

Sintering properties and low-temperature degradation behaviour of Y-TZP ceramics

C.H. Ting^{a,b}, S. Ramesh^{a,*}, N. Lwin^c and U. Sutharsini^d

^aCentre of Advanced Manufacturing and Materials Processing, Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia

^bDepartment of Mechanical and Material Engineering, Universiti Tunku Abdul Rahman, Jalan Genting Kelang, Setapak, Kuala Lumpur 53300, Malaysia

^cPhysics Department, Magway University, Myanmar

^dDepartment of Physics, University of Jaffna, Jaffna JA 40000, Sri Lanka

Y-TZP ceramics has outstanding mechanical properties and has been used for many engineering applications. However, a major drawback of this ceramic is the undesirable ageing-induced tetragonal to monoclinic phase transformation resulting in properties deterioration when exposed to steam environment. In the present work, the effect of sintering temperatures (1200 to 1500 °C) on mechanical properties, microstructure and low temperature ageing behaviour of the sintered Y-TZP samples were investigated. The sintered bodies were characterized to determine the bulk density, Young's modulus, Vickers hardness and fracture toughness. The sintered samples were exposed to superheated steam at 180 °C/10 bar vapor pressure and the extent of monoclinic phase development were measured at selected intervals. It was found that the relative density and Young's modulus of the sintered samples increased with sintering temperature and attained a maximum value of 99% and 211 MPa, respectively at 1400 °C. On the other hand, maximum Vickers hardness and fracture toughness of 14.4 GPa and 5.07 MPam^{1/2} respectively, was measured at 1350 °C. X-ray diffraction studies indicated that after 24 h of ageing, no traces of monoclinic phase was found in the Y-TZP having an average grain size of below 0.3 µm. The study found that sintering at 1350-1400 °C was optimum to produce sintered bodies having good ageing resistant without sacrificing the mechanical properties.

Key words: 3Y-TZP, Mechanical properties, Low-temperature degradation, Average grain size.

Introduction

Yttria-tetragonal zirconia polycrystals (Y-TZP) are increasingly being considered for engineering applications due to combinations of attractive properties including superior strength (> 1000 MPa) [1], high hardness and fracture toughness [2], high wear resistant [3], good thermal properties, chemical stability and smooth appearance. These superior mechanical properties of Y-TZP can be attributed to a phenomenon known as transformation toughening (TT) [4]. In this mechanism, the stress of a propagating crack will be absorbed by the metastable tetragonal (t) particles in the vicinity and transformed to the monoclinic (m) symmetry with an accompanying volume expansion of ~ 3 to 4%. The net effect is that higher level of stress would be required to maintain crack progression, thus explaining the high strength and toughness of the ceramic. The effectiveness of TT, however is controlled, in general by the amount of tetragonal phase retained and more specifically the stability of the (t) grains in the structure. The retention of the tetragonal structure to room temperature can be achieved by doping zirconia with yttria (2.5 to

3 mol%). On the other hand, the stability of the tetragonal particles is dependent on several factors which include the yttria content and distribution, processing technique and the present or absent of sintering additives [2, 5, 6].

In addition, the sintering conditions such as sintering techniques (e.g. hot pressing, HIPing, pressureless sintering and microwave sintering), soaking temperature, holding time and the ramp rates have a direct effect on the microstructure of the zirconia and this in turn will influence the mechanical properties of the zirconia. Chen and Brook [7] suggested that the temperature has the greatest effect on the bulk density of the ceramic rather than the holding time or the ramp rates. Gupta [8] reported that sintering at 1300 °C and 1500 °C caused the density of the zirconia to increase with time but sintering beyond 1500 °C was detrimental as the density was found to decrease with time. Lawson et al. [9] observed that although a high tetragonal phase retention (> 99%) could be retained in Y-TZPs sintered at 1250 °C using a long holding time of 12 hrs, the hardness of this ceramic was rather low (< 9 GPa). However these authors also reported that a two stage sintering (i.e. pre-sintering at 1250 °C for up to 12 hrs and then firing at 1450 °C for 2 hrs) resulted in enhanced densification, high tetragonal phase retention and good mechanical properties.

*Corresponding author:
Tel : +603-7967-5202
Fax: +603-7967-7621
E-mail: ramesh79@um.edu.my

However, one of the major problem with Y-TZP ceramic is the undesirable spontaneous transformation of tetragonal to monoclinic symmetry when exposed to humid environment at temperatures ranging from 100–300 °C [10, 11]. This phenomenon known as low-temperature degradation (LTD) or hydrothermal ageing spread from the surface into the body of the ceramic, causing compressive stresses induced by the volume expansion of the transformed monoclinic grains accompanied by crack formation and eventually results in fracture of the ceramic.

The mechanism of LTD still remains a subject of intense debate, but the presence of water or hydroxyls has been identified as the catalyst in accelerating the ageing-induced tetragonal to monoclinic phase transformation. Different approaches have been experimented to enhance the ageing resistance of Y-TZP such as altering the content and distribution of the yttria stabilizer and decreasing the tetragonal grain size. Some of the approaches taken have resulted in either a compromise on the mechanical properties, the use of expensive chemicals and process equipment and can even be labor intensive.

It is important to preserve the excellent mechanical properties of Y-TZP, especially the fracture toughness while suppressing the LTD in Y-TZP. The aim of present work was to study the effects of sintering temperatures on mechanical properties, microstructure and LTD behaviour of commercially viable 3 mol% Y-TZP powder.

Experimental Procedures

The as-received 3 mol% yttria-stabilized zirconia powder which was obtained from Kyoritsu, Japan had a total impurity concentration of about 0.1 wt% with SiO₂, Fe₂O₃, TiO₂ and Al₂O₃ as the major impurities. The Y-TZP powder had a specific surface area of 12 m²/g and a mean particle diameter of 300 nm. Green samples in the form of discs (20 mm diameter and 2.5 g) and rectangular bars (4 mm × 13 mm × 32 mm, 3 g) were pressed uniaxially at 0.3 MPa and cold isostatically pressed at 200 MPa. Sintering of green samples was done in air atmosphere using a box furnace (Carbolite, UK) at seven different temperatures, 1200, 1250, 1300, 1350, 1400, 1450, and 1500 °C for 2 h with heating rate of 10 °C/min. All disc specimens were ground on one surface by SiC papers of 120, 240, 600, 800, and 1000 grades progressively. Finally the ground samples were polished with 6 and 1 μm diamond paste prior to testing.

The bulk density of the sintered samples was measured by water immersion method using an analytical balance retrofitted with a density determination kit (Vibra HT, Japan) and the relative density was obtained by taking the theoretical density of Y-TZP as 6.07 g/cm³. The Young's modulus by sonic resonance was determined for rectangular samples using a commercial testing

instrument (GrindoSonic: MK5 "Industrial", Belgium). The instrument permits determination of the resonant frequency of a sample by monitoring and evaluating the vibrational harmonics of the sample by a transducer; the vibrations are physically induced in the sample by tapping. The modulus of elasticity was calculated using the experimentally determined resonant frequencies, according to ASTM E1876-97 standard [12].

Fracture toughness (K_{Ic}) and Vickers hardness measurements (Bowers, China) were made on polished samples using the Vickers indentation method. The indentation load was kept constant at 10 kgf and a loading time of 10 s was employed. The values of K_{Ic} were computed using the equation derived by Niihara et al. [13]. Average values were taken from five measurements.

Phase analysis by X-ray diffraction (XRD, Shimadzu XD-3A Series, Japan) of the samples was carried out under ambient conditions using Cu-Kα as the radiation source operating at 35 kV and 35 mA. The scan was conducted within the 2θ range of 27–36 ° at 0.02 ° 2θ step size and a count time of 0.5 s per step under ambient conditions. The crystalline phases present in the ceramic were identified by comparing with standard JCPDS files for (t)-ZrO₂ (No. 30 1468) and (m)-ZrO₂ (No. 37 1484). The fraction of the (t) and (m) phases were determined using the method of Toraya et al. [14].

The microstructure evolution of the sintered samples was observed using a field emission scanning electron microscopy (FE-SEM, Philips) and the grain size was measured from scanning electron micrographs using the line intercept analysis.

The low temperature degradation (LTD) was performed in an autoclave containing superheated steam at 180 °C/10 bar for periods up to 200 hrs. The amount monoclinic phase development was determined by XRD analysis as a function of ageing time.

Results and Discussion

The effect of sintering temperature on relative density of the samples is shown in Fig. 1. The lowest relative density measured was about 94% when sintered at 1200 °C and the densities increased at higher sintering temperatures. All the samples showed comparative density, in the range of 98–99% for the sintering temperature above 1250 °C. The maximum density was achieved at 1400 °C–1450 °C before decreasing slightly when sintered at 1500 °C. This decreased in density could be associated with grain coarsening at higher temperatures [15]. According to Inokoshi et al. [16], the decreased in bulk density of zirconia when sintered at higher sintering temperature of 1650 °C resulted in the partial transformation of the tetragonal phase into cubic and monoclinic phases thus resulting in a decreased in density of the Y-TZP sample.

The effect of sintering temperature on the Young's

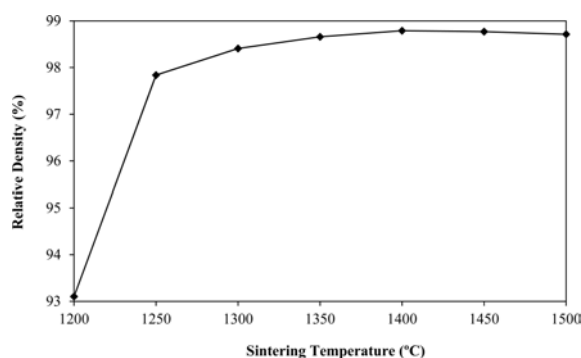


Fig. 1. Effect of sintering temperatures on the relative density of the Y-TZPs.

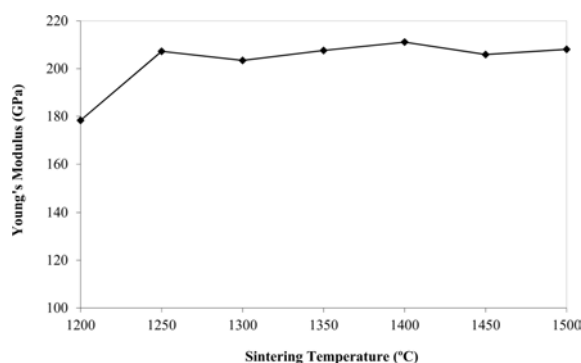


Fig. 2. Young's modulus variation as a function of sintering temperature.

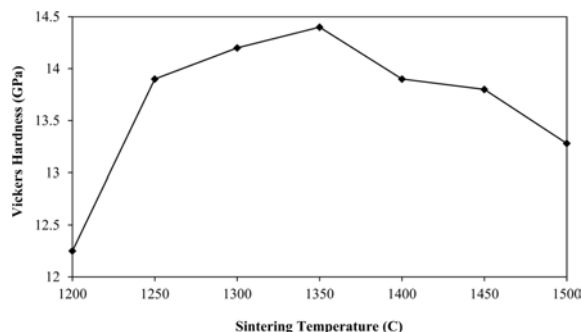


Fig. 3. Effect of sintering temperatures on the Vickers hardness of Y-TZPs.

modulus is presented in Fig. 2. It can be noted that the Young's modulus trend is in good agreement with that of the relative density. The Young's modulus of Y-TZP was low at 178 GPa when sintered at 1200 °C. However, as the sintering temperature increased, this was accompanied by an increased in the Young's modulus to above 200 GPa. In general, the Young's modulus of the ceramics fluctuated between the ranges of 203 to 211 GPa when sintered between 1250 to 1500 °C.

The effect of sintering temperature on the Vickers hardness is shown in Fig. 3. The hardness of the Y-TZP ceramic increases from a low of 12.2 GPa at 1200 °C to about 13.9 GPa at 1300 °C and gradually reaching a maximum of 14.4 GPa at 1350 °C. It can be inferred that this improvement in the hardness of Y-TZPs was

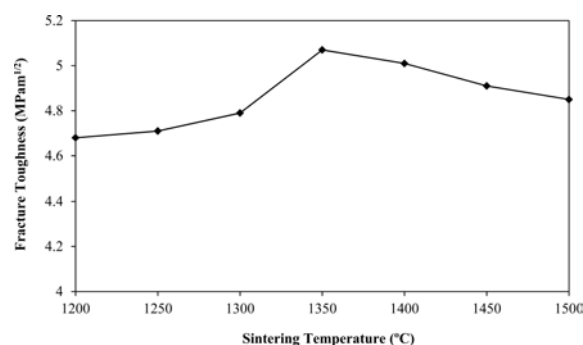


Fig. 4. Variation of fracture toughness for Y-TZP sintered at various temperatures.

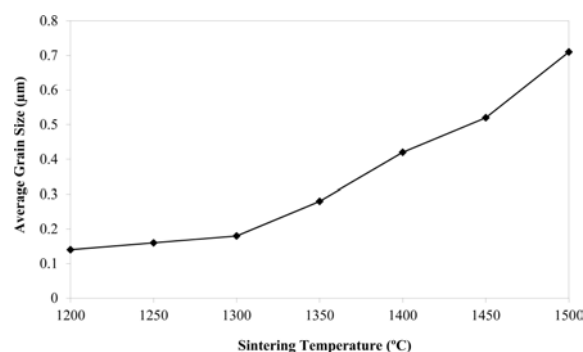


Fig. 5. Effect of sintering temperatures on the average grain size of the Y-TZPs.

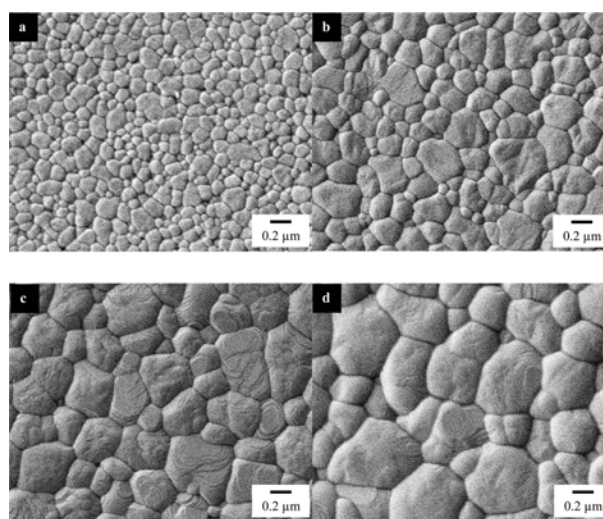


Fig. 6. Microstructure evolution of Y-TZP ceramics sintered at (a) 1250 °C, (b) 1350 °C, (c) 1450 °C and (d) 1500 °C.

due to the enhanced densification of the sintered body [17]. However, sintering above 1350 °C the hardness stated to decline, believed to be associated with grain coarsening associated with the cubic structure. This trend of Vickers hardness observed in the present work is in agreement with that reported by other researchers [17–19].

The influence of sintering temperature on the fracture toughness, K_{Ic} of Y-TZP is shown in Fig. 4. The K_{Ic} of the sintered samples increased gradually with temperature

reached a maximum of $5.07 \text{ MPam}^{1/2}$ at 1350°C . In general, the fracture toughness varied between 4.91 to $5.03 \text{ MPam}^{1/2}$ when sintered above 1400°C . This result indicated that the sintering temperature had marginal effect on the fracture toughness of the Y-TZP. Similar result was observed by Ramesh et al. [20] and the authors suggested that it was attributed to the homogenization over the stabilizer within the ZrO_2 grains of the Y-TZP powder, thus resulting in a more stable tetragonal grains.

Fig. 5 shows the effect of sintering temperature on the average grain size of Y-TZP. In general, it was found that the grain size increases with increasing sintering temperature from $0.2 \mu\text{m}$ to $0.71 \mu\text{m}$ as the sintering temperature increases from 1200°C to 1500°C . The Y-TZP sintered samples exhibited typical faceted unimodal grains with no pore inclusions. A uniform microstructure, composed of equiaxed grains was observed when sintered at 1250°C and above. However as the sintering increases, the grain growth rate for a few grains were relatively higher compared to the surrounding grains especially for samples when sintered at higher temperatures $\geq 1350^\circ\text{C}$ as evident from the SEM micrograph in Fig. 6. The large grains are 3 to 5 times larger than the smaller grains for the sample sintered at 1500°C . Larger grain size are generally observed for higher sintering temperatures

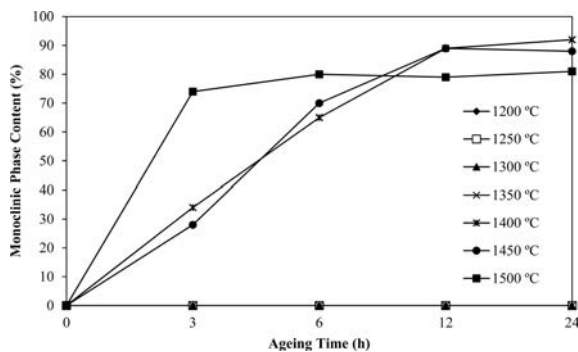


Fig. 7. Effect of hydrothermal ageing on the monoclinic phase development in Y-TZPs when exposed to superheated steam as a function of sintering temperatures.

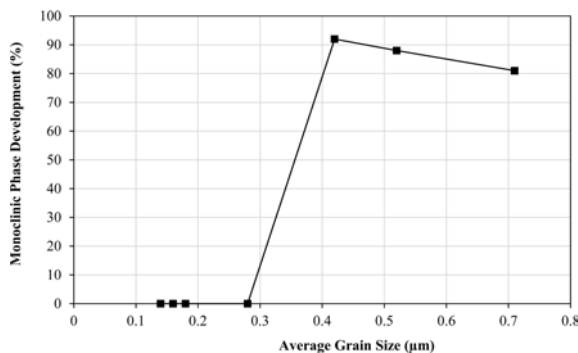


Fig. 8. Grain size dependence on the ageing-induced monoclinic phase development for Y-TZPs after exposure for 24 hrs in superheated steam.

and/or long sintering time (above 2 hrs) as is believed to be that of the cubic grains [21–24].

The effect of superheated steam (180°C and 10 bar pressure) on the tetragonal (t) to monoclinic (m) phase transformation of the Y-TZP samples is shown in Fig. 7. It was found that all samples sintered below 1400°C exhibited good resistance to LTD with no traces of monoclinic found after ageing up to 24 hrs. On the contrary, samples sintered $\geq 1400^\circ\text{C}$ were susceptible to LTD but at different rates. Samples with sintering temperature of 1400°C and 1450°C exhibited similar trend with lower LTD kinetics and achieved monoclinic saturation level at 90% within 12 hrs of exposure. The rate of LTD was rapid for sample sintered at 1500°C , reaching a saturated monoclinic level of about 80% within 3 hrs of exposure.

The present work revealed that the saturation monoclinic volume fraction of Y-TZP samples sintered at 1400°C and 1450°C reached about 90% after 12 hrs of hydrothermal ageing and the remaining 10% is believed to be of the tetragonal and/or cubic phase [16]. However, samples sintered at 1500°C has achieved saturation monoclinic content of about 80% after exposure for 3 hrs in superheated steam. It is envisaged that the cubic grains in this sample could act as a getter to draw out yttria stabilizer from the adjacent stable tetragonal grains, resulting in an enrichment of the yttria at grain boundary regions of the cubic grains. As a result, the tetragonal grains that had suffered from yttria depletion could become unstable and prone to hydrothermal ageing [21, 25].

The current work has shown that sample with an average grain size of about $0.7 \mu\text{m}$ for samples sintered at 1500°C was most sensitive to LTD. In contrast, Y-TZP having grain sizes of 0.14 to $0.28 \mu\text{m}$ (i.e. below $0.3 \mu\text{m}$) did not experience LTD as shown in Fig. 8, but samples with grains larger than $0.3 \mu\text{m}$ showed considerable phase transformation. Thus, this result indicated that $0.3 \mu\text{m}$ seemed to be the critical grain size below which the Y-TZP is not susceptible to hydrothermal ageing. This critical grain size observation has also been reported for other Y-TZPs when exposed to hydrothermal ageing test [2, 6, 17, 20, 26, 27]. It cannot be rule out that other factors such as starting powder, type of stabilizer, stabilizer content and distribution, and test conditions could also influence the LTD behavior of Y-TZP ceramics [28].

Conclusions

The influence of sintering temperatures on the properties and hydrothermal ageing behavior of Y-TZP has been investigated. The Y-TZP ceramics exhibited high density when sintered at temperature as low as 1250°C . Both relative density and Young's modulus of the Y-TZPs correlated well and increased with sintering temperature before reaching the maximum value at

98.9% and 211 GPa, respectively at 1400 °C. On the other hand, the maximum Vickers hardness of 14.4 GPa and fracture toughness of 5.07 MPam^{1/2} were recorded for ceramic sintered at 1350 °C. The grain size of the Y-TZP was found to increase almost linearly with increasing sintering temperature in the range of 1300 °C–1500 °C. All the Y-TZP ceramics sintered below 1400 °C exhibited no sign of ageing-induced monoclinic phase development after exposure in superheated steam at 180 °C and 1 MPa pressure for 24 hrs. It was revealed that samples having grain sizes above 0.3 µm were susceptible to hydrothermal ageing and in the extreme case exhibited more than 70% monoclinic phase after exposure for 3 hrs in superheated steam.

Acknowledgments

This study was supported under the FRGS grant no. FP056-2015A, PPP grant no. PG055-2015A and UTAR Research Fund (Project Number: IPSR/RMC/UTARRF/2014-C1/T10).

References

1. H. Tong, C.B. Tanaka, M.R. Kaizer and Y. Zhang, *Ceram. Inter.* 42 (2016) 1077-1085.
2. R. Singh, C. Gill, S. Lawson and G.P. Dransfield, *J. Mater. Sci.* 31 (1996) 6055-6062.
3. M. Valefi, B. Pathiraj, M. de Rooij, E. de Vries and D.J. Schipper, *J. Eur. Ceram. Soc.* 32 (2012) 4137-4147.
4. R.C. Garvie, R.H. Hannink and R.T. Pascoe, *Nature* 258 (1975) 703-704.
5. R. Stevens, in *Zirconia and Zirconia Ceramics*, Magnesium Elektron, Ltd. (1986) No. 113.
6. S. Ramesh, C. Gill, S. Lawson and G.P. Dransfield, *J. Mater. Sci.* 34 (1999) 5457-5467.
7. Y.L. Chen and R.J. Brook, *Br. Ceram. Trans. J.* 88 (1989) 7-12.
8. T.K. Gupta, *Science of Sintering* 10 (1978) 205-216.
9. S. Lawson, T.K. Sing, J.M. Smith, C. Gill and G.P. Dransfield, in *"Sintering Technology"* edited by R.M. German, G.L. Messing and R.G. Cornwall (Marcel Dekker Inc., N.Y., 1996) 473-480.
10. M. Cattani-Lorente, S.S. Scherrer, P. Ammann, M. Jobin, H.W.A. Wiskott, *Acta Biomaterialia* 7 (2011) 858-865.
11. M. Keuper, C. Berthold, K.G. Nickel, *Acta Biomaterialia* 10 (2014) 951-959.
12. ASTM Standard C1259-2008e1, "Standard test method for dynamic young's modulus, shear modulus, and poisson's ratio for advanced ceramics by impulse excitation of vibration," ASTM International, West Conshohocken, PA, 2008.
13. K. Niihara, R. Morena and D.P.H. Hasselman *J. Mater. Sci. Letts.* 1 (1982) 13-16.
14. H. Toraya, M. Yoshimura and S. Somiya, *J. Am. Ceram. Soc.* 67 (1984) C-119-C-121.
15. R.H.J. Hannink, P.M. Kelly and B.C. Muddle, *J. Am. Ceram. Soc.* 83 (2000) 461-487.
16. M. Inokoshi, F. Zhang, J. De Munck, S. Minakuchi, I. Naert, J. Vleugels, B. Van Meerbeek and K. Vanmeensel, *Dental Mater.* 30 (2014) 669-678.
17. S. Ramesh, M. Amiriyan, S. Meenaloshini, R. Tolouei, M. Hamdi, J. Pruboloksono and W.D. Teng, *Ceram. Inter.* 37 (2011) 3583-3590.
18. S.N.B. Hodgson, J. Cawley and M. Clubley, *J. Mater. Proc. Tech.* 92-93 (1999) 85-90.
19. S.N.B. Hodgson, J. Cawley and M. Clubley, *J. Mater. Proc. Tech.* 86 (1999) 139-145.
20. S.M. Kwa, S. Ramesh, L.T. Bang, Y.H. Wong, W.J. Kelvin Chew, C.Y. Tan, J. Purboloksono, H. Misran and W.D. Teng, *J. Ceram. Proc. Res.* 16 (2015) 193-198.
21. J. Chevalier, S. Deville, E. Münch, R. Jullian and F. Lair, *Biomaterials* 25 (2004) 5539-5545.
22. I. Denry and J.R. Kelly, *Dental Mater.* 24 (2008) 299-307.
23. L. Hallmann, A. Mehl, P. Ulmer, E. Reusser, J. Stadler, R. Zenobi, B. Stawarczyk, M. Özcan and C.H.F. Hämmerle, *J. Biomed. Mater. Res. -Part B Appl. Biomater.* 100 (2012) 447-456.
24. L. Ruiz and M.J. Readey, *J. Am. Ceram. Soc.* 79 (1996) 2331-2340.
25. H.G. Scott, *J. Mater. Sci.* 10 (1975) 1527-1535.
26. L. Hallmann, P. Ulmer, E. Reusser, M. Louvel, and C. H. F. Hämmerle, *J. Eur. Ceram. Soc.* 32 (2012) 4091-4104.
27. T. Kosmač and A. Kocjan, *J. Eur. Ceram. Soc.* 32 (2012) 2613-2622.
28. S. Lawson, *J. Eur. Ceram. Soc.* 15 (1995) 485-502.