Phase Formation, Microstructure and Mechanical Properties of ZrO₂ Modified-Dental Porcelain Ceramics

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ABSTRACT

The potential of a combination between single-step sintering and ZrO₂ additive as a simple ceramic fabrication method to obtain dental porcelain-based ceramic-nanocomposites with good mechanical properties was demonstrated. Influences of sintering condition on phase formation, densification, microstructure and mechanical properties of these porcelain ceramics were examined via XRD, SEM-EDX and Vickers indentation. It has been found that the choice of both sintering temperature and dwell time is one of the key factors controlling densification and leucite crystallization on the zirconia surface in dental porcelain ceramics.

Keywords: dental porcelain ceramics, leucite, sintering, strength.

1. INTRODUCTION

Leucite glass-ceramics are one of the significant restorative materials for dental applications owing to their suitable biocompatibility, wear resistance and esthetics. However, similar to other glass-ceramics, a major disadvantage to dentistry of porcelain-based ceramics is their brittleness, which often deteriorates their utilization in fields where high strength and toughness are required [1,2]. Several approaches have been introduced to minimize this limitation and improve the mechanical properties including a method of reinforcing the glassy matrix with high strength crystalline phases such as alumina (Al₂O₃), zirconia (ZrO₂) or leucite (KAlSi₂O₆) [2-4]. A significant milestone in this respect was established in the development of dental ceramics containing leucite crystalline phase because of their excellent thermal compatibility when bonding to metals and also a reinforcing agent in all ceramic restorations [5-7]. In general, most commercial porcelains for dental restorations are partially crystallized feldspathic glasses that consist of tetragonal-leucite crystals embedded in a glassy matrix. It has been reported that leucite glass-ceramics can
be fabricated by controlled crystallization of a glass via leucite additive, heat treatment and etc. [8-9]. In general, commercial dental porcelain ceramics contain some amount of leucite crystals sized \(\sim 5-10 \, \mu\text{m}\) causing extensive microcracking around these non-uniformed leucite crystals [8]. To overcome these problems, several efforts have been made to tailor the leucite morphology, volume fraction and distribution which is thought to affect the mechanical properties of these porcelain ceramics via heat treatment [4,9] or heat pressing [10].

According to a study on the effects of multiple firing and isothermal anneals on the leucite volume fraction reported by Mackert and Evan [11], it is established that measurable changes in the leucite concentration exist upon a variety of porcelain heat treatments. Although the study on the formation of leucite crystalline in porcelains has been reported by several researchers [7-9]; so far, attentions directly paid on the Zr-modified porcelain-based ceramics are very few. In connection with this, our earlier works [12] have demonstrated that the two-step sintering technique together with 20-wt% ZrO\(_2\) additive has considerable potential for the production of leucite/porcelain ceramic-nanocomposites. It was also found that the tempering time is a key factor to controlling dendritic morphology of leucite crystallization behavior and microstructural arrangement in ZrO\(_2\)-modified dental porcelain ceramics. However, no information regarding the mechanical properties of these materials is available. Moreover, effects of single-step sintering for the production of ZrO\(_2\)-modified dental porcelains have not yet been adequately characterized. Thus, in the present study, dental porcelain ceramics were fabricated by using both a single-step sintering and 20 wt% ZrO\(_2\) additive techniques. Their mechanical properties with respect to both firing temperature and dwell time were investigated, compared and explained on the basis of their composition, densification, and microstructural evolution.

2. MATERIALS AND METHODS

The starting materials were commercially available dental porcelain powders (Vita-VMK95, Vita Zahnfabrik, Bad Säckingen, Germany), which had particle size range of \(\sim 1.5-2.5 \, \mu\text{m}\). Porcelain powders were mixed with 20 wt% of zirconia powders (Sigma-Aldrich, purity > 99%) by using a rapid vibro-milling for 30 min [2,12]. The methods of mixing, drying, grinding and sieving of the products were similar to those employed in the preparation of the alumina-modified dental porcelain powders as described previously [2, 12]. Green samples were obtained by mixing powders with polyvinyl alcohol binder (PVA) via a slip-casting technique as recommended by the manufacturer [13], and then poured into a standard stainless steel mould with a normal-sized cavity of 30 mm \(\times\) 6 mm \(\times\) 2 mm, reproducing the desired dimensions and shapes [2, 12]. After moulding, the ceramics were fabricated by employing different firing schemes with heating rate of 25°C/min in a vacuum furnace (Multimat Touch & Press, Germany), with details listed in Table 1. During heating, the temperature was maintained at 500°C for 1 h to burn out the PVA binder. The dental porcelain, i.e. the control group (D0), was sintered at 1,060°C for 5 min. Further increase in the soaking time longer than 5 min results in melted samples probably due to a liquid-phase formation during the sintering process of dental porcelains [14]. The other groups of samples (coded D1-D9) were sintered by employing various firing temperature and dwell time. In contrast to those adopted by Chayada et al. [12], in this work, no second firing-step and quenching processes are required. Densities of
the final sintered products were determined by using the Archimedes principle. Phase formation and microstructural were examined by room temperature X-ray diffraction analysis (XRD; X’pert MPD, Philips Corp, Japan) using Ni-filtered Cu Kα radiation and field emission scanning electron microscopy (SEM; JSM-840A 6335 F, Jeol, Japan), respectively. The mean crystallite size was determined using the diffraction peak (400) of the leucite pattern by using Scherrer equation [15]. Lattice parameters of the leucite phase were determined from the d spacing for the (400) and (004) peaks for the tetragonal phase [4,12]. The grain size and morphologies of leucite phase in the sintered samples were determined from SEM micrographs. The chemical composition of the phase formed was also elucidated by an energy dispersive X-ray (EDX) analyzer with an ultra-thin window. EDX spectra were quantified with the virtual standard peaks supplied with the Oxford Instruments eXL software. In order to evaluate the mechanical properties of these samples, the characterization methods previously described in our earlier works [2] were performed. The uniaxial flexural strength was measured with the three-point bending technique and calculated as recommended by ISO 6872. Hardness and Young’s modulus were determined and calculated for all materials by the Vickers microhardness testing machine, and were measured as recommended by the ASTM C 1327-99 and C 1259-01, respectively. Fracture toughness was assessed using the indentation strength method. Hardness and elastic modulus are parameters of the equation used for calculation of the fracture toughness. The fracture toughness was calculated with the equation proposed by Fischer and Mark [16].

3. RESULTS AND DISCUSSION

The densification, leucite crystallization, microstructural evolution and mechanical behavior of the Zr-modified dental porcelain ceramics subjected to various sintering conditions are given in Table 1. In the sintering temperature range of 1,060-1,140°C, the density increases with increasing temperature. For a given sintering temperature, similar trend of the density is also observed with the extending of dwell time from 20 to 30 min. However, it can be seen that further increase in the dwell time to 40 min leads to the decrease of the density. This feature creates a maximum density value of about 2.88 g/cm³ which is comparable to the values reported by Chayada et al. (~2.76 g/cm³ [12]) where the two-step sintering technique was used. The increasing density with rising dwell time up to 30 min may be explained by the enhanced densification related to the effect of ZrO₂ [3,12]. Further increase in the dwell time causes a decrease in density values. This may be attributed to the suppression of atomic diffusion at probably too long soaking times resulting in an incomplete densification [12,17]. Similar behavior is also reported by Chayada et al. [12] for zirconia-modified dental porcelains derived from the two-step sintering technique. As is well known, the difference in thermal expansion between the tetragonal leucite crystals and the glassy matrix also provides tangential compressive stresses around the crystals that are thought responsible for significant strengthening in dental porcelain [4, 9]. The crystallization of a high expansion tetragonal leucite phase into a base glass is advantageous to increase its expansion coefficient to a level sufficient to allow efficient bonding to metals [18]. More recently, leucite has been used in all-ceramic materials, not for thermal compatibility, but as a reinforcing material for all-ceramic restorations [4, 9].

To study the crystalline phase development with different sintering conditions in each porcelain-based sample, the specimens were
Table 1. The sintering conditions employed for the production of samples and their physical properties.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sintering condition: Temperature/Dwell time (°C/min)</th>
<th>Density (g/dm³)</th>
<th>Leucite content (wt%)</th>
<th>Leucite crystalline size (± 2 nm)</th>
<th>Leucite particle size range (± 30 nm)</th>
<th>Flexural strength (MPa)</th>
<th>Fracture toughness (MPa m¹/²)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D0</td>
<td>1060/5</td>
<td>2.43</td>
<td>26.14</td>
<td>15.76</td>
<td>80-200</td>
<td>83.4 (±8.3)</td>
<td>1.01 (±0.10)</td>
<td>3.21 (±0.19)</td>
</tr>
<tr>
<td>D1</td>
<td>1060/20</td>
<td>2.66</td>
<td>23.52</td>
<td>7.74</td>
<td>35-150</td>
<td>154.6 (±15.5)</td>
<td>2.03 (±0.11)</td>
<td>7.20 (±1.01)</td>
</tr>
<tr>
<td>D2</td>
<td>1060/30</td>
<td>2.71</td>
<td>23.55</td>
<td>7.85</td>
<td>45-155</td>
<td>170.5 (±15.4)</td>
<td>2.20 (±0.10)</td>
<td>7.41 (±0.68)</td>
</tr>
<tr>
<td>D3</td>
<td>1060/40</td>
<td>2.69</td>
<td>23.74</td>
<td>8.32</td>
<td>52-161</td>
<td>169.2 (±16.7)</td>
<td>2.18 (±0.09)</td>
<td>7.33 (±0.64)</td>
</tr>
<tr>
<td>D4</td>
<td>1100/20</td>
<td>2.71</td>
<td>23.13</td>
<td>8.96</td>
<td>50-180</td>
<td>172.1 (±13.2)</td>
<td>2.24 (±0.09)</td>
<td>7.55 (±0.69)</td>
</tr>
<tr>
<td>D5</td>
<td>1100/30</td>
<td>2.78</td>
<td>24.70</td>
<td>11.26</td>
<td>60-190</td>
<td>184.3 (±14.7)</td>
<td>2.39 (±0.10)</td>
<td>7.98 (±0.43)</td>
</tr>
<tr>
<td>D6</td>
<td>1100/40</td>
<td>2.70</td>
<td>25.35</td>
<td>11.75</td>
<td>60-190</td>
<td>175.3 (±18.9)</td>
<td>2.36 (±0.13)</td>
<td>7.83 (±0.70)</td>
</tr>
<tr>
<td>D7</td>
<td>1140/20</td>
<td>2.86</td>
<td>23.09</td>
<td>12.18</td>
<td>60-220</td>
<td>185.7 (±15.5)</td>
<td>2.40 (±0.12)</td>
<td>8.01 (±0.58)</td>
</tr>
<tr>
<td>D8</td>
<td>1140/30</td>
<td>2.88</td>
<td>24.29</td>
<td>13.32</td>
<td>70-245</td>
<td>192.8 (±19.8)</td>
<td>2.50 (±0.16)</td>
<td>8.58 (±0.75)</td>
</tr>
<tr>
<td>D9</td>
<td>1140/40</td>
<td>2.87</td>
<td>24.77</td>
<td>15.87</td>
<td>70-250</td>
<td>186.1 (±14.3)</td>
<td>2.48 (±0.11)</td>
<td>8.43 (±0.67)</td>
</tr>
</tbody>
</table>
heat treated at various conditions (Table 1), followed by phase analysis using XRD technique. The X-ray diffraction patterns of both unfired and sintered dental porcelain ceramics in this study are given in Figure 1 (a and b), indicating a background of amorphous glassy phase and evidence of the formation of only leucite crystalline phase, which could be matched with JCPDS file no. 15-47, in agreement with other works [12, 18].

To a first approximation, this crystalline phase has a tetragonal leucite-type structure in space group $I4_1/a$ (no. 88) with cell parameters $a = 1,306$ pm and $c = 1,375$ pm [19], consistent with previous work reported by Mackert et al. [20] where the lattice parameters for tetragonal leucite at room temperature were $a = 13.197 \pm 0.013$ Å and $c = 13.819 \pm 0.016$ Å.

**Figure 1.** X-ray diffraction patterns of non-sintered (a) and sintered (b) dental ceramics, non-sintered (c) and sintered (d) D1 (e) D2, (f) D3, (g) D4, (h) D5, (i) D6, (j) D7, (k) D8 and (l) D9 samples.
As demonstrated in Figure 1(c-l), it can be seen that all samples showed almost identical XRD patterns. The strongest reflection in the majority of XRD traces derived from all 20-wt% ZrO₂-modified porcelain groups indicated a combination of monoclinic-zirconia which could be matched with JCPDS file no. 36-420 [21] and tetragonal-leucite phase. In addition, it should be noted that XRD peaks of leucite (323) and zirconia (111) at 2θ ~28.5° are superimposed, in agreement with previous studies [12]. In this study, no phase transformation of leucite can be detected at 1,060-1,140°C and the XRD patterns of the samples subjected to the sintering process for various dwell time from 20 to 40 min did not reveal the formation of any additional crystalline phases. This probably indicates the effectiveness of Zr as the leucite stabilizer, in analogous with those found for other similar systems [12,19].

In order to evaluate the relative amounts of tetragonal leucite phase in each group, the leucite peak at the (004) and (400) reflections and the zirconia peak at the (111) reflection were the peaks of interest (Figure 2). As suggested by Ong et al. [22], powder X-ray diffraction method can be used to approximate the amount of leucite phase in porcelain ceramics. It should be noted that for a given sintering temperature, some relationship was observed between the employed dwell times of 20-40 min and the concentration of leucite phase in the samples (Table 1). In this work, the amount of leucite phase in the ZrO₂-modified dental porcelain subjected to the sintering was found to slightly increase as a function of dwell time, consistent with those reported by Cheung and Darvell [23] for dental porcelains.

Figure 2. Enlarged X-ray diffraction patterns of all 20 wt% ZrO₂ modified-dental porcelain ceramics sintered at various conditions.
It has been found that by extending dwell time, some diffraction lines gradually sharpen, e.g., (004) and (400) peaks, an indication of a continuous increase in crystalline size and of the reduction of lattice strain. These observations point out that the prolonged heat treatment affects the leucite crystallite size.

Additionally, the crystallite size of leucite phase was estimated from these XRD patterns as also given in Table 1. The calculated crystallite size value was also found to increase with increasing both firing temperature and dwell time. Though, the relative intensities of the Bragg peaks exhibit independent of tempering time, it is well documented that, as Scherer's analysis provides only a measurement of the extension of the coherently diffracting domains, the crystallite sizes determined by this method can be significantly underestimated [15]. In addition to strain, factors such as defects, homogeneity of materials, the complex nature of the background due to amorphous matrix, processing variables and instrument effect can attribute to peak shape, making it almost impossible to extract a reliable crystallite size solely from XRD [15]. In this connection, SEM technique was also utilized for grain size measurement (Table 1 and Figure 3).

As shown in Figure 3 for the case of all 20-wt% Zr modified-dental porcelain ceramics, it can be seen that some leucite

Figure 3. SEM micrographs of all 20 wt% ZrO₂ modified-dental porcelain ceramics sintered at various conditions.
particulates which vary between 35 and 250 nm in size and are clustered together along the glassy matrix (closer observation is also given in Figure 4(c) indicating a “nanocomposite” structure [2, 12]) were initiated from the surface of zirconia grains. On the basis of this, the governing mechanism for the appearance of leucite phase in the glassy matrix is surface crystallization [11, 24]. All sintered samples showed two (or more) distinct phase structures with a glassy matrix phase reinforcing crystalline phase dispersed in the glassy matrix. In general, they have a very fine microstructure with agglomerates. It should be noted that dendritic-like leucite phase previously reported by several workers [12, 25] are also found here, especially for the samples subjected to high firing temperature or prolong dwell time [D5-D9]. These observations may be attributed to the influence of ZrO₂ additives as nucleating agents for leucite crystallization behavior, similar to those found in other similar glass-ceramic systems [12, 26].

Microstructural features of dental porcelain ceramics sintered at 1,060°C for 5 min (D0) are shown in Figure 4(a). It is seen that a smooth surface of typical porcelain glass-ceramics is observed, in agreement with those reported earlier [9, 12, 24]. SEM-EDX analysis of the dental porcelain ceramics (Figure 4(b)) marked as “Q” reveals the strong presence of silica and oxygen indicating the composition of glass matrix (Figure 4(d)). As shown in Figure 4(e) and (f), EDX spectra obtained from area “O” confirm the existence of all key elements related to the composition of leucite (KAlSi₂O₆) [19]. While EDX analysis of the large grain marked as “Q” shows only zirconia rich phase together with spectra of oxygen, indicating the existence of ZrO₂ additive. The results of SEM-EDX measurement supported the XRD observation discussed earlier (Figures 1 and 2).

Figure 4. Representative SEM micrographs of (a) dental porcelain, (b) D8 sample and (c) enlarged of (b) and their corresponding EDX analysis, indicating the chemical compositions of (d) glassy matrix, (e) leucite and (f) ZrO₂ phases, respectively.
Furthermore, there is no evidence of crack formation in the matrix or within the leucite crystals. From Figure 3, signs of leucite particle coalescence were visible in all Zr-modified porcelain samples which may have been driven by a reduction in interfacial energy when larger particles grow at the expense of smaller ones (Ostwald ripening) [27]. In this work, it is believed that apart from the sintering temperature affects, the prolonged soaking times may have allowed sufficient time for small particles below a critical size to dissolve and feed larger particles via a diffusion down the concentration gradient.

Impression of a Vickers indenter producing typical symmetry cracks, where the cracks propagate along the glassy phase of the matrix is illustrated in Figure 5(a,b), consistent with other similar porcelain-based ceramics [2,18]. While SEM image for ZrO₂-modified porcelains (D8) with maximum density value exhibits evidence of crack deflection (non-direct line) with the crystalline reinforced phase as shown in Figure 5(c,d), in agreement with literature [28]. The variations of mechanical properties with sintering conditions are also given in Table 1. For all ZrO₂-modified samples in the present work, the values of flexural strength, fracture toughness and hardness are slightly greater than that of dental porcelains (D0). Similar results have also been reported for other porcelain-base systems [2,28]. The results in Table 1 clearly indicate that the mechanical properties of the ZrO₂-modified dental porcelain ceramics depend on the densification derived from the sintering conditions. As listed in Table 1, maximum values of flexural strength, fracture toughness
and hardness increase from 154.6 MPa, 2.03 MPa-m^{1/2} and 7.20 GPa to 185.7 MPa, 2.40 MPa-m^{1/2} and 8.01 GPa as the sintering temperature increases from 1,060-1,140°C, with constant dwell time of 20 min. As also listed in Table 1, the similar tendency is also observed for the influence of dwell time from 20-30 min at a given sintering temperature. However, it is seen that the increase in the soaking time to 40 min results in a drop in the values of all mechanical properties, consistent with the densification results discussed earlier. This observation may be attributed to microstructural inhomogeneity of the porcelains as a result of leucite crystallization and/or agglomeration [14]. Consequently, the experimental work carried out here suggests that other factors such as the sintering conditions, the ZrO₂ additive, the leucite crystallization and microstructural arrangement clearly have some influence on the mechanical properties of the dental porcelain ceramics. Additional studies are essential to fully understand the mechanism of leucite crystallization and how this mechanism can be exploited in future to enhance or tailor the key mechanical properties of dental porcelain-based materials.

4. CONCLUSIONS

Results indicate that using different firing conditions (i.e. temperature and dwell time) to produce ZrO₂-modified dental porcelain ceramics greatly influences leucite crystallization, microstructure and mechanical properties of the resulting products. It has been concluded that using commercially available dental porcelain powders as the starting materials, a combination of the optimized firing condition and the addition of 20-wt% ZrO₂ has considerable potential for the production of leucite/porcelain ceramic-nanocomposites. It was also found that both the sintering temperature and dwell time are key factors in controlling dendritic morphology of leucite crystallization behavior and microstructural arrangement in Zr-modified dental porcelain ceramics.

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