Effect of Alumina Addition to Zirconia Nano-composite on Low Temperature Degradation Process and Biaxial Strength

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ABSTRACT

Ceramic dental materials have been considered as alternatives to metals for dental implants application. In this respect, zirconia tetragonal stabilized with %3 yttrium, is of great importance among the ceramic materials for endosseous dental implant application. Because of its good mechanical properties and color similar to tooth. The aim and novelty of this study was to design and prepare Y-TZP nano-composite to reduce the degradation process at low temperature by alumina addition and maintaining submicron grain sized. Also, flexural strength of nano-composite samples was evaluated. Toward this purpose, alumina-Y-TZP nano-composites containing 0–30 vol% alumina (denoted as A-Y-TZP 0-30) were fabricated using α-alumina and Y-TZP nano-sized by sintering pressure less method. The synthesized samples were characterized using x-ray diffraction, field emission scanning electron microscopy equipped with energy dispersive x-ray spectroscopy techniques. Nano-composite samples with high density (≥96%) and grain sized of ≤ 400 nm was obtained by sintering at 1270 °C for 170 min. After low temperature degradation test (LTD), A-Y-TZP20 and A-Y-TZP30 not showed monoclinic phase and the flexural strength in all of samples were higher than A-Y-TZP0. It was concluded that the grains were remained in submicron sized and A-Y-TZP20 and A-Y-TZP30 did not present biaxial strength reduction after LTD test.

Keywords: Alumina-zirconia nano-composite; Low temperature degradation process; Endosseous dental implant; Y-TZP matrix.

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1. Introduction

Intraosseous dental implant is one of the treatment methods for missing teeth replacement [1]. Titanium and its alloys have been used for fabrication of endosseous dental implants because of its biocompatibility and mechanical properties. But the gray color of the titanium may be disadvantageous and give rise to esthetic
problems, also, in the case of dental implant, biocompatibility depends on corrosion and mechanical characteristics of material. In spite of the high corrosion resistance and biocompatibility of titanium, in-vivo studies have shown evidences of titanium release into the body and accumulation in the tissue adjacent to the titanium implants and also in the lymph nodes [2]. Hence ceramic materials have been introduced as the alternatives to titanium implants. Among the ceramic material, zirconia has received increasing attentions in dentistry science due to its mechanical characteristics similar to metals [3], white color like teeth [4] and less adhesion of bacteria to the surface [5]. Depending on temperature zirconia can take three different crystal structure; monoclinic at room temperature, tetragonal at temperatures above 1170°C, and cubic at temperatures above 2370°C. Zirconia can be used as a meta-stable phase at room temperature with addition of several oxides including calcium oxide, magnesium oxide and yttrium oxide [6]. Zirconia ceramic has been studied in different applications such as: total knee and hip replacement, middle ear ossicular chain and dental implants (inlay, onlay, abutment and crown). For dental applications, tetragonal zirconia is usually stabilized by yttria (Y-TZP). The high strength and toughness of tetragonal zirconia stabilized with yttria arise from toughening phenomenon created by changing the crystal structure from tetragonal to monoclinic [7]. This phase change which is associated with volumetric expansion of almost between 3-7% causes a local pressure, leading to micro crack formation around phase transformed of zirconia tiny particles. This phase-transformation tends to occur in the stress concentration areas, especially in the areas of surface or intra lattice defects. This effectively suppresses the crack propagation resulting on the greater fracture toughness [6]. A part from this effect, tetragonal to monoclinic transformation may stem from hydrothermal aging in the wet environment of oral space. This phenomenon is usually known as low-temperature degradation by which the energy barrier for tetragonal to monoclinic transformation is reduced. This phenomenon is due to the formation of water components within the zirconia network which have not been fully known [8]. As a result tetragonal to monoclinic transformation gradually spreads over the surface and subsequently penetrates into the depth of material. This transformation slowly progresses at the temperature of oral space. The existence of large amounts of monoclinic phase is known to be deleterious to the mechanical properties of zirconia. Moreover, this may damage the long term clinical success of zirconia-based restorations [9]. A strategy to increase the hydrothermal stability of tetragonal phase of Y-TZP is the addition of alumina in order to inhibit the propagation of phase transformation into the bulk of the material. The higher the proportion of alumina phase, the greater the long-term stability of Y-TZP is achieved. Another strategy to reduce low-temperature degradation of zirconia is the grain size reduction using of nano-precursor for fabricating of intraosseous zirconia dental implants. Numerous researchers have studied the 3Y-TZP intraosseous implants by in-vivo method and some of these studies compared titanium implants with zirconia in terms of osseointegration in different bony tissues of body, particularly the jaw bone [10-12]. Besides, in these studies have been used Y-TZP and less have been noticed to low temperature degradation (LTD) in zirconia endosseous dental implant. Hence our study was designed to Y-TZP nano-composite structure and reduce the low temperature degradation process by alumina addition to Y-TZP matrix for endosseous dental implants application. The addition of nano sized alumina to zirconia maybe increases long term stability of Y-TZP during tetragonal-to-monoclinic phase transformation but also maybe a greater inhibitory effects on LTD process through the formation of submicron grain sized during controlled sintering process. This study was aimed at evaluating of LTD and flexural strength of A-Y-TZP nano-composite disks for intraosseous dental implant applications.

2. Experimental procedure
2.1. Preparation of nano-composites:
Nano-sized Al₂O₃ (α-Al₂O₃ purity >99/99%, average particle size of 13 nm, sigma aldrich, U.S.A) and Y-TZP (Y-TZP, Particle size 100 nm, sigma aldrich, U.S.A) powders were used as starting materials. Four different compounds were prepared by incorporating Al₂O₃ into the Y-TZP matrix including A-Y-TZP0 (0 vol.% Al₂O₃), A-Y-TZP10 (10 vol.% Al₂O₃), A-Y-TZP20 (20 vol.% Al₂O₃) and A-Y-TZP30 (30 vol.% Al₂O₃). Each powder mixture was ball-milled with a 125 ml zirconia jar and four 20 mm diameter zirconia balls at ambient temperature. Homogeneous mixing was performed using ball/powder mass ratio of 25:1, rotation...
speed of 150 rpm and time of 45 min. After sieving, the powders were uniaxially pressed into disks with dimension of Ø12×1.2 mm under a pressure of 150 MPa [13]. The obtained green compacts were sintered at 1270 °C for 170 min in air.

2.2. Microstructural and flexural strength characterizations

The phase composition of the samples was identified by x-ray diffraction (XRD, Philips x’pert mpd with cu kα radiation (λ=0.15418 mm) respectively). The XRD patterns were recorded in 2θ range of 20-80° with a scanning rate of 5°/min. The homogeneity of the as-ball milled samples was assessed using energy dispersive x-ray spectroscopy (EDAX). The microstructure of all samples were observed by field emission scanning electron microscopy (FESEM) (S-4160 Dektak3 and ICMM-CSIC of Madrid) after three-point bending test and flexural strength evaluation. The average grain size of zirconia were determined using FESEM observations of nano-composite samples. The density of sintered samples were measured using kern system (ALS Series) following the porosity of sintered samples were assessed by Archimedes method (ASTM C 373–88) (see Table 1) [14]. The flexural strength of disk specimens was assessed by three-point bending test [15] using zwick/roell z050 testing machine under a cross head speed of 0.5 mm/min.

Table 1- Relative porosity of ceramic samples sintered at the temperature of 1270 °C

<table>
<thead>
<tr>
<th>Samples</th>
<th>0% vol</th>
<th>10% vol</th>
<th>20% vol</th>
<th>30% vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-3Y-TZP</td>
<td>0.04918</td>
<td>0.03174</td>
<td>0.03125</td>
<td>0.03330</td>
</tr>
</tbody>
</table>

2.3. Optimization of sintering process

ISO-13356 specifies 1400 °C for sintering of a biocompatible ceramic bone-substitute material based on yttrium-stabilized tetragonal zirconia (Y-TZP) with micrometer grain sized. Which is used as material for surgical implants [16]. In this study precursors for the manufacture of nano-composite disks were nano sized. Since the high surface area of primary nano particles provides an extremely large driving force for grain growth. The sintering of nano-composite samples requires process optimization in terms of time and temperature to achieve refined zirconia grains with submicron sized. When the grain size is less than 0.2 µm the transformation is not possible, conversely when zirconia have larger grain size (≥1 µm) phase transformation spontaneously occur, and this results in zirconia less stability [17]. In this study, the sintering temperature was studied in 1200-1400 °C temperature range [18-19]. Density evaluating completely was done during evaluation of different temperatures for the sintered samples (Table 2).

Table 2- Relative density of ceramic samples sintered at various temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1200 °C</th>
<th>1250 °C</th>
<th>1270 °C</th>
<th>1300 °C</th>
<th>1400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-3Y-TZP</td>
<td>96.05</td>
<td>95.51</td>
<td>94.33</td>
<td>93.11</td>
<td>92.98</td>
</tr>
<tr>
<td>A-3Y-TZP</td>
<td>88.89</td>
<td>90.54</td>
<td>96.63</td>
<td>88.18</td>
<td>82.01</td>
</tr>
<tr>
<td>A-3Y-TZP</td>
<td>90.75</td>
<td>90.75</td>
<td>96.99</td>
<td>89.23</td>
<td>83.60</td>
</tr>
<tr>
<td>A-3Y-TZP</td>
<td>90.80</td>
<td>90.80</td>
<td>96.83</td>
<td>88.69</td>
<td>80.55</td>
</tr>
</tbody>
</table>

2.4. Low temperature degradation behavior of alumina-zirconia nano-composites

Before the LTD test, the disks were polished to obtain a mirror-like plane and annealed at 1200°C for 1h in air to eliminate the stress-induced transformed layers [13]. Subsequently, the samples were immersed in hot water and kept in autoclave for 5 h. It was estimated that this treatment at 134°C for 1h corresponds to ~4 years in-vivo [20]. The biaxial flexural strength test and XRD analysis were executed after the LTD test.

3. Results and discussion

In dental implantology Y-TZP has been
proposed for endosseous dental implant application (hot isostatic pressed with biaxial strength: 900-1000 MPa and Fracture toughness: 8-9 MPa/m^{1/2}) [10-12]. But less have been noticed to LTD process in Y-TZP. Therefore our hypothesis was designed to reduce LTD in Y-TZP by alumina addition to Y-TZP matrix and maintaining submicron grain sized. The content of monoclinic phase in Y-TZP raw material for surgical implants was determined by ISO 13356 (%≤ 25) [16]. According to the data given in Table.2, the density of nano-composite samples is initially increased by increasing the temperature, reaching the maximum value at 1270°C, and then decreased by further temperature rising up to 1400 °C. In addition, the porosity measurement shows the porosity percentage less than %5. Based on schottky-barrier model positively charged grain boundary core expels oxygen vacancies and absorbs Al^{+3} action causing the oxygen vacancy depletion in the space charge layer. Increasing the temperature to above 1270 °C results in a higher amount of Al amorphous phase in triple junctions probably due to the Al release from ZrO_{2} solid solution [23]. Also, the density of Al-rich amorphous phase is lower than tetragonal-ZrO_{2} [21]. The density of nano-composite samples is decreased through temperature rising over 1270 °C. Besides, high density is important for zirconia dental applications especially in load bearing position. The high density for all of nano-composite samples was provide in 1270 °C. Based on the results of density measurements (Table 2), the sintering at 1270 °C was chosen as the optimum consolidation process by which the zirconia grains remained in sub-micron range. It is well-established that the zirconia grain size significantly affects the tetragonal-to-monoclinic transformation in Y-TZP ceramics. Numerous researchers have reported that reducing the average grain sized in zirconia-based ceramics is beneficial to stability of tetragonal phase, and there by retards the LTD [8]. Tsukuma et. al. [22] found that in zirconia with the grain size of ≥1 μm, a significant tetragonal-to-monoclinic transformation, reducing the strength of material and for the grains with ≥0.6 μm, the resistance to aging phenomenon is decreased. The FESEM image of A-Y-TZP20 nano-composite with a high density of 96% shows the pore size is less than 100 nm (yellow arrow); besides, recrystallization of the structure is evident as illustrated in Fig. 1-a. The FESEM image of A-Y-TZP20 nano-composite also reveals the presence of nanocomposite grains with size of ≤ 400 nm, the grains with ≤ 100 nm size were remarkably abundant. The EDAX analysis (Fig. 1-b and 1-c) and x-ray mapping (Fig. 1-d) confirm the homogeneous mixing of alumina and zirconia in A-Y-TZP20 nano-composite after sintering in 1270 °C. In this study the A-Y-
TZP nano-composites with different amounts of alumina (0-30 vol. %) were sintered in 1270 °C. Fig. 2, shows the XRD patterns of starting materials. It is observed that both tetragonal and monoclinic phases are present in the phase composition of Y-TZP. Fig. 3, demonstrates the XRD pattern of pure Y-TZP and three A-Y-TZP nano-composites after sintering at 1270 °C. Which only A-Y-TZP30 contain no monoclinic phase. With increasing the sintering temperature to 1400 °C, monoclinic phase is formed in all samples except A-Y-TZP20 (Fig. 4). As for A-Y-TZP10, the extent of monoclinic phase formed at sintering temperature of 1400°C is higher as compared to 1270 °C. Based on Garvie and Nicholson’s formula [23], mass fraction of monoclinic phase \( (X_m) \) present in different samples sintered at 1270 °C is calculated as follows:

\[
X_m = \frac{I_{m}(-111) + I_{m}(111)}{I_{m}(-111) + I_{m}(111) + I_{t}(101)} \quad \text{(eq. 1)}
\]

Where \( X_m \) is the mass fraction of monoclinic phase, \( I_{m}(-111) \) is the intensity of monoclinic peak at \( 2\theta = 28.2° \), \( I_{m}(111) \) is the intensity of monoclinic peak at \( 2\theta = 31.5° \), and \( I_{t}(101) \) is the intensity of tetragonal peak at \( 2\theta = 30.2° \). Volume fraction \( (V_m) \) of monoclinic phase was calculated using the equation (2) as proposed by Toraya et al. [24].

\[
V_m = 1.311 X_m / (1 + 0.311 X_m) \quad \text{(eq. 2)}
\]

Where \( V_m \) is the volume fraction of monoclinic phase and \( X_m \) is the mass fraction of monoclinic phase. According to equation (2), the volume fraction of monoclinic phase in Y-TZP (raw material), A-Y-TZP0, A-Y-TZP10, A-Y-TZP20 and A-Y-TZP30 was calculated to be 0.194, 0.018, 1.384, 0.087, and 0, respectively. Monoclinic phase is brittle and reduces mechanical properties. With increasing the alumina content, the extent of monoclinic phase is decreased indicating that alumina incorporation suppresses the formation of monoclinic phase in Y-TZP. Based on the previous reports [25], hydrothermal stability can be achieved for Y-TZP by addition of alumina with homogenous distribution within the Y-TZP matrix. Therefore, in this study, EDAX analysis was done on A-Y-TZP10, A-Y-TZP20 and A-Y-TZP30 after ball milling. The results of EDAX analysis (Fig. 5) and x-ray mapping confirm the homogeneous mixing of alumina and Y-TZP in A-Y-TZP10 nano-composite following ball milling. In this study, alumina nano-particles was used to control of low temperature degradation process. Since the primary raw material contains some monoclinic phase, the XRD pattern related to samples after aging process \((T=132 °C,\)

...
P=0.2Bar) (Fig. 6) shows this point. Among the nano-composite samples only A-Y-TZP10 contain monoclinic phase. It seems that small amount of alumina has no significant suppressing effect on formation of monoclinic phase, while, the comparison between the XRD patterns of pre- and post-LTD, A-Y-TZP20 reveals the presence of monoclinic phase only before the LTD. It appears that a negligible tetragonal-to-monoclinic phase transformation occurs for A-Y-TZP20. So that with polishing before LTD, monoclinic phase is not observed (Fig. 6). Borchers et. al. [26] found no significant effect of low temperature degradation on the flexural strength of Y-TZP dental ceramics. In their study tetragonal-to-monoclinic phase transformation was observed after aging. Kosmac et. al. [27] and Ban et. al. [28] observed the flexural strength reduction for the samples aged at 134°C. In this study flexural strength evaluation after aging process (Fig. 7) showed that a slight decrease is obtained only for A-Y-TZP10 nano-composite disk. This behavior stemmed from the existence of monoclinic phase after aging process of A-Y-TZP10, in consistence with findings of Lorente et. al. [29]
during a study on low temperature degradation process in Y-TZP ceramic. Fig. 8, presents the effect of Al$_2$O$_3$ addition on biaxial strength of the sintered samples. The biaxial flexural strength is initially increased by increasing Al$_2$O$_3$ content up to 20 vol.%, reaching a maximum of 871 MPa after which decreased to 612 MPa for A-Y-TZP30 sample. According to the fracture mechanics for ceramic materials, the strength depends on the fracture energy and fracture origin. Strength is also affected by the micro structural features such as grain size, toughening mechanisms like toughening induced by phase transformation, and micro cracks deflection [13]. This decrease in biaxial strength for A-Y-TZP30 sample can be explained by the fact that the threshold of tetragonal-to-monoclinic transformation is changed for this sample. On the other hand, the alumina addition in case of A-Y-TZP10 and A-Y-TZP20 decreases the threshold of phase transformation resulting in the higher biaxial strength values of 700 and 871 MPa, respectively for A-Y-TZP10 and A-Y-TZP20. In contrast, the threshold of transformation in case of A-Y-TZP30 is increased leading to the sample failure before phase transformation. Fig. 9, illustrates the FESEM images from the samples failed after biaxial strength test. As illustrated in Fig. 9, micro-cracks are observed on the surface of several grains of A-Y-TZP nano-composites particularly for A-Y-TZP10 and A-Y-TZP20. It seems that after loading on the samples, stress-induced phase transformation mechanism is activated and the higher biaxial strength of A-Y-TZP10 and A-Y-TZP20 retards early failure. However, in the case of A-Y-TZP30, in which the transformation threshold is increased, the failure take place resulting in a severe cracking inter grains, in consistence with findings of Xu et. al. [30] that compared the evaluation methods of fracture toughness in Y-TZP ceramics. Therefore, with increasing the threshold of transformation in case of A-Y-TZP30, is reduced some extent biaxial strength as compare as the other nano-composite samples.

Fig. 8- Variations in biaxial flexural strength of nanocomposites versus alumina content.

Fig. 9- FESEM images from (A) A-3Y-TZP10, (B) A-3Y-TZP20 and (C) A-3Y-TZP30 after flexural strength test.
Based on the Lange et al. [31] reports, the factors affecting the change of tetragonal zirconia grains include stabilizer content, grain size and matrix forces that constrain the grains. On the other hand, alumina addition to A-Y-TZP nano-composite enhances the rigidity of matrix and consequently increases the critical stress required for initiating tetragonal-to-monoclinic transformation and thereby rises the overall strength [32]. This case is clearly visible for A-Y-TZP30. However, controlling the hydrothermal aging of Y-TZP still remains a challenge. It has been reported that the addition of Al₂O₃ to Y-TZP can inhibit the tetragonal-to-monoclinic transformation [32]. Although grains in all of samples remained in submicron sized but monoclinic phase appearance in A-Y-TZP10 sample don’t suppress following alumina addition. Hence, the flexural strength of A-Y-TZP10 slightly reduced as compared prior to LTD test. In this study, flexural strength in all of nano-composite samples was higher than A-Y-TZP0.

4. Conclusions

Al₂O₃/Y-TZP nano-composites containing 0–30 vol% Al₂O₃ were fabricated by pressure less sintering method. The effect of Al₂O₃ content on flexural strength and low temperature degradation of Y-TZP ceramics were assessed. The following conclusions can be drawn: monoclinic phase and flexural strength reduction were found after LTD test for A-Y-TZP30. It was observed that the addition of small amount of alumina (10 vol. %) has no suppressing effect on formation of monoclinic phase, leading to slightly flexural strength reduction for A-Y-TZP10 as compared to other samples after aging process. The biaxial flexural strength was increased with alumina content except A-Y-TZP30. As evidenced by FESEM images after flexural strength test, it appears that stress-induced phase transformation is the main mechanism for increasing of flexural strength for all samples except A-Y-TZP30. Based on this study, seems the alumina addition to Y-TZP matrix in high volume (20% vol or 30% vol) suppress monoclinic phase appearance. This effect is useful for LTD control but flexural strength in A-Y-TZP30 is reduced as compared to A-Y-TZP10 and A-Y-TZP20.

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References


