\textsubscript{2}O\textsubscript{3}/0.5 wt% and 0.6 wt% Al\textsubscript{2}O\textsubscript{3}/0.4 wt% MnO\textsubscript{2} and exposed to Ringer’s solution at room temperature in sterile environment for up to 8 weeks. The weights of degraded samples were measured at weeks 1, 2, 4, 6 and 8 of immersion period. Both quantitative (weight loss) and qualitative (morphological change via SEM) analyses were carried out to quantify and identify the degradation. The SEM images determined the formation of porous structure and the increase in grain size.

composition and 466.92 nm for the 0.6 wt% Al\textsubscript{2}O\textsubscript{3}/0.4 wt% MnO\textsubscript{2} was obtained.

A comparison between Figs. 8 and 9 revealed a coarser structure in Fig. 9, with the grain size being roughly 15% greater than in 0.5 wt% Al\textsubscript{2}O\textsubscript{3}/0.5 wt% MnO\textsubscript{2} specimens. The average grain size changes with sintering temperature and also with the method employed due to the different heating mechanisms that take place and processing times that are required. A higher sintering temperature causes the grain boundaries between grains to disperse and this caused the two grains to
Two sets of samples for each group were used for each week to obtain an average weight values. The total number of samples used for the degradation tests was 24 samples. The results presented in Table 4 showed a successive decrease in measured weights for both groups of samples with the progress of immersion period up to 8 weeks that indicated the degradation of the samples. In sample with dopant composition of 0.5 wt% Al₂O₃/0.5 wt% MnO₂, the maximum
weight loss at week 8 was observed to be 1.07%. Similarly, the samples containing 0.6 wt% Al₂O₃/0.4 wt% MnO₂ showed the maximum weight loss of 0.66%, which was considerably lesser than that of samples with 0.5 wt% Al₂O₃/0.5 wt% MnO₂ dopants. This was obvious that the samples containing 0.5 wt% Al₂O₃/0.5 wt% MnO₂ dopants experienced more weight loss over the immersion period of 8 weeks than that the samples containing 0.6 wt% Al₂O₃/0.4 wt% MnO₂ dopants. The weight loss could be attributed to the increase in porosity. Another study also revealed that the ceramic material was prone to degradation due to environmental exposure [2].

The second method used to identify the presence of degradation in the doped 3Y-TZF samples was SEM imaging. At each interval (i.e. 0, 1, 2, 4, 6, 8 weeks), the samples underwent SEM imaging to analyse if there was an increase of size in the porous structures. Scanning electron microstructure (SEM) images of the samples containing 0.5 wt% Al₂O₃/0.5 wt% MnO₂ immersed in Ringer’s solution in sequence from the initial week (controlled samples) up till the final week (week 8) is shown in Fig. 10. It was observed that the pore size increased for every sample as the immersion period increased. For the 0.5 wt% Al₂O₃/0.5 wt% MnO₂ samples, the initial porous size was seen to be 882.28 nm, observed from the first week with

Fig. 11 – SEM image showing the porous structures of the samples (a) week 0; (b) week 1; (c) week 2; (d) week 4; (e) week 6; (f) week 8 containing 0.6 wt% Al₂O₃/0.4 wt% MnO₂.
the controlled samples and the final porous size recorded was 1572.36 nm respectively. Degradation of the material starts to occur with increasing immersion period in Ringer’s solution at 37 °C, resulting in grain size and pore size to increase. This observation indicated that the weight loss of the sample is linearly proportional to the increase in grain size of the sample. It has been identified that material variables such as powder processing techniques, compositions which include yttria content and dopants, sintering conditions, and hence microstructural characteristics such as grain size and the presence of grain boundary phase are all salient factors controlling the ageing behaviour of 3Y-TZP ceramics.

Similarly, the scanning electron microstructure (SEM) images of the samples containing 0.6 wt% Al₂O₃/0.4 wt% MnO₂ immersed in Ringer’s solution in sequence from the initial week (controlled samples) up till the final week (week 8) is shown in Fig. 11. The porous sizes of the 0.6 wt% Al₂O₃/0.4 wt% MnO₂-doped Y-TZP sample were measured during SEM. The initial porous size recorded at week 0 was 832.44 nm, whereas, the final porous size recorded at week 8 was 2542.6 nm, respectively. In this observation it was also seen that the porous size increased as the immersion period increased.

4. Conclusions

The incorporation of Al₂O₃ and MnO₂ dopants improved the physical and mechanical properties of 3Y-TZP bioceramics. It was observed that the addition of 0.6 wt% Al₂O₃ and 0.4 wt% MnO₂ dopants exhibited maximum increase in the density (6.09 g/cm³), the fracture toughness (9.8 MPa m½) and the flexural strength (900 MPa) of the material. The microstructures of 3Y-TZPs containing 0.6 wt% Al₂O₃ and 0.4 wt% MnO₂ were single phase and composed of fine, equiaxed tetragonal grains. The best performing samples recorded a value of 445.02 m and 466.92 nm, which was much lower than the critical grain size value of commercial Y-TZP (500 nm), which indicated the addition of dopants contributed to the reduction in grain size and finally an increase in density. Besides, superior ageing resistance was exhibited by 3Y-TZP containing 0.6 wt% Al₂O₃ and 0.4 wt% MnO₂ sintered at 1450 °C. The sintering temperature of 1450 °C was found to be the optimum for all 3Y-TZPs to achieve >98% of theoretical density (6.1 g/cm³). Overall, the addition of Al₂O₃ and MnO₂ dopants could be an effective means for sintering and consolidating 3Y-TZP commercial materials potentially for hip implants due to the resulting finer microstructure, enhanced mechanical properties, and superior ageing resistance.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

The authors would like to thank the Ministry of Science, Technology and Innovation (MOSTI), Malaysia for providing the financial support under the grant No. 02-02-03-SF0251 to conduct this work. In addition, the supports provided by UNITEN and HUKM in carrying out this research are also gratefully acknowledged.

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