

## Research Article

# Microstructure and Mechanical Properties of Microwave Sintered $\text{ZrO}_2$ Bioceramics with $\text{TiO}_2$ Addition

Hsien-Nan Kuo,<sup>1</sup> Jyh-Horng Chou,<sup>1,2,3</sup> and Tung-Kuan Liu<sup>1</sup>

<sup>1</sup>*Institute of Engineering Science and Technology, National Kaohsiung First University of Science and Technology, 1 University Road, Kaohsiung 824, Taiwan*

<sup>2</sup>*Department of Electrical Engineering, National Kaohsiung University of Applied Sciences, 415 Chien-Kung Road, Kaohsiung 807, Taiwan*

<sup>3</sup>*Department of Healthcare Administration and Medical Informatics, Kaohsiung Medical University, 100 Shih-Chuan 1st Road, Kaohsiung 807, Taiwan*

Correspondence should be addressed to Hsien-Nan Kuo; [andykuo8165@gmail.com](mailto:andykuo8165@gmail.com)

Received 27 April 2016; Accepted 23 June 2016

Academic Editor: Alberto Borboni

Copyright © 2016 Hsien-Nan Kuo et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The microwave sintered zirconia ceramics with 0, 1, 3, and 5 wt%  $\text{TiO}_2$  addition at a low sintering temperature of  $1300^\circ\text{C}$  and a short holding time of 1 hour were investigated. Effect of contents of  $\text{TiO}_2$  addition on microstructure and mechanical properties of microwave sintered zirconia bioceramics was reported. In the sintered samples, the main phase is monoclinic zirconia ( $m\text{-ZrO}_2$ ) phase and minor phase is tetragonal zirconia ( $t\text{-ZrO}_2$ ) phase. The grain sizes increased with increasing the  $\text{TiO}_2$  contents under the sintering temperature of  $1300^\circ\text{C}$ . Although the  $\text{TiO}_2$  phase was not detected in the XRD pattern, Ti and O elements were detected in the EDS analysis. The presence of  $\text{TiO}_2$  effectively improved grain growth of the  $\text{ZrO}_2$  ceramics. The Vickers hardness was in the range of 125 to 300 Hv and increased with the increase of  $\text{TiO}_2$  contents. Sintering temperature dependence on the Vickers hardness was also investigated from  $1150^\circ\text{C}$  to  $1300^\circ\text{C}$ , showing the increase of Vickers hardness with the increase of the sintering temperature as well as  $\text{TiO}_2$  addition.

## 1. Introduction

Zirconia ( $\text{ZrO}_2$ ) has become one of the most important ceramic materials since 1970s because of the discovery of transformation toughening mechanisms. There are three different polymorphs which existed in pure zirconia, such as monoclinic (m), tetragonal (t), and cubic (c) phases [1, 2]. It is well known that the monoclinic phase existed and is stable at room temperature up to  $1170^\circ\text{C}$ ; the tetragonal phase is formed and is stable at temperatures above  $1170^\circ\text{C}$  up to  $2370^\circ\text{C}$ ; and the cubic phase is stable above  $2370^\circ\text{C}$  [3]. These existent phases depend on the temperature and compositional ranges under equilibrium conditions. Moreover,  $\text{ZrO}_2$  ceramic shows many special properties, such as high elastic modulus, high fracture toughness, high wear resistance, suitable ionic conductivity, chemical inertness, and high melting temperature [2, 4]. Because of such excellent physical and chemical properties,  $\text{ZrO}_2$  ceramic is attractive

to be a biomaterial and is a popular alternative to alumina as dental bioceramic [5–7].

To increase its industrial applicability, it is desired to retain the tetragonal phase at room temperature to provide favorable mechanical properties. Namely, methods for keeping the  $\text{ZrO}_2$  based solid solution as the tetragonal (t) phase and preventing deleterious  $t \rightarrow m$  phase transformation during cooling after sintering shall be developed [2, 6]. In past, many research efforts reported that a proper percentage of stabilizers such as  $\text{Y}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{MgO}$  could be used to hold the tetragonal phase from  $1170^\circ\text{C}$  to the room temperature, inhibiting the happening of crack propagation and providing relatively high fracture toughness [2, 6–9]. In addition, the combination of uniform grain size and densification of the  $\text{ZrO}_2$  based ceramics can in turn improve the mechanical properties [9]. Therefore, the processing of starting powders, composition, and sintering condition such as sintering time and temperature

are important parameters to prepare the high quality bioceramics.

It is known that, in conventional solid state sintering, the heat is transmitted radiantly to the surface of the material and reaches the internal core of the material by thermal conduction [10]. The sintered piece has approximately 22~25% shrinkage after final sintering. Typically, conventional solid state sintering may not provide uniform heating distribution and requires extended sintering process from 8 to 10 hours for the sintering of ZrO<sub>2</sub> dental sample, causing much energy consumption [7].

Microwave sintering technology has been used for sintering ceramic materials. In the microwave sintering environment, the suitable material absorbs energy through dielectric heating, and the temperature is more uniformly distributed in the ceramic material [11–14]. Since microwave sintering technology has many attractive features, including uniform heating distribution, rapid volumetric heating, and low cost, it leads to the higher production rates and lower energy consumption. Compared to the conventional sintering technology, it makes the process commercially attractive. Estimates of energy saving are 25% to 95% [14]. However, high purity ZrO<sub>2</sub> is a low absorber of microwave energy. Therefore, addition of TiO<sub>2</sub> into high purity ZrO<sub>2</sub> was provided to improve the microwave coupling at a given temperature [10, 15]. It is expected that microwave sintering would have a lower temperature (below 1400°C) and a shorter process (2 hours) than conventional sintering [16]. The sintering temperature, the heating rate, and the sintering time can affect the grain size, density, and mechanical properties of the sintered ZrO<sub>2</sub> ceramic.

In this paper, the aim of this study is to investigate the effect of TiO<sub>2</sub> content on the microstructure and mechanical properties of the microwave sintered ZrO<sub>2</sub> with TiO<sub>2</sub> addition at a low sintering temperature and a short holding time. In addition, the relation between the microstructure and mechanical properties is also discussed. Moreover, the dependence of the sintering temperature on the Vickers hardness was also investigated from 1150°C to 1300°C to verify the importance of TiO<sub>2</sub> addition.

## 2. Materials and Methods

In this study, starting powders used ZrO<sub>2</sub> with purity of 99.9% and TiO<sub>2</sub> with purity of 99.85%. Four composite samples were prepared by adding TiO<sub>2</sub> content from 0, 1, 3, and 5 wt% into ZrO<sub>2</sub>, respectively. The powders were mixed by wet ball-milling for 12 h in ethanol, using high purity zirconia balls as medium to achieve a homogeneous mixture. After milling, the mixed powders were dried at 90°C for 10 h. The dried powders were mechanically grounded and added with 10 wt% PVA solution. Five green samples, for each composition, with a diameter of 10 mm and a thickness of 1 mm were formed by uniaxially pressing. The samples were microwave sintered at the sintering temperatures of 1150, 1200, 1250, and 1300°C for a holding time of 1 hour in microwave oven. The heating rate was varied as 100°C/min up to 300°C for 1 h to burn out the binder and 100°C/min up to the final temperature under air atmosphere. The sintered samples were naturally

cooled to the room temperature. In the study, the microwave furnace (Therm Wave Mod. III), with a continuously variable power of 2.45 GHz microwaves up to 1.3 kW, was used. To provide indirect heating of the powders, silicon carbide (SiC), having a very strong heating response to 2.45 GHz microwaves, was used as a susceptor. The samples were placed in the center of the susceptor and the sintering temperature was measured by insertion of a thermal couple around the susceptor.

After sintering, the diameter and thickness of each sintered sample were measured with a digital caliper to calculate the shrinkage percent. The crystalline phases of the composite specimens were conducted by using X-ray diffraction (XRD, Bruker D8 Advance) analysis with CuK $\alpha$  radiation of  $\lambda = 1.5406 \text{ \AA}$  using a Ni filter and with a secondary graphite monochromator. A scanning range of  $2\theta = 20^\circ \sim 60^\circ$  with a step of  $0.03^\circ$  and 0.4 s as a count time per step was used. The morphology of the sintered samples was examined by scanning electron microscope (SEM, HORIBA EX-200) with the function of energy dispersive spectroscopy (EDS). The average grain size of the microwave sintered samples was obtained by analyzing SEM images using the linear intercept method on the fracture surfaces. The hardness of the sintered samples was conducted at room temperature by a micro-Vickers hardness tester (HM-113, Japan) with an indent load of 5 g held for 6 s on the surface of the microwave sintered samples. The measurement was repeated five times for each sample. With removal of the largest and smallest values during the measurement, the average value was determined to be the measured result.

## 3. Results and Discussion

**3.1. XRD Analysis.** Figure 1 shows the XRD patterns of the microwave sintered ZrO<sub>2</sub> samples with addition of 0, 1, 3, and 5 wt% TiO<sub>2</sub> contents at 1300°C for 1 h. The main diffraction patterns of the tetragonal phase are around  $2\theta = 30^\circ, 51^\circ,$  and  $60^\circ$ . In these patterns, it was found that the diffraction patterns with reflections in  $2\theta = 28^\circ$  and  $31^\circ$  were related to the main phase of monoclinic zirconia and low diffraction intensity with reflection in  $2\theta = 50.36^\circ$  was related to second phase of tetragonal zirconia in the sintered samples for different TiO<sub>2</sub> content [2, 6]. As reported in many researches, low-temperature cubic and tetragonal phases are meta-stable and would be converted into the monoclinic phase during cooling. Typically, the addition of stabilizers, such as Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, CaO, and MgO, to pure ZrO<sub>2</sub> can provide multiphases which coexisted in a material, known as Partially Stabilized Zirconia (PSZ) [1, 2]. In this study, the addition of TiO<sub>2</sub> seemed not to prevent  $t \rightarrow m$  phase transformation during cooling. The result might be caused from the sintering temperature of 1300°C and the holding time of 1 hour which were much lower than conventional sintering temperature and time for the stabilizer [8]. However, the intensities of main monoclinic (m) phases with reflections in  $2\theta = 28^\circ$  and  $31^\circ$  both slightly decreased with increasing TiO<sub>2</sub> content, indicating TiO<sub>2</sub> additions into pure ZrO<sub>2</sub> still have an effect on the phase transformation.

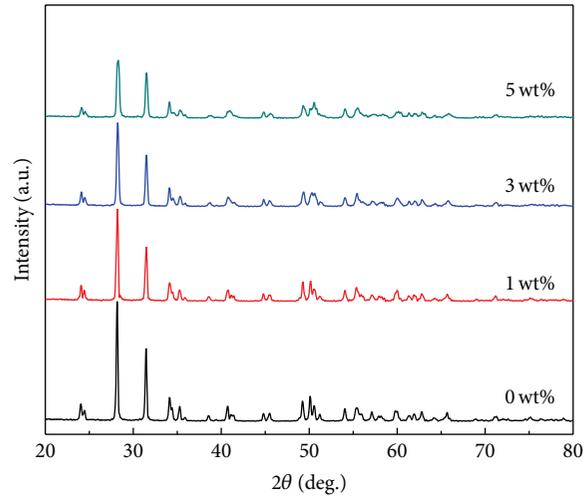


FIGURE 1: XRD patterns of the microwave sintered ZrO<sub>2</sub> samples with addition of 0, 1, 3, and 5 wt% TiO<sub>2</sub> contents.

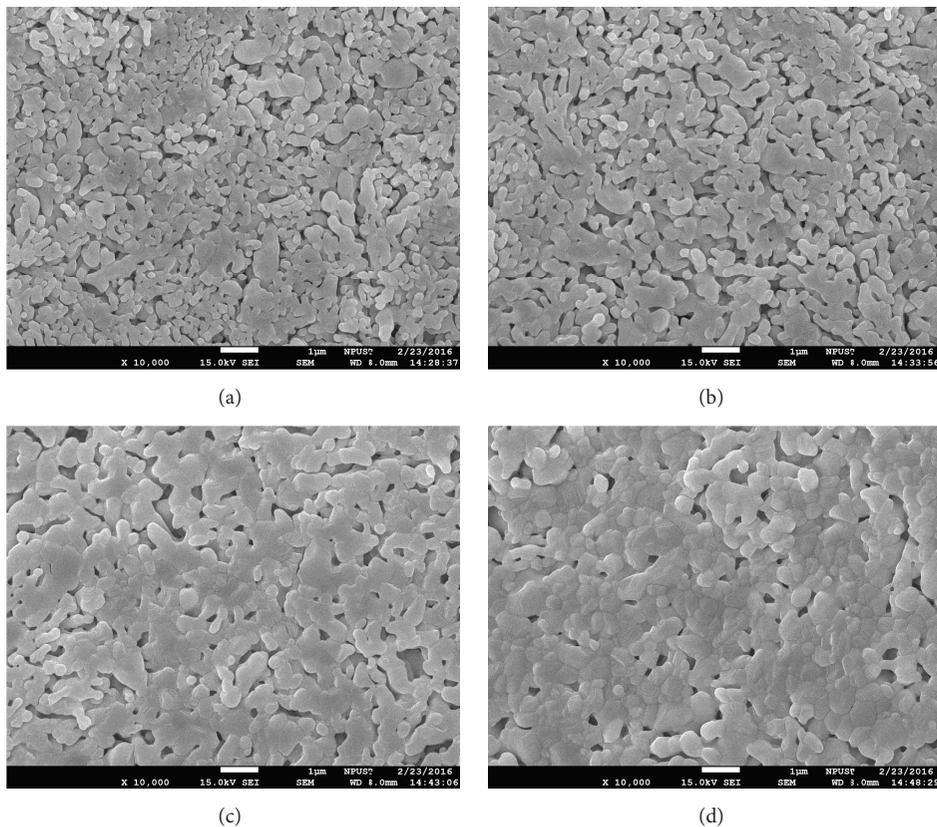


FIGURE 2: SEM of the microwave sintered ZrO<sub>2</sub> ceramics with addition of (a) 0, (b) 1, (c) 3, and (d) 5 wt% TiO<sub>2</sub> contents.

**3.2. Microstructure.** Under the microwave sintering temperature of 1300°C and the holding time of 1 hour, the linear shrinkage of the microwave sintered ZrO<sub>2</sub> samples with different additions was approximately 16%. With the density measurement, the relative densities of microwave sintered ZrO<sub>2</sub> ceramics with TiO<sub>2</sub> addition achieved around 88% to 90%. Figure 2 shows SEM results of the microwave sintered ZrO<sub>2</sub> ceramics with addition of (a) 0, (b) 1, (c) 3, and (d) 5 wt%

TiO<sub>2</sub> contents at 1300°C in 1 h. It is clearly observed that the grain sizes increased with increasing TiO<sub>2</sub> contents. The grain sizes were 420 nm, 650 nm, 890 nm, and 1060 nm with the addition of TiO<sub>2</sub> content with 0, 1, 3, and 5 wt%, respectively. The result indicated that the addition of TiO<sub>2</sub> in ZrO<sub>2</sub> ceramic could improve the grain growth and enhance the microwave sintering. Since the TiO<sub>2</sub> phase was not detected in the XRD pattern, the TiO<sub>2</sub> phase might be too small to be detected and

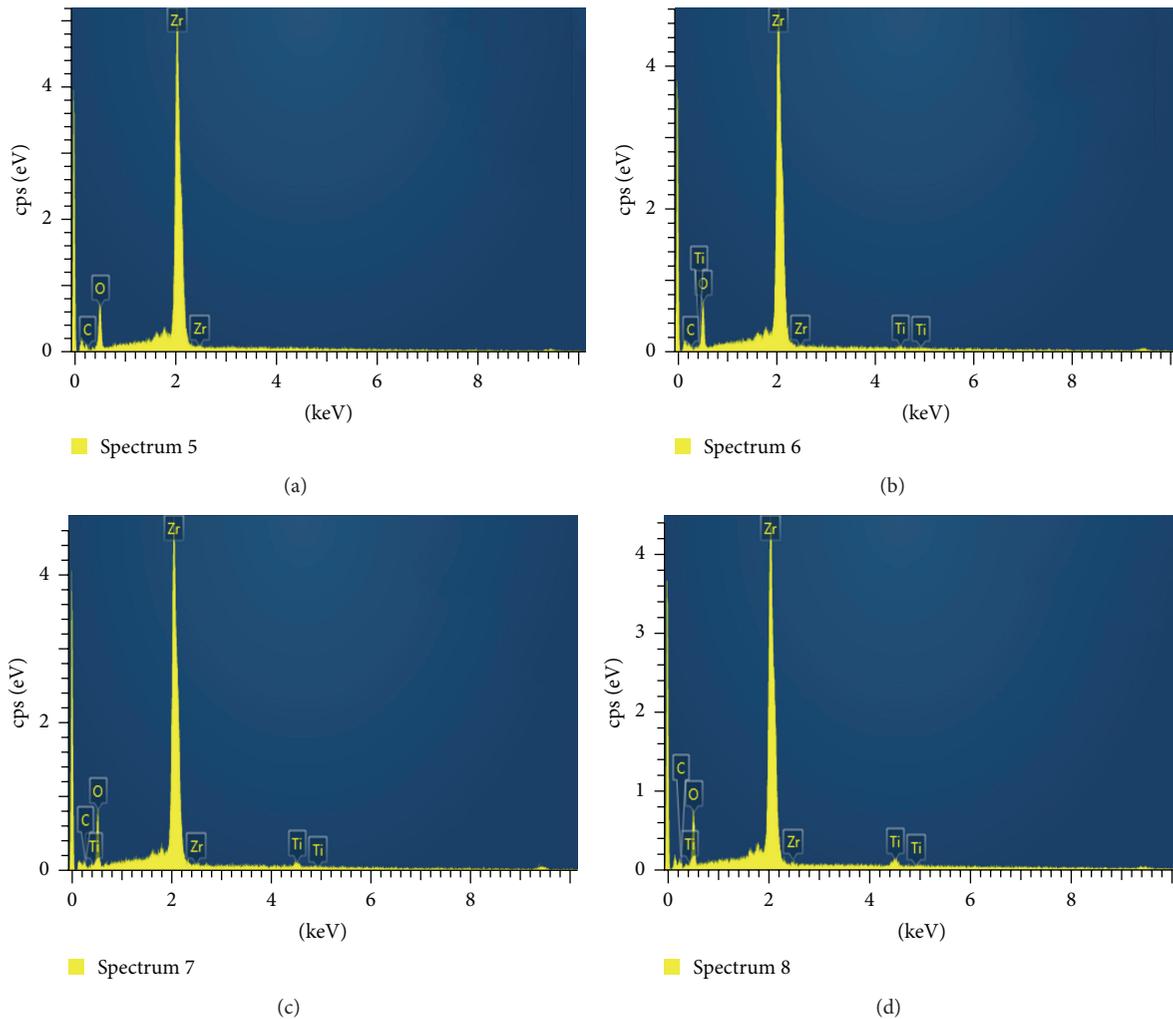


FIGURE 3: EDS analysis of the microwave sintered  $ZrO_2$  ceramics with addition of (a) 0, (b) 1, (c) 3, and (d) 5 wt%  $TiO_2$  contents.

$TiO_2$  addition was embedded around the  $ZrO_2$  grain and/or within the  $ZrO_2$  grain. Although the sintered samples did not achieve the full densification, it shall be noted that even at such a low temperature and a short holding time the  $ZrO_2$  grains were eventually coalesced with each other. At the triple junctions of the  $ZrO_2$  grains, some micro pores were present. It is known that the appearance of pores would increase the diffusion distance between  $ZrO_2$  grains, thus reducing the driving force for pore shrinkage of the sintered ceramics [6].

Figure 3 shows EDS analysis of the microwave sintered  $ZrO_2$  ceramics with addition of (a) 0, (b) 1, (c) 3, and (d) 5 wt%  $TiO_2$  contents. The EDS results verified that the content of  $TiO_2$  increased actually with increasing  $TiO_2$  addition. Although the  $TiO_2$  phase was not detected in the XRD pattern, Ti and O elements were detected in the EDS analysis. The presence of  $TiO_2$  on the grain and/or grain boundaries effectively improved the grain growth of the  $ZrO_2$  grains.

**3.3. Mechanical Properties.** Figure 4 shows the Vickers hardness of the  $ZrO_2$  ceramics with addition of 0, 1, 3, and 5 wt%  $TiO_2$  contents. Despite the errors associated with the measurement, it is found that the Vickers hardness of

the  $ZrO_2$  ceramic with addition of 0, 1, 3, and 5 wt%  $TiO_2$  contents was 125, 150, 250, and 300 Hv, respectively. The hardness values are low if the sintered samples are designed for dental use, since the sintered samples did not achieve the full densification under such a low temperature and a short holding time. Optical microscope of the  $ZrO_2$  ceramics with addition of (a) 0, (b) 1, (c) 3, and (d) 5 wt%  $TiO_2$  contents was shown in Figure 5. It is clearly observed that, under the same indent load, the lengths of the cross-indentation were decreased with increasing  $TiO_2$  contents. Thus, the larger length of the Vickers hardness indicated the shorter length of the cross-indentation. Typically, many factors would affect the Vickers hardness of ceramic materials, including the intrinsic deformability of the ceramic and the extrinsic microstructural features such as existent phases, grain size, crystal orientation, porosity, and boundary constitution [6, 8]. Under the microwave sintering temperature of  $1300^\circ C$  and the holding time of 1 hour, the main phase of monoclinic zirconia and second phase of tetragonal zirconia coexisted in the sintered samples with different  $TiO_2$  content, and the amount of the main phase was much larger than that of the second phase, as discussed in Figure 1. However, the grain

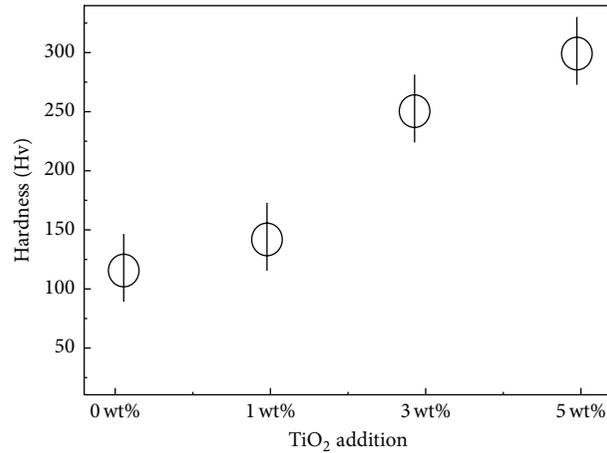


FIGURE 4: Vickers hardness of the ZrO<sub>2</sub> ceramics with addition of 0, 1, 3, and 5 wt% TiO<sub>2</sub> contents.

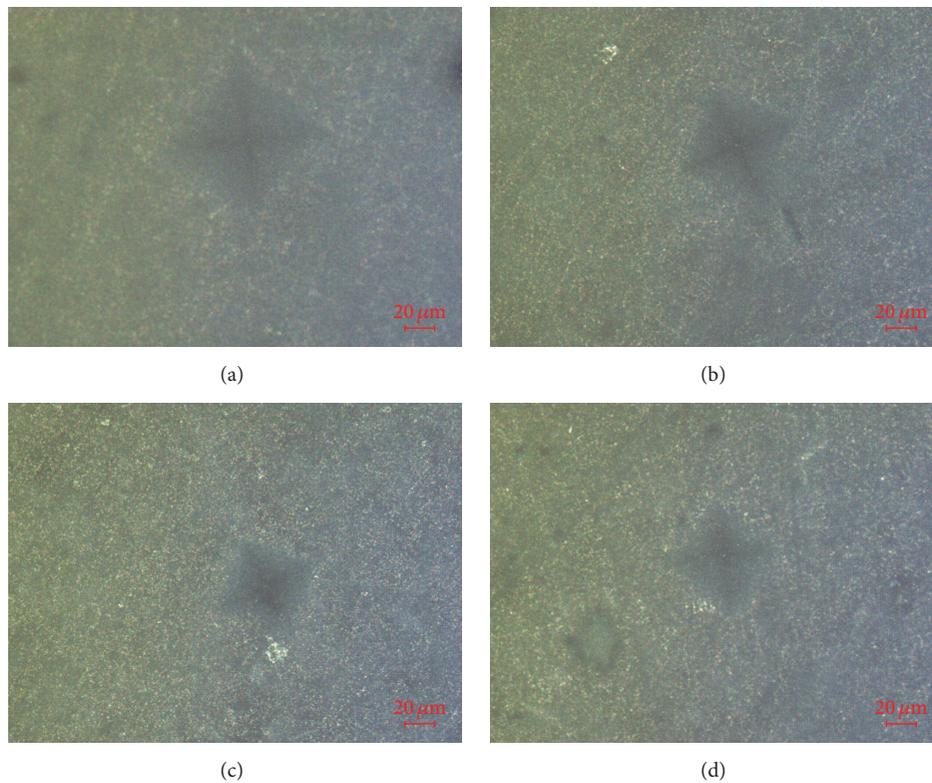


FIGURE 5: Optical microscope of the ZrO<sub>2</sub> ceramics with addition of (a) 0, (b) 1, (c) 3, and (d) 5 wt% TiO<sub>2</sub> contents (the scale bar is 20 μm.).

sizes increased and the microwave sintering enhanced with increasing TiO<sub>2</sub> contents. Thus, it is suggested that in this study the hardness of ZrO<sub>2</sub> was mainly influenced by the enhanced microwave sintering with TiO<sub>2</sub> addition.

Figure 6 shows further the Vickers hardness of the ZrO<sub>2</sub> ceramics with addition of 0, 1, 3, and 5 wt% TiO<sub>2</sub> contents under different sintering temperatures. It is actually found that, with increasing the sintering temperature from 1150°C to 1300°C, the Vickers hardness of the ZrO<sub>2</sub> ceramics increased in spite of TiO<sub>2</sub> contents. The increase was not obvious from 1150°C to 1200°C and then enhanced after 1200°C.

Moreover, for the same sintering temperature, the Vickers hardness of ZrO<sub>2</sub> was enlarged by doping with TiO<sub>2</sub> in spite of the content. Namely, TiO<sub>2</sub> addition into the ZrO<sub>2</sub> ceramics actually improved the Vickers hardness of the ZrO<sub>2</sub> ceramics under the microwave sintering. Figure 7 shows the optical microscope of the ZrO<sub>2</sub> ceramics with addition of 5 wt% TiO<sub>2</sub> contents sintered at (a) 1150°C, (b) 1200°C, (c) 1250°C, and (d) 1300°C. It is verified that, with higher sintering temperature, the length of the cross-indentation decreased due to the increase of the Vickers hardness. From the above results, it is summarized that TiO<sub>2</sub> content plays

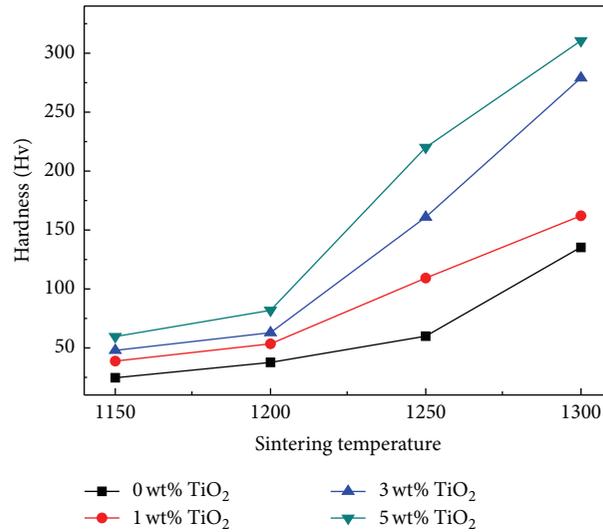


FIGURE 6: Vickers hardness of the ZrO<sub>2</sub> ceramics with addition of 0, 1, 3, and 5 wt% TiO<sub>2</sub> contents under different sintering temperatures.

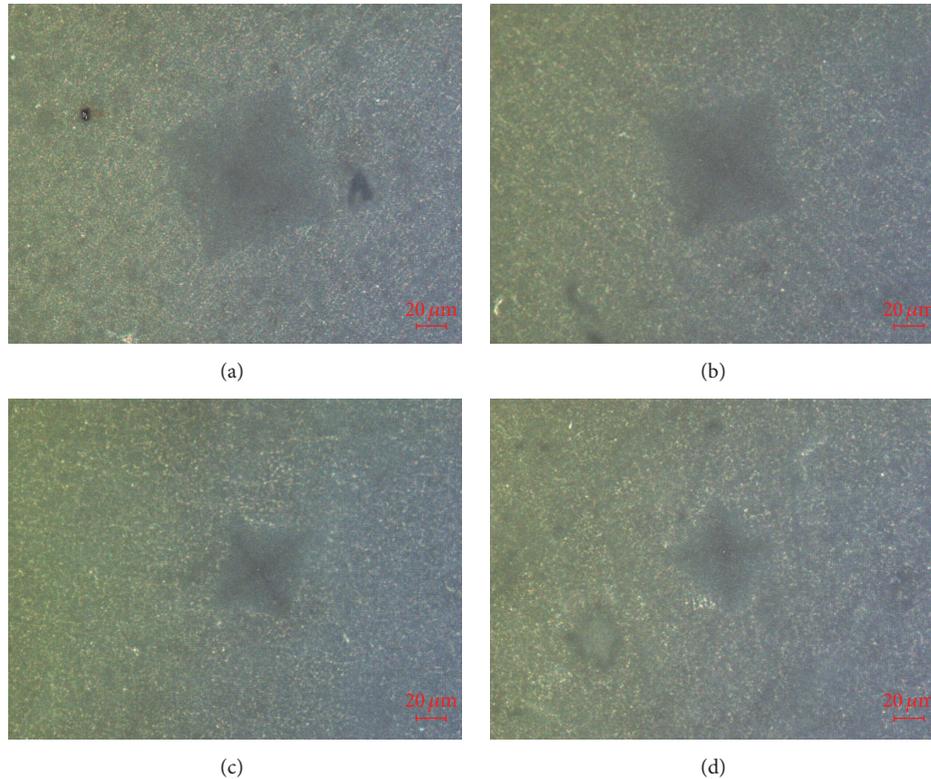


FIGURE 7: Optical microscope of the ZrO<sub>2</sub> ceramics with addition of 5 wt% TiO<sub>2</sub> contents sintered at (a) 1150°C, (b) 1200°C, (c) 1250°C, and (d) 1300°C (the scale bar is 20 μm.).

an important role in the crystallite phases, microstructures, and mechanical properties of microwave sintered ZrO<sub>2</sub> ceramics with TiO<sub>2</sub> addition. In the future, the sintering temperature shall be high and/or the sintering holding time shall be also longer to achieve the full densification and enough Vickers hardness of the ZrO<sub>2</sub> ceramics for the dental use.

#### 4. Conclusions

This paper investigated the effect of contents of TiO<sub>2</sub> addition on microstructure and mechanical properties of microwave sintered zirconia bioceramics for the dental use. The zirconia ceramics with 1, 3, and 5 wt% TiO<sub>2</sub> addition were sintered using the microwave energy at the sintering temperature of

1300°C. For different TiO<sub>2</sub> content, the main phase was the monoclinic zirconia (m-ZrO<sub>2</sub>) phase and second phase was tetragonal zirconia (t-ZrO<sub>2</sub>) phase. For all sintered samples, the grain growth was nearly completed. The grain sizes increased with increasing TiO<sub>2</sub> contents, indicating that TiO<sub>2</sub> addition effectively improved the grain growth of the ZrO<sub>2</sub> grains. The Vickers hardness increased with TiO<sub>2</sub> contents in the range from 125 to 300 Hv. Moreover, the Vickers hardness of ZrO<sub>2</sub> was enlarged by doping with TiO<sub>2</sub> in spite of the content under the same sintering temperature from 1150°C to 1300°C. Based on the study results, the microwave sintering is verified to be used to sinter ZrO<sub>2</sub> bioceramics with a low sintering temperature, and TiO<sub>2</sub> addition plays an important role in the crystallite phases, microstructures, and mechanical properties of microwave sintered ZrO<sub>2</sub> ceramics.

### Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

### Authors' Contributions

Hsien-Nan Kuo and Jyh-Horng Chou contributed to design of experiments and composed the paper. Hsien-Nan Kuo performed experiments and data analysis.

### Acknowledgments

The authors would like to thank the Advanced Electronic Materials Laboratory and Precision Instrument Center of National Pingtung University of Science and Technology for supporting the experimental equipment. This work was supported by the Ministry of Science and Technology, Taiwan, under Grant no. NSC 102-2221-E-151-021-MY3.

### References

- [1] S. Pilathadka, D. Vahalová, and T. Vosáhlo, "The Zirconia: a new dental ceramic material. An overview," *Prague medical report*, vol. 108, no. 1, pp. 5–12, 2007.
- [2] I. Denry and J. R. Kelly, "State of the art of zirconia for dental applications," *Dental Materials*, vol. 24, no. 3, pp. 299–307, 2008.
- [3] R. H. J. Hannink, P. M. Kelly, and B. C. Muddle, "Transformation toughening in zirconia-containing ceramics," *Journal of the American Ceramic Society*, vol. 83, no. 3, pp. 461–487, 2000.
- [4] S. R. Choi and N. P. Bansal, "Mechanical behavior of zirconia/alumina composites," *Ceramics International*, vol. 31, no. 1, pp. 39–46, 2005.
- [5] K. G. Kanade, J. O. Baeg, S. K. Apte, T. L. Prakash, and B. B. Kale, "Synthesis and characterization of nanocrystallined zirconia by hydrothermal method," *Materials Research Bulletin*, vol. 43, no. 3, pp. 723–729, 2008.
- [6] M. J. Abden, M. K. Islam, and J. D. Afroze, "Microstructure and mechanical properties of 3YSZ ceramics reinforced with Al<sub>2</sub>O<sub>3</sub> particles," *International Journal of Materials Engineering*, vol. 4, no. 4, pp. 2166–5389, 2014.
- [7] S. Ban, H. Sato, Y. Suehiro, H. Nakanishi, and M. Nawa, "Biaxial flexure strength and low temperature degradation of Ce-TZP/Al<sub>2</sub>O<sub>3</sub> nanocomposite and Y-TZP as dental restoratives," *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, vol. 87, no. 2, pp. 492–498, 2008.
- [8] J. Chevalier, L. Gremillard, A. V. Virkar, and D. R. Clarke, "The tetragonal-monoclinic transformation in zirconia: lessons learned and future trends," *Journal of the American Ceramic Society*, vol. 92, no. 9, pp. 1901–1920, 2009.
- [9] J. LLorca, J. Y. Pastor, P. Poza et al., "Influence of the Y<sub>2</sub>O<sub>3</sub> content and temperature on the mechanical properties of melt-grown Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> eutectics," *Journal of the American Ceramic Society*, vol. 87, no. 4, pp. 633–639, 2004.
- [10] D. D. Upadhyaya, A. Ghosh, G. K. Dey, R. Prasad, and A. K. Suri, "Microwave sintering of zirconia ceramics," *Journal of Materials Science*, vol. 36, no. 19, pp. 4707–4710, 2001.
- [11] H.-Y. Chen, M.-H. Weng, S.-J. Chang, and R.-Y. Yang, "Preparation of sr<sub>2</sub>SiO<sub>4</sub>:Eu<sup>3+</sup> phosphors by microwave-assisted sintering and their luminescent properties," *Ceramics International*, vol. 38, no. 1, pp. 125–130, 2012.
- [12] R.-Y. Yang, M. H. Weng, H.-Y. Chen, C.-M. Hsiung, and S.-H. Chen, "The influence of Eu<sup>3+</sup> doping on photoluminescent properties of red emitting phosphor YInGe<sub>2</sub>O<sub>7</sub>:Eu<sup>3+</sup> by microwave assisted and conventional sintering method," *Journal of Luminescence*, vol. 132, no. 2, pp. 478–483, 2012.
- [13] C. Laberty-Robert, F. Ansart, C. Deloget, M. Gaudon, and A. Rousset, "Dense yttria stabilized zirconia: sintering and microstructure," *Ceramics International*, vol. 29, no. 2, pp. 151–158, 2003.
- [14] A. A. Almazdi, H. K. Khajah, H. E. Monaco, and A. Kim, "Applying microwave technology to sintering dental zirconia," *Journal of Prosthetic Dentistry*, no. 12, pp. 60181–60184, 2012.
- [15] Y. Takigawa, Y. Naka, and K. Higashi, "Effect of titania doping on phase stability of zirconia bioceramics in hot water," *Materials Transactions*, vol. 48, no. 3, pp. 332–336, 2007.
- [16] A. Marinis, S. A. Aquilino, P. S. Lund et al., "Fracture toughness of yttria-stabilized zirconia sintered in conventional and microwave ovens," *Journal of Prosthetic Dentistry*, vol. 109, no. 3, pp. 165–171, 2013.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

