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Contributed Paper

Influence of Sintering Temperature on Phase Formation, Microstructure and Mechanical Properties of the Recycled Ceramic Body Derived from CAD/CAM Dental Zirconia Waste

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ABSTRACT

Dental zirconia (ZrO_2) debris derived from computer aided design and computer aided manufacturing (CAD/CAM) waste was initially vibro-milled into nanosized ZrO_2 powders prior to ceramic fabrication. The optimal pressureless sintering temperature for the production of ZrO_2 ceramics was suggested via analysis of phase formation, microstructure, densification and mechanical properties results obtained from a combination of X-ray diffraction (XRD), scanning electron microscopy (SEM), Archimedes principle, Vickers hardness testing and three-point flexural strength techniques. The strength data was further analyzed using the one-way ANOVA with Scheffe post hoc test ($p = 0.05$) and Weibull analysis. Weibull modulus, characteristic strength and SEM characterizations were accomplished in the fracture mode. In general, it was found that no phases other than tetragonal ZrO_2 were observed in the samples sintered below $1100\text{ }^\circ\text{C}$ whilst a coexistence of both monoclinic- and tetragonal- ZrO_2 phases was found in the samples experienced higher sintering temperatures. Larger average grain sizes were observed for the samples sintered at higher temperature, whereas their porosities could be reduced resulting in an increasing of the relative density. This work demonstrated that both of physical and mechanical properties of the recycled ceramics derived from CAD/CAM dental ZrO_2 waste could be significantly tailored via the choice of sintering temperature at $1100\text{ }^\circ\text{C}$ which provides the most comparable properties to the commercial dental ZrO_2 pre-sintered block, showing the appropriation for CAD/CAM machining.

Keywords: dental zirconia, waste, sintering, phase formation, mechanical properties

1. INTRODUCTION

In recent years, zirconia (ZrO_2) ceramics have been utilized as one of the good choices available for manufacturing of dental prostheses via computer aided design and computer aided manufacturing (CAD/CAM) technology [1]. However, in these convenient and very rapid processes, dental ZrO_2 -based pre-sintered block debris (*i.e.* waste) obtained after being fabricated by soft machining is generally occurred [2] and generating a loss of about 30% of material [1]. In order to minimize an environmental impact together with raising value-added enhancement from these wastes, we are interested in recycling the ZrO_2 debris for the fabrication of ceramic body with characteristics comparable to those of freshly ZrO_2 pre-sintered blocks specified for such CAD/CAM machining. In connection with this, early attempt to reuse waste 3 mol% yttria-stabilized tetragonal zirconia (3Y-TZP) was performed by Kamiya *et al.* [3] where hydrothermal treatment and sintering temperature between 1450 and 1550 °C were examined. It was found that though the physical and mechanical properties of recycled ceramics were inferior than that of the original 3Y-TZP ceramics, this trend seems not only to be inevitable for the recycled 3Y-TZP but it might also be possible to apply as a recycling system for sintered ZrO_2 bodies. Elgayar *et al.* [2] later demonstrated an alternative cost reduction technique where 2 wt% of waste ZrO_2 powders from CAD/CAM systems were mixed with fresh ZrO_2 powders before shaping and sintering at 1250 °C for 4 h, resulting the ceramics with comparable flexural strength (1012 ± 101 MPa) to the controlled (*i.e.* 0 wt% of waste ZrO_2 adding) ZrO_2 ceramics (1090 ± 98 MPa). Moreover, in recent years, Silva *et al.* [4] reported the potential to recycle the wasted ZrO_2 powders derived from the machining

process of dental crowns and bridges via uniaxial and isostatic pressing techniques in comparison with the commercial ones. It is likely that the samples produced by using an isostatic pressing exhibited a reasonable physical and mechanical properties, comparable to those of the commercial ones indicating the potential to recycle these materials in the same process. However, there are no works with attention paid directly on the potential investigation of ZrO_2 block development for CAD/CAM process by using 100% waste dental ZrO_2 debris via a simple ceramic processing.

In our earlier work [5], a vibro-milling method was designed for production of nanosized ZrO_2 powders derived from CAD/CAM ZrO_2 waste. Interestingly, so far, no work has been done on investigation of further taking these ZrO_2 nanopowders to produce ZrO_2 ceramics. To perform this experiment, normal pressureless sintering technique is interested in terms of its simplicity, flexibility and cost-effective for the ceramic fabrication [6]. As is well-documented [6], varying sintering conditions can cause the changes of both physical and mechanical properties of ZrO_2 ceramics. Especially, sintering temperature is one of the key parameters controlling the properties of ZrO_2 ceramics. Therefore, in this work, effect of sintering temperatures on phase formation, microstructure, densification and mechanical properties of the recycled ceramics fabricated from CAD/CAM dental ZrO_2 waste is investigated and discussed in comparison with the as-received dental ZrO_2 -based pre-sintered block debris as the control sample. The potential of the present approach as an alternative way to recycle ZrO_2 waste is be explored. Moreover, important questions such as how the sintering temperature affects

both physical and mechanical properties of recycled ceramics and what is the optimal sintering temperature to produce ZrO_2 ceramic body suitable for potential forming dental prostheses via CAD/CAM machining are also addressed.

2. MATERIALS AND METHODS

2.1 Preparation of Ceramic Body from CAD/CAM Dental ZrO_2 Waste

Dental ZrO_2 -based pre-sintered block (BruxZir[®] shaded zirconia milling blanks) debris was collected in vacuum system after the daily CAD/CAM machining of prostheses from a dental laboratory of Hexa Ceram Co., Ltd. As-received powders were washed using deionized water to remove dust and any possible contamination and finally dried at 120 °C for 24 h in an oven to remove the water content in waste zirconia powders. The rapid mechanical milling technique was employed to produce ZrO_2 nanopowders by vibro-milling these coarse powders for 2 h, as detail given in our earlier publication [5]. After powder treatment process, ceramic fabrication was achieved without adding any binder by simply uniaxial pressing the obtained nanopowders as pellets (~15 mm in diameter and ~7 mm thick) in a uniaxial die press at 100 MPa. Each pellet (green body) was placed in an alumina plate and sintered in air at temperature ranging from 950 to 1250 °C with dwell-time of 2 h and heating/cooling rates of 5 °C min^{-1} applied.

2.2 Characterization of Ceramic Body

All recycled ceramic bodies together with the as-received dental ZrO_2 -based pre-sintered block debris (the control) were subsequently characterized by room temperature X-ray diffraction (XRD; Rigaku, MiniFlex II and SmartLab), using Ni-filtered CuK_{α} radiation to identify phase formation

of all samples. The tetragonality factor (c/a) of the sintered ceramics was calculated from the XRD patterns. Shrinkage testing was measured from the thickness, diameter and volume of all fabricated ZrO_2 samples before and after sintering processes by using vernier caliper (digimatic, Mitutoyo). Before studying the microstructural development of the ceramics by using SEM (JEOL JSM-840A) technique, the fracture surfaces of all samples were sputtering-coated with gold. Grain size of all samples was directly determined from the SEM micrographs and linear intercept method, respectively. The relative density was calculated from the ratio of the measured bulk density using Mettler Toledo density kit following Archimedes' principle by immersing the sample into a water-based liquid to the theoretical density, which was taken as 6.1 g/cm^3 [7].

To determine the mechanical properties of the ceramic bodies, hardness values of all samples were determined by using the Vickers hardness measurement (STARTECH SMV-1000) with a conventional diamond pyramid indenter. The diagonals of each indentation were measured using an optical microscope. The Vickers hardness (H_v) values of each condition were subjected to a load of 10 kgf and a holding times of 15 s in ten different areas for each sample. Fracture toughness (K_{Ic}) was then determined by measuring the crack length emanating from the indentation center as indicated by the equation of Anstis *et al.* [8]. To assess fracture reliability of the sintered ceramics, three-point flexural strength (total number of specimens, $N = 120$; number of samples per group $n = 20$) was measured according to the ISO 6872:2008 [9]. After sintering, the final dimensions of all the specimens were 1.2 mm \times 4 mm \times 25 mm. The specimens were then placed in an appropriate sample holder and loaded in a Universal testing machine

(Tira test 2420, Tira Maschinenbau GmbH, Rauenstein, Germany) at a crosshead speed of 1 mm/min until failure. The specimens were tested dry at room temperature. Finally, the flexural strength of the samples was calculated by employing an equation of Stawarczyk *et al.* [9]. Statistical analysis of flexural strength data between materials was obtained with one-way ANOVA, followed by least significant difference (LSD) t-test ($\alpha = 0.05$, SPSS 16.0) and Scheffe post hoc test at a significance level (p) of 0.05. In addition, the Weibull moduli were calculated from 20 flexural strength data according to the conditions advocated by Nohut *et al.* [10].

3. RESULTS AND DISCUSSIONS

Apart from the applications of ZrO_2 -based ceramics itself, it is well-documented that ZrO_2 particles with metastable tetragonal phase have normally been used as a dispersed phase in several advanced ceramics to enhance their mechanical properties (e.g. tensile strength, wear resistance and fracture toughness). Therefore, to further examine the influence of different sintering temperatures on phase formation of the as-prepared ZrO_2 ceramics, XRD technique was employed. The XRD patterns of recycled ZrO_2 ceramics experienced sintering temperatures ranging from 950 to 1250 °C together with as-received dental ZrO_2 -based pre-sintered block debris (the control) are shown in Figure 1(a). The results indicated that all ceramics sintered at 950 to 1050 °C show tetragonal (t) ZrO_2 phase, which could be matched with the JCPDS file number 17-0923 with lattice constants $a = 5.12 \text{ \AA}$ and $c = 5.25 \text{ \AA}$ and is stable at room temperature. However, the recycled ZrO_2 ceramics sintered at 1100 to 1250 °C clearly show both (t) ZrO_2 major phase as well as little amount of

monoclinic (m) ZrO_2 phase, which could be matched with the JCPDS file number 37-1484 with lattice parameters $a = 5.312 \text{ \AA}$, $b = 5.212 \text{ \AA}$, $c = 5.147 \text{ \AA}$ and $\beta = 99.128^\circ$ as a minor phase. In addition, no evidence of other peaks corresponding to any new phase was observed for all samples, which is consistent with those observed by Kamiya *et al.* [3] and Shojai *et al.* [11]. This is clear from the data collected in the 2θ range of 27 to 34°, within which the main peaks of all ZrO_2 polymorphs must appear, as shown in Figure 1(b). These results revealed that very weak m ($\bar{1}11$) and m (111) peaks were observed in the recycled ZrO_2 ceramics sintered above 1050 °C when strong t (111) peak of all samples was adjusted into the same level. The m ($\bar{1}11$) and m (111) peaks became relatively stronger with increasing sintering temperature. To obtain the comparable quantities, the weight percent of (m) ZrO_2 phase content in each sample may, in principle, be estimated from the intensities of the most intense X-ray reflections for the (t) and (m) phases by employing the following equation:

$$\text{wt.\% monoclinic phase} = \left(\frac{I_{m(\bar{1}11)}}{I_{t(111)} + I_{m(\bar{1}11)}} \right) \quad (1)$$

This equation which is similar to those extensively used in the field of ceramics [12], should be seen as a first approximation since its applicability requires comparable maximum absolute intensities of the pair of (t) and (m) ZrO_2 peaks being used [12]. Here I_m and I_t refer to the intensities of m ($\bar{1}11$) and t (111) peaks, respectively. On the other hand, if the expected ratio between the intensities of the two monoclinic peaks (*i.e.* m ($\bar{1}11$) and m (111)) is known and the intensity of m (111) peak can be accurately determined [13, 14], then the integrated intensity ratio (X_m) is also used apart from

eq. (1) as:

$$X_m = \frac{I_{m(\bar{1}11)} + I_{m(111)}}{I_{m(\bar{1}11)} + I_{m(\bar{1}11)} + I_{t(111)}} \quad (2)$$

where the subscripts *m* and *t* refer to the monoclinic and tetragonal phases, respectively and $I_{(hkl)}$ refers to the integration of the diffraction line intensity indicated by its Miller indices. Eq. (2) was originally intended to identify the fraction of weight percent of (m) ZrO₂ phase in a polymorphic mixture of ZrO₂ by constructing linear calibration curves for X_m as a function of the actual weight fraction of monoclinic. Nevertheless, a linear intensity concentration relationship is established from the hypothesis that the intensities of peak are equal to sum of the (m) peaks $I_{m(\bar{1}11)} + I_{m(111)}$, which are not strictly correct [14] because the possible errors introduced into the analytical procedure due to preferred orientation of ZrO₂ grains during the sample preparation for XRD measurement, known mixtures of (t) and (m) ZrO₂ were carefully prepared and analyzed [15]. To determine the relative contents of the phases present, eqs. (1) and (2) have been applied to these XRD patterns. The results for the two equations are compared (tabulated in Table 1) as a function of sintering temperatures. It was found that the (m) ZrO₂ content derived from eq. (2) is higher than that from eq. (1). This might be due mainly to an error from the measurement of the integrated intensities of partially overlapping m (111) and t (111) reflections [13] or an unequal $I_{t(111)}$ to the sum of $I_{m(\bar{1}11)}$ and $I_{m(111)}$ [14] as mentioned earlier. In addition, they show that the qualitative concentrations of (m) ZrO₂ phase calculated from both equations tend to increase significantly whereas the qualitative concentrations of (t) ZrO₂ phase tend to decrease when higher sintering temperatures were applied, which is in agreement with other works [16]. With

increasing the sintering temperature, (m) content is increased which could be due to grain growth [16]. Moreover, the (m) phase could be also noticed in the control sample. This could be due to due to the martensitic (t) to (m) phase transformation induced by mechanical stress during CAD/CAM process [5]. Therefore, the amount of (m) phase in the control sample is not calculated here. Since the amount of transformable (t) phase is crucial to explain the relationship between phase transformation and mechanical properties, the transformability of the (t) phase in the recycled ceramics sintered at 1100 °C and 1250 °C was also studied. These two samples were chosen as the representatives for the employed lowest and highest sintering temperatures which cause the phase transformation from (t) to (m) in this study. The ceramics were crushed and grinded in an alumina mortar for 5 minutes to obtain the fine powders and the changes in the amount of (m) phase content were determined in comparison with the non-grinded ceramics [17]. The results are shown in Figure 2 and Table 2. It was found that the ceramics sintered at 1100 °C and 1250 °C have the transformable (t) phase ~2.1(4.3)% and ~1.1(1.9)%, respectively. Literally, higher transformability should cause better mechanical properties such as higher fracture toughness or higher flexural strength due to the (t) → (m) transformation toughening [17]. In this case, the sample sintered at 1250 °C provides superior mechanical properties (Table 3) even though the transformability fraction of (t) phase is lower than that of the ceramics sintered at 1100 °C. Therefore, the tetragonal phase amount should not be only the factor which is responsible for the improvement of mechanical properties here since there are other variable factors. For example, higher relative densities obtained from the ceramics

sintered at higher temperatures might cause higher values of those mechanical properties. However, for practical application aspect, the better way to determine the appropriate sintering temperature should

be the referring to the reference sample which is the as-received dental ZrO₂-based pre-sintered block debris (the control) in the present work which would be discussed later.

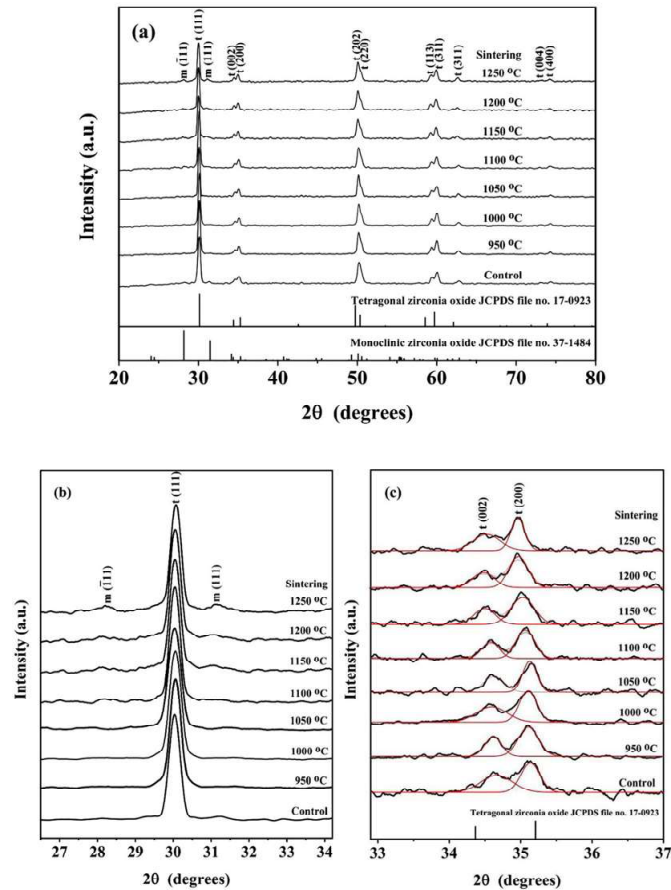


Figure 1(a). XRD patterns of as-received dental ZrO₂-based pre-sintered block (control) and recycled ZrO₂ ceramics sintered at various temperatures, (b) enlarged zone of (a) showing the relative ratios of the t (111), m ($\bar{1}\bar{1}\bar{1}$) and m (111) peaks and (c) enlarged zone of (a) showing relative ratios of the t (002)/t (200) peaks (data taken using the Rigaku, MiniFlex II X-ray diffractometer).

Table 1. Calculated monoclinic/tetragonal ZrO₂ phases as a function of sintering temperatures.

Sintering (°C/h)	Qualitative concentrations of ZrO ₂ phase calculated by eq. (1)		Qualitative concentrations of ZrO ₂ phase calculated by eq. (2)	
	Monoclinic wt. (%)	Tetragonal wt. (%)	Monoclinic wt. (%)	Tetragonal wt. (%)
1100/2	11.51	88.49	22.57	77.43
1150/2	17.85	82.15	29.73	70.27
1200/2	19.01	80.99	32.85	67.15
1250/2	23.07	76.93	35.82	64.18

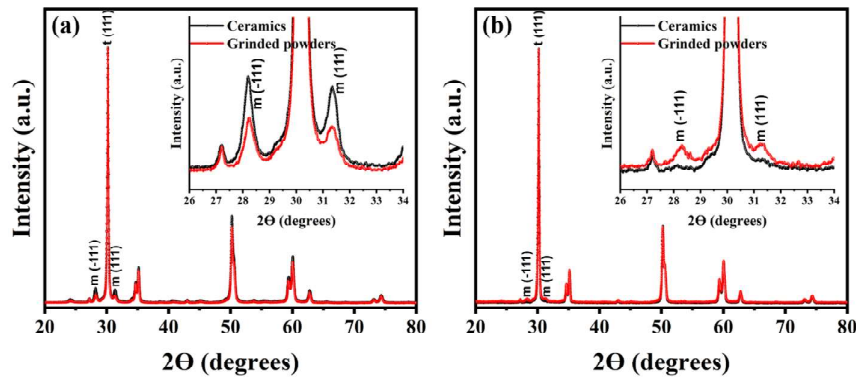


Figure 2. XRD patterns of recycled ZrO_2 ceramics sintered at (a) 1100 °C and (b) 1250 °C and their grinded powders (data taken using the Rigaku, SmartLab X-ray diffractometer).

Table 2. Calculated monoclinic/tetragonal ZrO_2 phases of the recycled ceramics before and after grinding.

Sintering (°C/h)	Qualitative concentrations of ZrO_2 phase calculated by eq. (1)			Qualitative concentrations of ZrO_2 phase calculated by eq. (2)		
	Monoclinic wt. (%)	Tetragonal wt. (%)	Transformable tetragonal fraction (%)	Monoclinic wt. (%)	Tetragonal wt. (%)	Transformable tetragonal fraction (%)
1100/2 before	6.13	93.87	2.1	11.30	88.70	4.3
1100/2 after	4.15	95.85		7.50	92.50	
1250/2 before	1.39	98.61	1.1	3.05	96.95	1.9
1250/2 after	2.48	97.52		4.90	95.10	

Also, the relative intensities of the Bragg peaks, the variation of $t(002)$ and $t(200)$ peaks splitting seem to be observed from XRD patterns. Zooming in these regions around 2θ of 33 to 37° could clarify this detailed alteration, as presented in Figure 1(c). It is seen that the XRD patterns of all samples show the presence of both (002) and (200) peaks confirming their tetragonal symmetries. Considering the cases of recycled ZrO_2 ceramics, the degree of (002)/(200) peaks splitting tend to increase after sintering from 950 to 1050 °C, and then gradually decrease with further increasing of the sintering temperature from 1100 to 1250 °C. It may be associated with (t) to (m) phase transformation causing many stresses and strains of both thermal and mechanical treatments during sintering process to be included in the ZrO_2 containing tetragonal

phase [18]. These findings certainly affect the tetragonality ($c_{(002)}/a_{(200)}$) factors of the tetragonal ZrO_2 phase. The estimated c/a values for all samples are given in Table 3 as a function of the sintering temperature. It may be concluded that changing of c/a ratio is associated with phase transformation causing an internal mechanical stress from heat treatment included in structure, in agreement with earlier work [19]. Now, it can be summarized that sintering temperatures in the range 950 to 1050 °C may be appropriate to fabricate the recycled ZrO_2 ceramic blocks because this condition seems to provide the pure phase after comparing with the control. To further identify the optimal sintering temperature for the production of recycled ZrO_2 ceramics, SEM technique was performed to reveal the microstructural evolution of these samples.

Table 3. Sintering behaviors of ZrO₂ ceramics derived from different fabrication technique.

Materials	Processing [Ref.]	Sintering (°C/h)	Tetragonality (c/a)	Physical properties		Mechanical properties					
				Relative density ^a (%)	Grain size range/mean ^b (nm)	Vickers hardness (GPa)	Fracture toughness (MPa·m ^{1/2})	Flexural strength (MPa)			
Control		-	1.00895	60.30	48.89-108.10/98.80	2.30±0.06	1.15±0.14	71.25±19.55			
ZrO ₂ ceramics (this work)	Normal sintering	950/2	1.01013	55.34	31.54-108.89/84.91	1.48±0.12	0.86±0.16	9.87±6.77			
		1000/2	1.01028	68.53	41.99-137.90/88.88	2.48±0.10	1.20±0.10	14.26±8.33			
		1050/2	1.01072	75.86	54.26-140.89/95.70	5.01±0.14	2.21±0.11	27.36±13.10			
		1100/2	1.01151	78.21	57.03-144.79/98.59	5.37±0.17	2.82±0.16	60.67±25.43			
		1150/2	1.00952	84.27	80.99-186.33/130.12	6.50±0.20	3.13±0.10	120.93±49.86			
		1200/2	1.00873	86.98	101.19-187.61/145.25	7.52±0.13	3.61±0.21	160.84±67.28			
		1250/2	1.00853	91.28	114.76-209.63/190.77	8.44±0.25	4.32±0.28	212.00±38.60			
		800/2	-	50.08	-	0.94	0.43	-	-		
		8500/2	-	52.24	-	1.07	0.61	-	-		
		900/2	-	54.24	-	1.15	0.86	-	-		
Y-TZP ceramics	Normal sintering [7]	950/2	-	56.73	-	1.55	0.94	-	-		
		1000/2	-	69.38	-	2.81	1.13	-	-		
		1050/2	-	78.20	-	5.15	2.25	-	-		
		1350/2	-	94.57	-	10.94±0.34	5.14±0.25	-	-		
		1400/2	-	96.89	-	11.48±0.21	5.08±0.23	-	-		
		1450/2	-	97.57	-	12.37±0.37	4.82±0.26	-	-		
		1500/2	-	98.05	-	11.97±0.39	5.47±0.34	-	-		
		1550/2	-	99.11	-	12.19±0.31	5.20±0.26	-	-		
		1490/2	-	97.62	-	-	-	628.30±40.60	-		
		1530/2	-	98.25	-	-	-	693.32±85.33	-		
Y-TZP ceramics	Normal sintering [27]	1570/2	-	99.41	-	-	-	708.70±49.14	-		
		1610/2	-	98.77	-	-	-	628.30±40.60	-		
		1100/2	-	97.15	-	1.65	-	-	-		
		1150/2	-	97.21	-	2.35	-	-	-		
		1200/2	-	97.65	-	5.85	-	-	-		
		1250/2	-	99.08	-	9.45	-	-	-		
		ZrO ₂ ceramics	Cold isostatic pressing with normal sintering [28]	1150/2	-	97.21	-	1.65	-	-	-
				1200/2	-	97.65	-	5.85	-	-	-

^aEstimated precision of the density is ± 1%. ^bEstimated precision of the grain size is ± 0.1%.

As shown in Figure 3, surface micrograph of as-received dental ZrO₂-based pre-sintered block debris (control) is similar to those of recycled ZrO₂ ceramics sintered at 950 to 1100 °C. In general, these samples exhibit small grain size and loosely bonded grains consisted of many pores. When the sintering temperatures were increased over 1100 °C, it can be seen that the grain size enlarged continuously while the pore size decreased obviously and the adjoining of grains was dramatically improved. Average values of grain size measured by the linear intercept method are revealed in Figure 4 and Table 3. Two distinct regions are observed according to the change of average grain size as a function of sintering temperature. In the first region (950 to 1100 °C), the average grain size gradually increases from ~84 to 95 nm. At a low sintering temperature, the point contacts between particles grew into necks which represented the initial state of sintering. Whereas in the second region (1150 to 1250 °C), the average grain size drastically increases from ~161 to 299 nm because the grain growth became increasingly active due to the higher sintering temperature [6]. Moreover, the increase in grain size resulted from a high sintering temperature, which activated grain boundary diffusion and lattice diffusion leading to continuous growth, resulting in a slight reduction of pores [11]. Thus, the shrinkage in thickness, diameter and volume of recycled ZrO₂ ceramics in each sample were investigated as shown in Figure 5. The results show that the samples experienced lower sintering temperatures from 950 °C and 1000 °C exhibit a lower shrinkage. When sintering temperature is increased from 1050 to 1250 °C, the shrinkage of the samples tends to increase significantly. The increase of shrinkage with increasing temperature was attributed to elimination of pore by interconnecting

between grains [11]. To produce recycled ZrO₂ ceramic bodies for forming dental prostheses via CAD/CAM machining, the relative density of ZrO₂ ceramics must be considered. The relative densities of recycled ZrO₂ ceramics are shown in Figure 4 and Table 3. It can be seen that ceramics with higher relative density are obtained after experiencing higher sintering temperature, in agreement with Liang *et al.* [7] and Shojai *et al.* [11] because of the increased elimination of porosities under enhanced diffusion at higher temperatures as corresponded with microstructure investigation previously given in Figure 3. Clearly, the grains expand further and particles contacted more with each other. It is likely that the decrease in the pore numbers leads to an increase of densification after applying higher sintering temperatures [11]. This is in agreement with the result of SEM observations (Figure 3). Microstructure and densification changes observed here thereby lay the fundamental to understand the influence of sintering temperature on mechanical properties of these materials.

In connection with this, the mechanical properties of recycled ZrO₂ ceramics experienced various sintering temperatures were explored in comparison with those of as-received dental ZrO₂-based pre-sintered block debris (control). Also depicted in Table 3, it was found that the Vickers hardness values of recycled ZrO₂ ceramic samples increase slowly with increasing sintering temperature up to 1050 °C, whereas the hardness values increase rapidly when sintering temperatures exceed 1050 °C were employed. Increasing in hardness was likely caused by densification, resulting in the formation of strong bonding along the grain boundaries among ZrO₂ grains, which is in agreement with Kamiya *et al.* [3]. Moreover, the different amounts of porosity and larger grain size of the samples

sintered at higher sintering temperatures may be the important factors leading to different hardness values [3, 6, 11]. From Table 3, it is seen that the recycled ZrO_2 ceramics sintered at 1000 °C exhibit similar hardness with the control block debris,

indicating an empirical optimum sintering temperature for this work. On the other hand, recycled ZrO_2 ceramics sintered at the temperature above 1050 °C may cause the wear of the milling instruments and surface defects of ZrO_2 ceramic blocks.

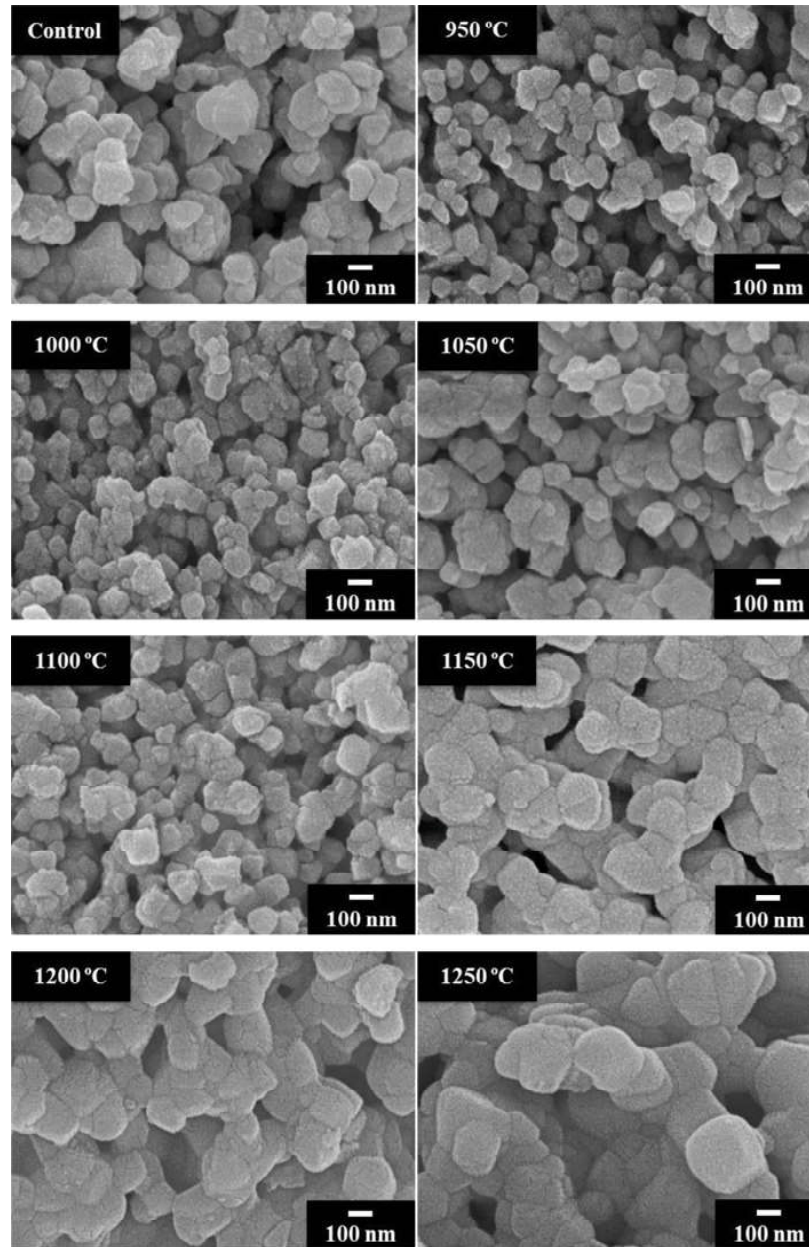


Figure 3. SEM images of as-received dental ZrO_2 -based pre-sintered block (control) and as-sintered recycled ZrO_2 ceramics sintered at various temperatures.

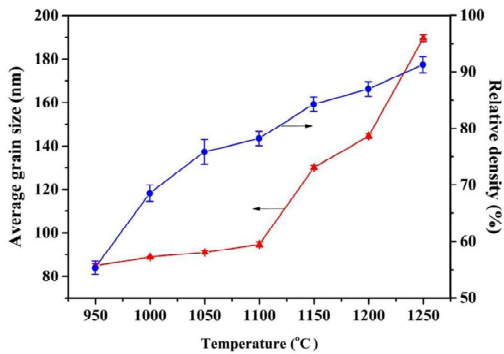


Figure 4. Variation of grain size and density with sintering temperature for recycled ZrO_2 ceramics sintered at various temperatures.

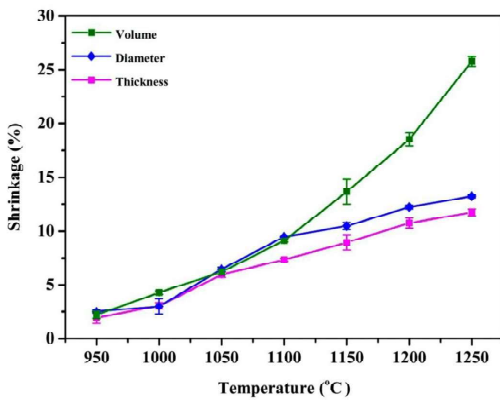


Figure 5. Variation of a shrinkage in volume, shrinkage in diameter and shrinkage in thickness of recycled ZrO_2 ceramics sintered at various temperatures.

As is well-documented, the applied stress from mechanical testing can cause the microstructural changes and phase switching of ZrO_2 ceramics, with the associated volume expansion. Phase transformation puts the crack propagation into compression and restricts its further growth. This mechanism of transformation toughening enhances the fracture toughness. Related to this, the results of the fracture toughness test of samples after sintering at different temperatures are given in Table 3. As expected, the fracture toughness values of the recycled ZrO_2 ceramics increase gradually as the sintering temperature increases. Generally, sintering temperature has the

direct impact on the phase content through influencing the grain size, which has an effect on (t) ZrO_2 stability. It affects the transformability of (t) ZrO_2 which is much dependent on its grain size, *i.e.*, the larger grain size is more transformable [15]. This increase in fracture toughness is likely related to the increase in matrix grain size [3, 6]. In addition, the K_{IC} improvement is partly attributed to the different relative density of recycled ZrO_2 ceramics because sintered samples with higher relative densities exhibited greater fracture toughness values [20]. Moreover, decreasing of porosity in microstructure may be related to increase of K_{IC} . Therefore, the results indicated that the toughness values of recycled ZrO_2 ceramics sintered at 1000 °C can be comparable to toughness value of as-received dental ZrO_2 -based pre-sintered block debris (control).

In connection with this, the SEM technique was employed to further examine the fracture microstructure evolution of these recycled ZrO_2 ceramics. It is obvious that the sintering temperature influenced the fracture surface of recycled ZrO_2 ceramic samples as shown in Figure 6. Studies found that fracture surfaces of the recycled ZrO_2 ceramics sintered at 950 to 1250 °C and the as-received dental ZrO_2 -based pre-sintered block debris (control) exhibit intergranular predominantly, indicating that the grain boundaries are mechanically softer than the grains [21]. As the temperature increased to 1250 °C, homogeneous microstructure of the recycled ZrO_2 ceramics is observed with low degree of porosity similar to that found in the commercial material. Moreover, samples show a fracture surface containing highly dense faceted grain packing and the presence of sharp grain boundary edges (marked the circle as shown in Figure 6). These faceted grains exhibited both

intergranular and transgranular fracture where proportion of each mode of fracture depends on the sintering temperatures [20]. As shown in Figure 3, these factors may

contribute to greater flexural strength values. Furthermore, the changes in flexural strength can be related with the decreasing of porosity in sintered recycled ZrO_2 ceramics [10].

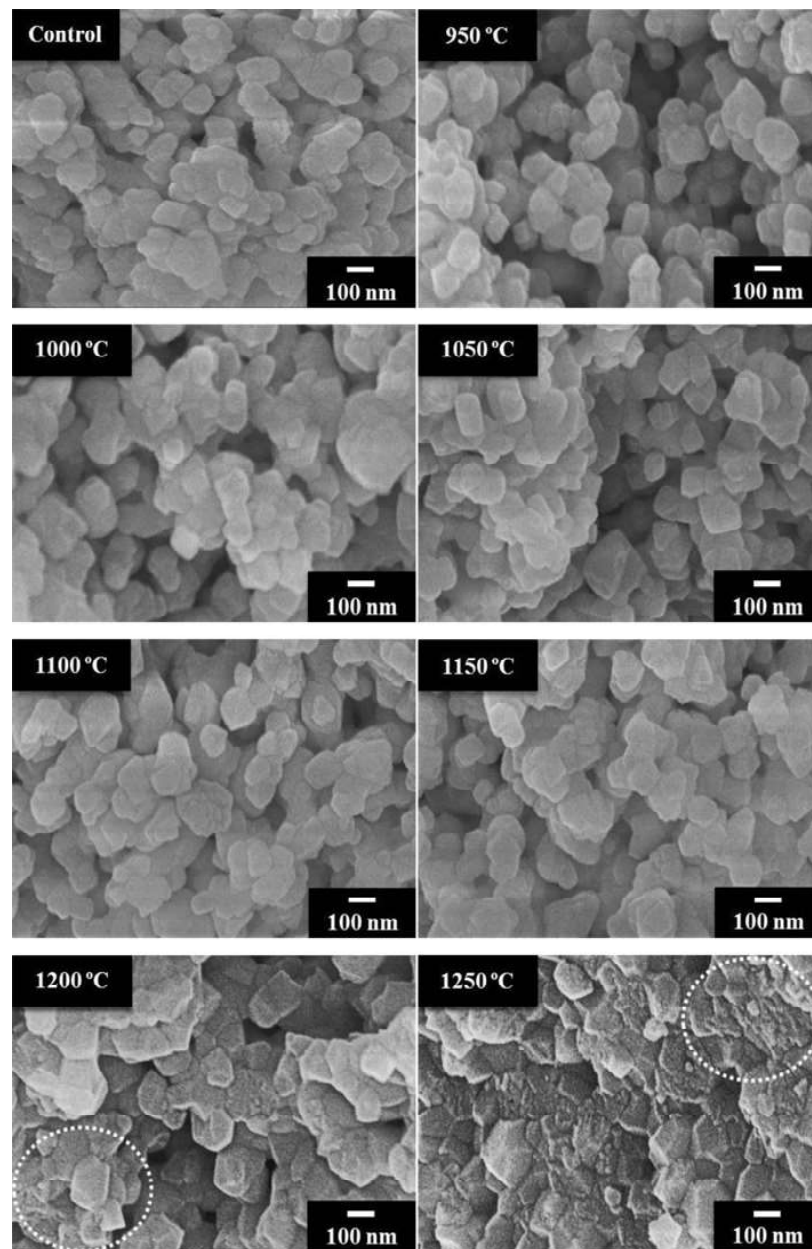


Figure 6. SEM images of fracture surfaces of as-received dental ZrO_2 -based pre-sintered block (control) and as-sintered recycled ZrO_2 ceramics sintered at various temperatures.

To investigate the flexural strength values for all material conditions, significant differences by one-way ANOVA analysis and Scheffé post hoc test were calculated for strength data (Table 4) with SPSS software. After calculation, there is a significant difference between the each group of samples at flexural strength values ($P < 0.05$). In this connection, the fracture data for all material conditions is represented in a Weibull plot (Figure 7) and the data for each condition was then analyzed following Weibull statistical distribution function. It was observed that curve changing in Weibull distribution for the control and recycled ZrO_2 ceramics after applying various sintering temperatures depends on the applied stress due to difference of strength in specimens during testing [22]. Moreover, it can be observed that slopes of the Weibull fit for flexural strength values show wider distributions for the recycled ZrO_2 ceramics sintered at 950 to 1100 °C and narrower for those sintered at 1150 to 1250 °C and the as-received dental ZrO_2 -based pre-sintered block debris. The microstructural homogeneity in fracture surface (Figure 6) also influences the distribution of stresses. The corresponding statistical Weibull parameters derived for each condition are given in Table 5. It should

be noted that the Weibull modulus (m) of dental ZrO_2 -based pre-sintered block debris is $m = 3.69$. For recycled ZrO_2 ceramics sintered at 950 to 1250 °C, m values increase from 1.74 to 6.53, respectively. This m changing can be monitored in the increase of slope of the Weibull fit for each sintering temperature (Figure 7). Variation of the strength or asymmetrical strength distribution is probably due mainly to flaws and microcracks within the microstructure can be represented by using the m value [23, 24]. A lower m value means that the samples contain more flaws and defects. Whilst, a higher m value reflects a smaller error range and therefore better structural reliability [23]. For the Weibull characteristic, strength (σ_0) is the strength happening for a particular test specimen. It is obvious that the σ_0 values are in good agreement with the mechanical strength regarding difference of flexural strength values (Table 3) and homogenous microstructure (Figure 6). Moreover, the $\sigma_{0.05}$ for all samples are also presented since the limits for fractural strength for reliable use in dentistry are recommended to be set at a failure probability = 5% [25]. It was found that the $\sigma_{0.05}$ values show the same trend as the σ_0 values.

Table 4. Summary of one-way ANOVA for flexural strength data of recycled ZrO_2 ceramics after sintered at various temperatures.

Sample groups of flexural strength data	Sun of Squares (SS)	df	Mean Square (MS)	F	Sig.
Between groups	769912.205	7	109987.458	140.692	< 0.01
Within groups	118827.987	152	781.763		
Total	888740.192	159			

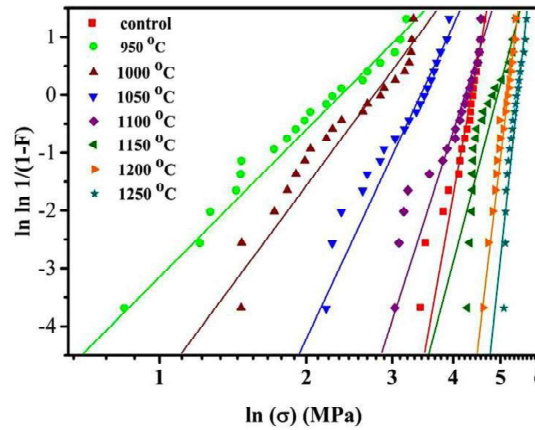


Figure 7. Weibull plots of uniaxial flexure strength for as-received dental ZrO₂-based pre-sintered block (control) and recycled ZrO₂ ceramics sintered at various temperatures.

Table 5. Weibull regression analysis for flexural strength data of recycled ZrO₂ ceramics after sintered at various temperatures.

Materials	Processing [Ref.]	Sintering (°C/h)	<i>m</i> Value	σ_0	$\sigma_{0.05}$ (MPa)
Control		-	3.69	76.93	34.46
ZrO ₂ ceramics (this work)	Normal sintering	950/2	1.74	11.38	2.07
		1000/2	1.86	16.14	3.27
		1050/2	2.21	30.73	8.05
		1100/2	2.33	66.87	18.71
		1150/2	2.82	137.91	48.14
		1200/2	5.70	174.01	103.41
		1250/2	6.53	229.90	145.89
Y-TZP ceramics	Normal sintering [24]	1350/2	10.0	-	-

* There is no significant Weibull statistical different ($p > 0.05$) between materials with the same superscript letters. *m* value is the Weibull modulus; σ_0 is the Weibull characteristic strength and $\sigma_{0.05}$ is the stress levels at 5 % probability of failure.

Finally, in order to check whether the physical and mechanical properties of recycled ZrO₂ ceramics achieved in the current work are in acceptable ranges, the determined values for the relative density, hardness, fracture toughness and flexural strength are compared with the related research reported by other groups [19, 26-28] as presented in Table 3. Especially, the flexural strength could be considered as the ideal mechanical properties

of the pre-sintered block for CAD/CAM since the company reports this value for commercial purpose [29]. Due to this, the range of most desirable flexural strength as dental block for CAD/CAM machining should be in the same range as the control sample which are ~51-91 MPa as tabulated in Table 3. Considering this point, the recycled ZrO₂ ceramics sintered at 1100 °C could be evaluated as the possible candidate as dental

block for CAD/CAM machining since they provide the comparable flexural strength ($\sim 35\text{-}86$ MPa). Moreover, it was found that the key properties of the ceramic body developed in the present study are comparable with other ZrO_2 ceramic products. Employing higher sintering temperature range (1350-1610 °C) by Hasanuzzaman *et al.* [26] and Hua *et al.* [27] than our work was found beneficial for the mechanical properties. However, their results show that using higher sintering temperatures did not provide much improved physical and mechanical properties compared to the lowest sintering temperature designed in each work, unlike significantly observed in our work. It was found that the different porosity of samples could be an important factor leading to differences of hardness and fracture toughness values [30, 31]. This could guide us to design a reasonable upper limit that we might not need to employ too high sintering temperature to achieve the products with comparable properties as the control (*i.e.* the as-received dental ZrO_2 -based pre-sintered block debris for the present work). Moreover, comparing the relative density values of ZrO_2 ceramics derived from this present work versus Hao *et al.* [28] as shown in Table 3 was found that employing the cold isostatic pressing technique in their case [28] can produce ZrO_2 ceramics with higher density than using uniaxial die pressing as in our case, at the same temperature (1100 to 1250 °C). This may be due to better particle packing uniformity for their case. However, the pressure in cold isostatic pressing must be released slowly since the air is originally compressed within the powders [6]. Thus, conventional sintering is still more attractive sintering method to produce ceramic products, mainly due to its simplicity and reasonable cost compared to other methods in terms of the recycling

issues of these wastes for the future and also the effectiveness of manufacturing points of view.

In this work, it can be summarized that the physical and mechanical properties of recycled ZrO_2 ceramics via normal sintering process are gently dependent on the sintering temperature as presented in Table 3. Furthermore, the grain size and the distribution played an important role in influencing the densification behavior and mechanical properties. Consideration of all findings related to both physical and mechanical properties, recycled ZrO_2 ceramics sintered at 1100 °C may be suitable selection of sintered condition in forming dental prostheses via CAD/CAM machining from the sintered ceramic body in the future. This is due to the most comparable properties with as-received dental ZrO_2 -based pre-sintered block debris (control). However, further works are recommended especially the investigation with attention paid on other key properties, such as transparency or biocompatibility for better practical and versatile clinical applications.

4. CONCLUSION

The influence of sintering temperature on phase formation, microstructure, densification and mechanical properties of ZrO_2 -based ceramics derived from recycled ZrO_2 nanopowders has been investigated. No phases other than tetragonal ZrO_2 were observed in ceramics sintered at 950 to 1050 °C but the monoclinic- and the tetragonal- ZrO_2 phases were observed at sintering temperatures from 1100 to 1250 °C. Grain size, density and shrinkage of recycled ZrO_2 ceramics increased with the increase of sintering temperature. Moreover, sintering conditions play critical role on mechanical properties of the recycled ZrO_2 ceramics. Comparing the measured properties of the

recycled ceramics sintered at 1100 °C with the control results demonstrated that the present approach is a promising strategy to recycle CAD/CAM ZrO₂ wastes.

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REFERENCES

- [1] de Assis L.C.L., de Magnago R.O., da Silva C.A.A., Habibe A.F., Villanova G.R.L. and dos Santos C., *Mater. Sci. Forum*, 2014; **798-799**: 632-637. DOI 10.4028/www.scientific.net/MSF.798-799.632.
- [2] Elgayar I. and Aboushelib M.N., *Int. J. Chem. Appl. Biol. Sci.*, 2014; **1**: S132-S134. DOI 10.4103/2348-0734.146957.
- [3] Kamiya M., Mori Y., Kojima T., Sasai R. and Itoh H., *J. Mater. Cycles Waste Manag.*, 2007; **9**: 27-33. DOI 10.1007/s10163-006-0168-3.
- [4] Silva Y.B.F., Acchar W. and Silva V.M., *Mater. Sci. Forum*, 2017; **881**: 387-391. DOI 10.4028/www.scientific.net/MSF.881.387.
- [5] Sriboonpeng C., Nonkumwong J., Srisombat L. and Ananta S., *Chiang Mai J. Sci.*, 2017; **44**: 1100-1112.
- [6] Moulson A.J. and Herbert J.M., *Electroceramics Materials, Properties and Applications*, 2nd Edn., John Wiley and Sons, New York, 2003.
- [7] Liang X., Qiu Y., Zhou S., Hu X., Yu G. and Deng X., *J. Univ. Sci. Technol. B*, 2008; **6**: 764-768. DOI 10.1016/S1005-8850(08)60284-4.
- [8] Anstis G.R., Chantikul P., Lawn B.R. and Marshall D.B., *J. Am. Ceram. Soc.*, 1981; **64**: 533-538. DOI 10.1111/j.1151-2916.1981.tb10320.x.
- [9] Stawarczyk B., Ozcan M., Hallmann L., Ender A., Mehl A. and Hammerlet C.H.F., *Clin. Oral Invest.*, 2013; **17**: 269-274. DOI 10.1007/s00784-012-0692-6.
- [10] Nohut S. and Lu C., *Ceram. Int.*, 2012; **38**: 4979-4990. DOI 10.1016/j.ceramint.2012.02.093.
- [11] Shojai F. and Mantyla T.A., *J. Mater. Sci.*, 2001; **36**: 3437-3446. DOI 10.1023/A:1017908011672.
- [12] Tipakontitikul R. and Ananta S., *Mater. Lett.*, 2004; **58**: 449-454. DOI 10.1016/S0167-577X(03)00523-8.
- [13] Toraya H., Yoshimura M. and Somiya S., *J. Am. Ceram. Soc.*, 1984; **67**: C-119-C-121. DOI 10.1111/j.1151-2916.1984.tb19715.x.
- [14] Schmid H.K., *J. Am. Ceram. Soc.*, 1987; **70**: 367-376. DOI 10.1111/j.1151-2916.1987.tb05009.x.
- [15] Whitney E.D., *Trans. Faraday Soc.*, 1965; **61**: 1991-2000. DOI 10.1039/TF9656101991.
- [16] a) Li J., Tang Z., Zhang Z. and Luo S., *Mater. Sci. Eng. B*, 2003; **99**: 321-324. DOI 10.1016/S0921-5107(02)00563-9., b) Kawai Y., Uo M., Wang Y., Kono S., Ohnuki S. and Watari F., *Dent. Mater. J.*, 2011; **30**: 286-292. DOI 10.4012/dmj.2010-175, c) Lu F., Zhang J., Huang M., Namavar F., Ewing R.C., and Jie L., *J. Phys. Chem. C*, 2011; **115**: 7193-7201.

- DOI /10.1021/jp109558s, d) Cheema T. A. and Garnweitner G., *CrystEng Comm*, 2014; **16**: 3366-3375. DOI 10.1039/c3ce42392a.
- [17] Khor K.A. and Yang J., *Mater. Lett.*, 1997; **31**: 23-27. DOI 10.1016/S0167-577X(96)00245-5.
- [18] Gupta T.K., Bechtold J.H., Kuznicki R.C., Cadoff L.H. and Rossing B.R., *J. Mater. Sci.*, 1977; **12**: 2421-2426. DOI 10.1007/BF00553928.
- [19] Jue J.F. and Virkar A.V., *J. Mater. Sci.*, 1990; **73**: 3650-3657. DOI 10.1111/j.1151-2916.1990.tb04271.x.
- [20] Fan J., Lin T., Hu F., Yu Y., Ibrahima M., Zheng R., Huang S. and Ma J., *Ceram. Int.*, 2017; **43**: 3647-3653. DOI 10.1016/j.ceramint.2016.11.204.
- [21] Gao L., Hong J.S., Miyamoto H. and Torre S.D.D.L., *J. Eur. Ceram. Soc.*, 2000; **20**: 2149-2152. DOI 10.1016/S0955-2219(00)00086-8.
- [22] Danzer R., Supancic P., Pascual J. and Lube T., *Ceram. Int.*, 2007; **74**: 2919-2932. DOI 10.1016/j.engfracmech.2006.05.028.
- [23] Siarampi E., Kontonasaki E., Papadopoulou L., Kantiranis N., Zormpa T., Paraskevopoulos K.M. and Koidis P., *J. Prosthet. Dent.*, 2012; **108**: 84-95. DOI 10.1016/S0022-3913(12)60112-7.
- [24] dos Santos C., Santos F.A. and Elias C.N., *Key Eng. Mater.*, 2009; **396**: 603-606. DOI 10.4028/www.scientific.net/KEM.396-398.603.
- [25] Juniora S.A.R., Ferracane J.L., Bona A.D., *Dent. Mater.*, 2008; **24**: 421-431. DOI 10.1016/j.dental.2007.05.013.
- [26] Hasanuzzaman M., Rafferty A., Olabi A.G. and Prescott T., *Int. J. Nanopart.*, 2008; **1**: 50-65. DOI 10.1504/IJNM.2007.014572.
- [27] Hua Z., Zhang B., Chen J., Sun L. and Zhang Y., *Key Eng. Mater.*, 2012; **519**: 273-276. DOI 10.4028/www.scientific.net/KEM.519.273.
- [28] Hao C.C., Muchtar A., Amat N.F., Ghazali M.J. and Yahaya N., *Adv. Mater. Res.*, 2014; **89**: 6591-595. DOI 10.4028/www.scientific.net/AMR.896.591.
- [29] BruxZir®. "BRUXZIR® SHADED MILLING BLANKS" bruxzir.com. <http://bruxzir.com/wp-content/uploads/2018/02/bruxzir-solid-zirconia-shaded-milling-blanks-instructions-for-use.pdf> (accessed July 7, 2018).
- [30] Limpichaipanit A., Jiansirisomboon S. and Tunkasiri T., *Sci. Eng. Compos. Mater.*, DOI 10.1515/secm-2014-0353.
- [31] Limpichaipanit A. and Tunkasiri T., *Adv. Appl. Ceram.*, 2016; **115**: 349-353. DOI 10.1080/17436753.2016.1155293.