

HIGH-FREQUENCY INDUCTION HEAT SINTERING OF ULTRA-FINE Al_2O_3 -(ZrO_2 +X%MOL Y_2O_3) BIOCERAMICS

Khalil Abdelrazek Khalil

Permanent: Aswan High Institute of Energy, South Valley University,
Aswan, Egypt

Currently: Division of Advanced Materials Engineering, RCIT, Chonbuk
National University, Jeonju 561-756, South Korea

E-mail: khalil305@hotmail.com

(Received June 15, 2006 Accepted July 9, 2006)

ABSTRACT- Alumina–zirconia composites Al_2O_3 –20 vol. % yttria stabilized zirconia containing two types of yttria stabilized zirconia: 3mol% yttria doped ZrO_2 (3YSZ) and 8mol% yttria doped ZrO_2 (8YSZ) were consolidated very rapidly to full density by high frequency induction heat sintering (HFIHS). A comparison between 3YSZ and 8YSZ as a second phase toughening alumina has been made. Effects of sintering temperature on the mechanical properties have been studied. The consolidated samples were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The microhardness, strength and toughness of the composites are determined. The results showed that, 3YSZ is the most effective as a second phase toughening alumina than 8YSZ. Al_2O_3 -3YSZ composites with higher mechanical properties and small grain size developed through this technique.

KEYWORDS: High frequency induction heat sintering, Yttria stabilized zirconia, toughness, hardness, nanostructures.

1. INTRODUCTION

Among the bioinert ceramics used in surgical practice the most popular are those based on aluminum oxide (corundum) [1]. Disadvantages of all bioceramic materials are their low crack resistance compared to metals, practically complete absence of ductility, and difficulties of manipulation and adjustment during a surgical operation (particularly high strength ceramics) [1, 2]. A suitable method of improving the mechanical properties is based on the synthesis of composites made of alumina and other second phases [3, 4]. As toughening phase yttria stabilized zirconia (YSZ) was chosen because of its very good mechanical properties, good biocompatibility and chemical compatibility with the ceramic [5-10]. Pure zirconia is monoclinic at room temperature and changes to the denser tetragonal form at about 1,000°C, which involves a large volume change and creates cracks within its structures [11]. A smaller addition of stabilizer to the pure zirconia will bring its structure into a tetragonal phase at a temperature higher than 1,000°C, and a mixture of cubic phase and monoclinic (or tetragonal)-phase at a lower

temperature. This solid solution material is termed as partially yttria stabilized zirconia (PSZ). Usually such PSZ consists of larger than 3-4 mol% of Y_2O_3 . PSZ is a transformation-toughened material. Addition of more than 8 mol% of Y_2O_3 (13.75 wt%) into the zirconia structure in a certain degree results in a solid solution, which is a cubic form and has no phase transformation during heating from room temperature up to 2,500 °C and cooling. This solid solution material is termed as fully yttria stabilized zirconia. On the other hand, the technique of high-frequency induction heat sintering (HFIHS) has been shown to be an effective sintering method which can successfully consolidate ceramics and metallic powders to near theoretical density [12 – 15]. The HFIHS process is a sintering method for the rapid sintering of nanostructured hard metals in a very short time of high-temperature exposure with pressure application. This process is a non-contact technique which provides localized heating through custom-designed coils. It allows the right amount of heat to be applied exactly where it is needed for an exact period of time, ensuring controlled and accurate performance that can be easily repeated.

The objective of this study was to compromise between 3YSZ and 8YSZ as a second phases toughening alumina matrix. The composite powders were first synthesized by wet-milling technique and then sintered at different temperatures by HFIHS. The microstructure and mechanical properties were investigated and discussed.

2. EXPERIMENTAL PROGRAM

2.1 Materials And Processing

Nanocrystalline alumina ($\alpha-Al_2O_3$, purity 99.5%), 3 and 8 mol% yttria stabilized zirconia (3 and 8 YSZ, purity 99.9%) supplied by Nanostructured & Amorphous Metals, Inc., USA were used in this study. The initial powder mixture was composed of 80 vol% alumina and 20 vol% (3 or 8 mol %) yttria stabilized zirconia. All powders were mixed in a Universal Mill using polyethylene bottles and zirconia balls with a ball-to-powder weight ratio of 30:1 and a powder-to-alcohol weight ratio of about 2:1. Mixing was performed at a horizontal rotation velocity of 250 rpm for 24 h. The mixing conditions were the same for all powders. After mixing, the slurries were dried at 60 °C in a vacuum drying oven. The mixed powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the HFIHS machine. Details of this apparatus were introduced elsewhere [12, 13]. The system was first evacuated to a vacuum of 28×10^{-2} torr and then a uniaxial pressure was applied. An induced current (about 50 kHz) was then activated and maintained until densification was observed, indicating the occurrence of the sintering and the concomitant shrinkage of the sample. The choice of induced current was based on preliminary experiments aimed at determining the highest heating rate (highest current) that results in sample temperatures below the melting point of the material used and homogeneous distribution of sintering temperature. At the end of the process, the current was turned off and the sample cooled to room temperature at a rate which was determined to be approximately 500°C/min (final stage). After sintering, the samples were cut into bars with a dimension of 4×3×18 mm for subsequent indentation and microscopy observations. The specimens were machined using a diamond grinder and polished with diamond paste to 1 μ m. The relative density of the sintered sample was measured by the Archimedes principals. The

strength measurement was conducted with mechanical tester Shimadza AG-20KNG using a three-point bending method with a span length of 10 mm and a crosshead speed of 0.5 mm/min. Vickers hardness and toughness were measured by performing indentations at a load of 20 kg and holding time of 15 s. The determination of hardness and fracture toughness at ambient temperature followed the pattern ASTM C 1421-99. Fracture toughness is given by the values of K_{IC} . The factor K_{IC} was determined using the direct crack measurement method. The fracture surfaces were coated with gold using Polaron SC 7640 Sputter Coater to avoid charging during the SEM observation. The microstructure observations of the coated fracture surfaces were investigated using a JSM – 6400 Scanning Electron Microscope (SEM) (Oxford, UK). Phase identification was performed on samples cut from the center of sintered bodies using X-ray diffractometry (XRD) on a Philips PW1050 X-ray diffractometer.

3. RESULTS AND DISCUSSION

3.1 Effect Of Sintering Temperature On Density

Figure 1 (a) and (b) shows the density and relative density of Al_2O_3 -20vol% 3YSZ and Al_2O_3 -20vol% 8YSZ as a function of sintering temperature under the same conditions (60 MPa applied pressure and 200 °C/min heating rate). The relative densities of the specimens increased with increase in sintering temperature. It can be noticed that, despite the short sintering time when the current was applied, the density was improved with increasing sintering temperature, reached to maximum at a temperature of 1400 °C. However, the density almost remains constant beyond 1400°C. The high sintering efficiency could be explained from two aspects. First, the high pressure applied could accelerate the densification process. Second, the powder is heated in a very short time and high-temperature exposure when the heat is transferred to the product via electromagnetic waves.

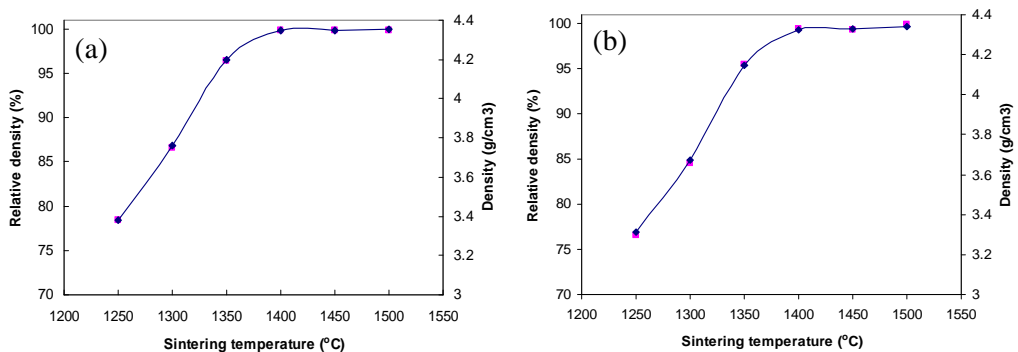


Fig. 1: Effect of sintering temperatures on density and relative density (a) Al_2O_3 +3YSZ, (b) Al_2O_3 +8YSZ

Figure 2 shows a comparison between densities of Al_2O_3 -20vol% 3YSZ and Al_2O_3 -20vol% 8YSZ as a function of sintering temperature, under the same sintering conditions. It is clear that, the density of Al_2O_3 -20vol% 3YSZ is higher than that of

Al_2O_3 -20vol% 8YSZ. This due to the density of 3YSZ is higher than that of the 8YSZ.

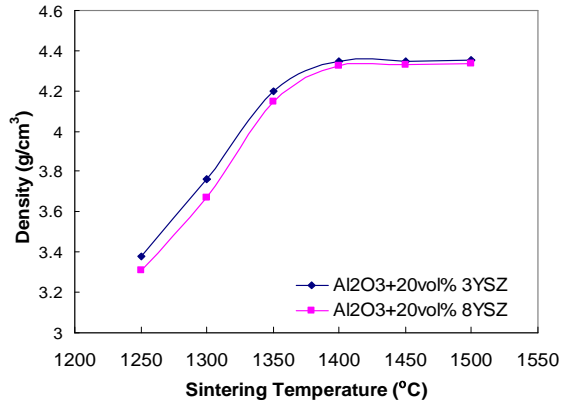


Fig. 2: Sintering temperatures vs. density for Al_2O_3 +3YSZ and Al_2O_3 +8YSZ

3.2 Effect Of Sintering Temperature On Mechanical Properties

Figure 3 (a) to (d) shows XRD data of the as received 3YSZ powders, as received 8YSZ powders, Al_2O_3 and Al_2O_3 + 3YSZ after sintering and Al_2O_3 and Al_2O_3 + 8YSZ after sintering, respectively.

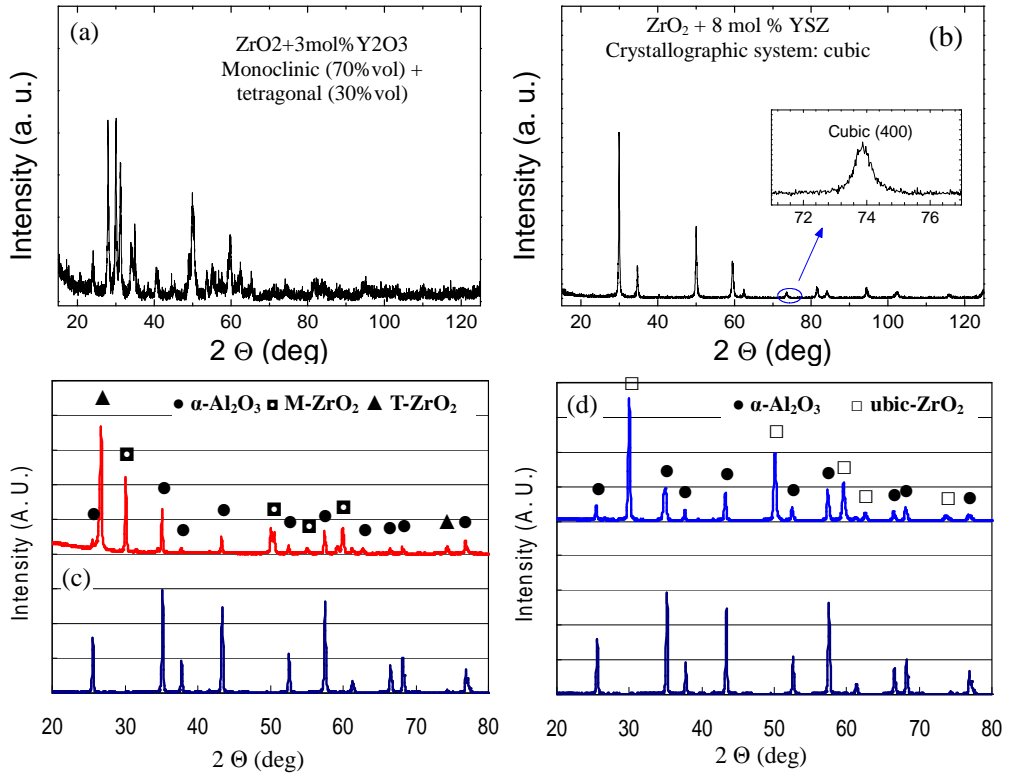


Fig. 3: XRD patterns of (a) as received 3YSZ powders (b) as received 8YSZ powders (c) Al₂O₃ and Al₂O₃ + 3YSZ after sintering and (d) Al₂O₃ and Al₂O₃ + 8YSZ after sintering.

XRD results showed that, all peaks of the Al₂O₃ are consistent with the peaks of the α-Al₂O₃ phase. The initial 3YSZ is consisted of 70%vol monoclinic and 30%vol tetragonal phase, **Figure 3 (a)**, while, the initial 8YSZ is consisted of cubic phase, **Figure 3 (b)**. After sintering, **Figure 3 (c)**, the compacted Al₂O₃ + 3YSZ powders consisted of α-Al₂O₃ as a major phase with the coexistence of monoclinic and tetragonal phase of ZrO₂+3mol% Y₂O₃ with the possibility of some transformation from tetragonal-to-monoclinic occurred during heating. No other phase was detected after sintering, which means no chemical reaction between α-Al₂O₃ and 3YSZ phase occurred during sintering. The compacted Al₂O₃ + 3YSZ powders consisted of α-Al₂O₃ as a major phase with the coexistence of cubic phase only of ZrO₂ + 8mol% Y₂O₃, **Fig. 3 (d)**. No other phase was detected after sintering, which means no chemical reaction between α-Al₂O₃ and 8YSZ phase and also no transformation from cubic to another phase occurred during sintering.

Vickers impressions had been carried through the surfaces of each one of the samples. These were already sectioned from the center of the sintered specimens and then polished. After taking the diagonal length measurements, the values of the Vickers hardness (GPa) were calculated using the following equation [16]:

$$H_v = 0.0018544 \left(\frac{P}{d^2} \right) \quad (1)$$

Where: H_V = Vickers hardness (GPa); P = applied load (N); d = arithmetic mean of the two diagonal length (mm). Each Vickers impression presented two pairs of radial cracks emerging from the corners. The equation used to determine the plane-strain fracture toughness (K_{IC}) values [16] is as follows:

$$K_{IC} = 0.016 \left(\frac{E}{H} \right)^{1/2} \frac{P}{C^{3/2}} \quad (2)$$

Where: K_{IC} = fracture toughness ($\text{MPa} \cdot \text{m}^{1/2}$); P = applied load (N); E = Young's modulus (GPa); H = hardness (GPa); and C = diagonal crack length (m). Young's modulus was obtained by rule of mixtures starting from 380 GPa for Alumina and 210 GPa for yttria stabilized zirconia [17- 20].

The relationship between Vickers hardness and fracture toughness of the Al_2O_3 -3YSZ and Al_2O_3 -8YSZ composites sintered by HFIHS as a function of sintering temperature are shown in **Fig. 4 (a)** and **(b)**. As was expected, the Vickers hardness and toughness increased with increasing temperature. The higher hardness and fracture toughness were obtained when 3YSZ was used as a second toughening phase. The hardness and toughness of the Al_2O_3 -3YSZ sintered composites reached 18 GPa and $6.8 \text{ MPa} \cdot \text{m}^{1/2}$ respectively, whereas the hardness and toughness of the Al_2O_3 -8YSZ sintered composites reached only 17 GPa and $5.7 \text{ MPa} \cdot \text{m}^{1/2}$ respectively. Induced stress may be the explanation for the toughening in 3YSZ. The induced stress explanation depends upon the tetragonal-to-monoclinic transformation, once the application temperature over pass the transformation temperature at about 1000°C . The pure zirconia particles in 3YSZ can retain the high-temperature tetragonal phase. Stress energies from propagating cracks cause the transition from the metastable tetragonal to the stable monoclinic zirconia. The energy used by this transformation is sufficient to slow or stop propagation of the cracks. A typical indentation of Al_2O_3 -3YSZ and Al_2O_3 -8YSZ sample is shown in **Fig. 5**.

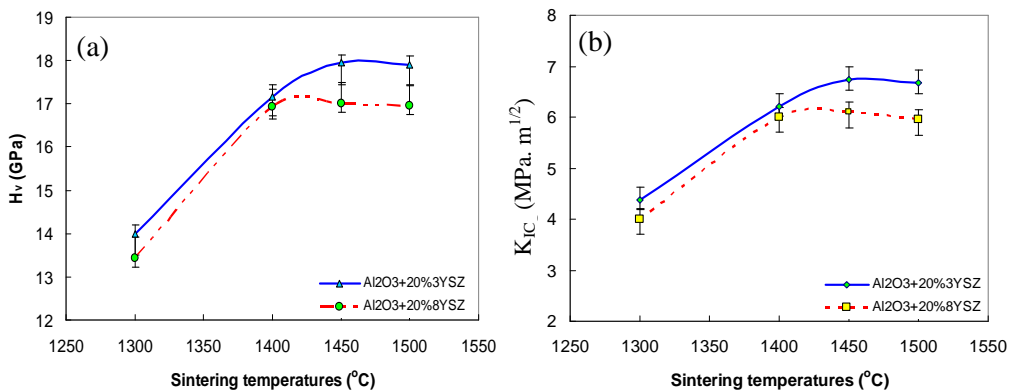


Fig. 4: Effect of sintering temperatures on (a) hardness (b) fracture toughness for Al_2O_3 +3YSZ and Al_2O_3 +8YSZ.

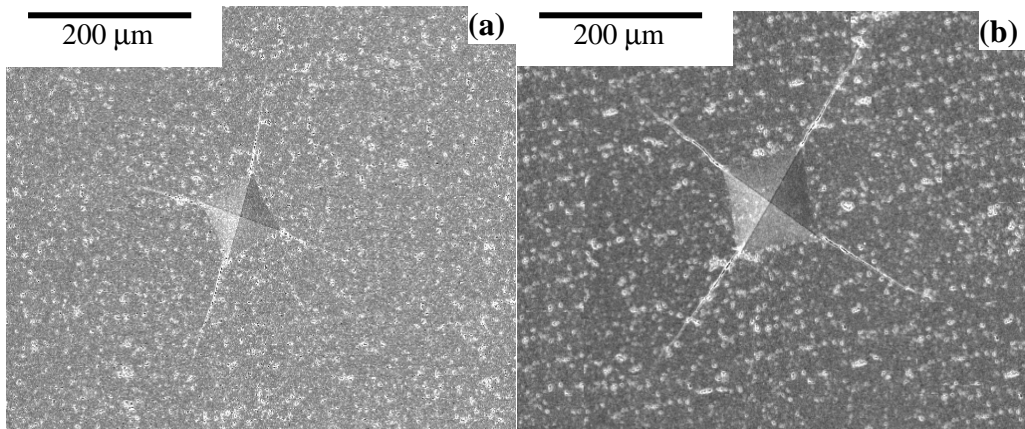


Fig. 5: Vickers hardness indentation of (a) $\text{Al}_2\text{O}_3+3\text{YSZ}$, (b) $\text{Al}_2\text{O}_3+8\text{YSZ}$, load 200 N.

Figure 6 shows bending strength of the $\text{Al}_2\text{O}_3-20\text{vol}\%$ 3YSZ and $\text{Al}_2\text{O}_3-20\text{vol}\%$ 8YSZ composites sintered by HFIHS as a function of sintering temperature. The flexural strength increased with increasing temperature, reached to the maximum value at $1450\text{ }^\circ\text{C}$, the bending strength did not vary with the sintering temperature. The strength of the $\text{Al}_2\text{O}_3-3\text{YSZ}$ sintered composites reached 970 MPa, whereas the strength of the $\text{Al}_2\text{O}_3-8\text{YSZ}$ reached only 895 MPa.

3.3 Microstructural Features

In general, sintered samples with higher relative densities exhibit greater mechanical properties. However, there is also an influence of microstructural uniformity on mechanical properties. **Figure 7** shows SEM micrographs of the fracture surface of the $\text{Al}_2\text{O}_3+\text{YSZ}$ samples sintered at $1400\text{ }^\circ\text{C}$, $\text{Al}_2\text{O}_3+3\text{YSZ}$ and $\text{Al}_2\text{O}_3+8\text{YSZ}$. In **Fig. 7 (a)** $\text{Al}_2\text{O}_3+3\text{YSZ}$, showed highly homogeneous microstructures without agglomerates. The grain size is relatively small compared to that in **Fig. 7 (b)**. These provided better densification, less porosity in the sample and no abnormally grown alumina grains. The intragranular fracture mode was dominant during fracture, indicating the presence of stiff grain-boundaries. When using 8YSZ as a second phase toughening alumina, **Fig. 7 (b)**, the grain size rapidly increased and abnormal grains appeared.

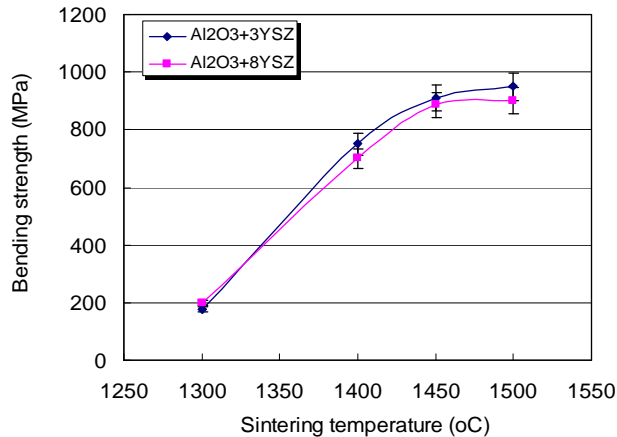


Fig. 6: Sintering temperatures vs. flexural strength for Al₂O₃+3YSZ and Al₂O₃+8YSZ.

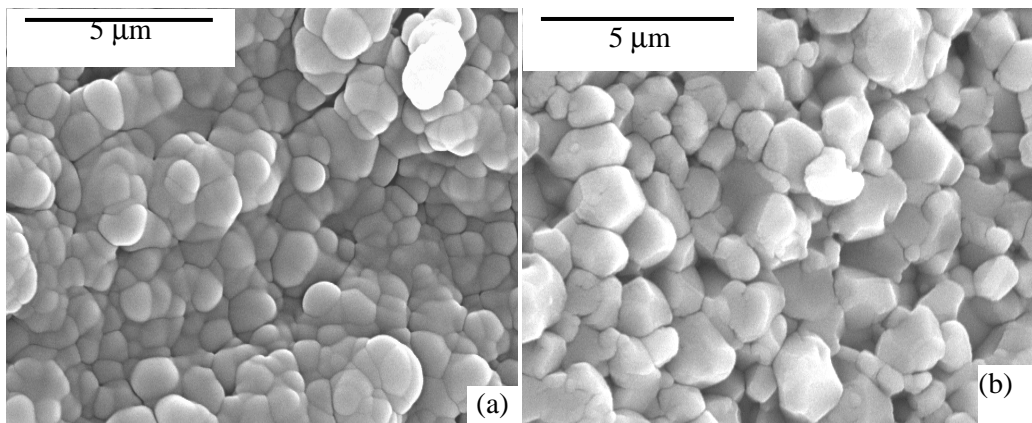


Fig. 7: SEM micrographs of Al₂O₃+YSZ samples sintered at 1400 °C (a) Al₂O₃+3YSZ, (b) Al₂O₃+8YSZ.

4. CONCLUSION

From the present investigation the following conclusions can be obtained:

1. Two second phase 20 vol. % – (ZrO₂+3 and 8% mol Y₂O₃) were mixed with high pure alumina and consolidated very rapidly to full density by HFIHS.
2. The mechanical and microstructure properties of the alumina compacts were significantly improved by using both of ZrO₂+3 and 8%mol Y₂O₃, however, the results showed that, 3YSZ is most effective as a second phase toughening Alumina then 8YSZ due to tetragonal-to-monoclinic phase transformation.
3. The hardness and toughness of the Al₂O₃–3YSZ sintered composites reached 18 GPa and 6.8 MPa.m^{1/2} respectively, whereas the hardness and toughness of the Al₂O₃–8YSZ sintered composites reached only 17 GPa and 5.7 MPa.m^{1/2} respectively.
4. The strength of the Al₂O₃–3YSZ sintered composites reached as high as 970 MPa, whereas the strength of the Al₂O₃–8YSZ reached only 895 MPa.

5. ACKNOWLEDGEMENTS

This work was supported by the Korean Research Foundation Grant Funded by Korea Government (MOEHRD) (KRF-2005-210-D00042)

6. REFERENCES

- [1] V. A. Dubok, Bioceramics, yesterday, today, tomorrow, powder metallurgy and metal ceramics, Vol. 39, No. 7-8, pp. 381-394, 2000.
- [2] A. Marti, Inert bioceramics (Al_2O_3 , ZrO_2) for medical application, Injury, Int. J. Care Injured 31 (2000) S-D 33-36
- [3] Maria Cecilia Correa de sa e Benevides de Moraes, Carlos Nelson Elias, et al., Mechanical properties of Alumina- Zirconia Composites for Ceramic Abutments, Materials Research, vol. 7, No. 4, pp. 643 – 649, 2004
- [4] M. Szutkowska, Fracture resistance behavior of alumina zirconia composites, Journal of Material Processing Technology, Vol. 153-154, No. 10, Pp 868-874, 2004.
- [5] S. Tekeli, M. Erdogan, and B Aktas, Influence of α - Al_2O_3 addition on sintering and grain growth behavior of 8 mol% Y_2O_3 - stabilized cubic Zirconia (c- ZrO_2), Ceramic International, No. 30, pp 2203 – 2209, 2004
- [6] R. Choi and N. P. Bansal, Mechanical behavior of Zirconia / alumina composites, Ceramic International, No. 31, pp 39 – 46, 2005
- [7] D. Basu and B. K. Sarkar, Effect of Zirconia addition on the fatigue behavior of fine grained alumina, Bulletin of Material science, Vol. 24, No. 2, pp 101-104, 2001
- [8] C. Fernandez, E. Verne, et al., Optimization of the synthesis of glass- ceramic matrix biocomposites by the “ response surface methodology”, Journal of European Ceramic Society, Vol. 23, pp 1031 – 1038, 2003
- [9] Jinsheng Hong, Lian Gao, et al, Spark plasma sintering and mechanical properties of $\text{ZrO}_2(\text{Y}_2\text{O}_3) - \text{Al}_2\text{O}_3$ composites, Materials Letters, vol. 43, pp. 27 – 31, 2000
- [10] L.Gao, H. Z. Wang, et al., $\text{SiC-ZrO}_2(3\text{Y})-\text{Al}_2\text{O}_3$ nanocomposites superfast densified by spark plasma sintering, Nanostructured Materials, vol. 11, No. 1, pp. 43 – 49, 1999.
- [11] W.H. Tuan, R.Z. Chen, T.C. Wang, C.H. Cheng and P.S. Kuo, Mechanical properties of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites, Journal of the European Ceramic Society, Vol. 22, pp. 2827–2833, 2002
- [12] S. W. Kim and K. A. Khalil, High-Frequency Induction Heat Sintering of Mechanically Alloyed Alumina–Yttria-Stabilized Zirconia Nano-Bioceramics, Journal of American Ceramic Society, vol. 89, No. 4. pp. 1280-1285, 2006.
- [13] K. A. Khalil and S. W. Kim, Densification of ZTA bioceramic composites by high-frequency induction heating, The 4th Korean-Sino Conference on Advanced Manufacturing Technology, pp. 145-149, 2005.
- [14] Hwan-Cheol Kim , Dong Young Oh , Synthesis of WC and dense WC-5Vol.%Co hard materials by high- frequency induction heated combustion, Materials Science and Engineering A, Vol. 368, pp 10 – 17, 2004
- [15] Hwan-Cheol Kim, Dong Young Oh, et al., Synthesis of WC and dense WC- x Vol.% Co hard materials by high- frequency induction heated combustion method,

- International Journal of Refractory & Hard Materials, Vol. 22, pp. 41-49, 2004
- [16] G.R. Anstis, P. Chantikul, B.R. Lawn and D.B. Marshall, A. critical evaluation of indentation techniques for measuring fracture toughness: I direct crack measurements, Journal of American Ceramic Society, vol. 64, No. 9, pp. 533-538, 1981.
- [17] C. Piconi and G. Maccauro, Review, Zirconia as a ceramic biomaterial, Biomaterial, vol. 20, pp 1 – 25, 1999
- [18] R.H.J Hannink, Transformation toughening in Zirconia-Containing Ceramics, Journal of American Ceramic Society, vol. 83, No. 3, pp. 461-487, 2000.
- [19] A. Bravo-Leon, Y. Morikawa, et al., Fracture toughness of nanocrystalline tetragonal zirconia with low yttria content, Acta Materialia, vol. 50, pp. 4555-4562, 2002.
- [20] R. S. Mishra, Journal of American Ceramic Society, vol. 79, pp. 2989-2992, 1996.

التلبيد باستخدام الحرارة الناتجة عن الحث الذاتي للتيار عالي التردد لحبيبات متناهية الصغر في الحجم من مركب البابو سيراميك الومنيا- زركونيا المدعمة بنسبتين مختلفتين من اليتريا

مركبات من الالومينا والزركونيا المستقرة بنائيا بإضافة كميتين مختلفتين من اكسيد اليتريم تم تصليدهم بالتلبيد بسرعة شديدة إلى ما يقرب الكثافة النظرية باستخدام (**High Frequency Induction Heat Sintering**). تم عمل مقارنه بين استخدام الزركونيا المدعمة بـ 3 مول % يتريا والآخرى المدعمة بـ 8 مول % يتريا كمقوى لزيادة الخواص الميكانيكية للالومينا. تم دراسة تأثير درجة حرارة التلبيد على الخواص الميكانيكية لكلا المركبين. تم تقييم المنتج باستخدام أشعة اكس وميكروسكوب المسح الالكتروني لدراسة مدى التغير الحادث في البنية الميكروسكوبية للمنتج. الصلادة الميكروسكوبية والمتانة ومقاومة المركب الملبد للكسر تم تحديدها أيضا. أثبتت النتائج ما يلي: الزركونيا المدعمة بـ 3 مول % يتريا تعتبر مؤثرة ايجابيا كعنصر مدعم للالومينا عن تلك الاخرى التي استخدم فيها الزركونيا المدعمة بـ 8 مول % يتريا. مركب يحتوى على الالومينا والزركونيا المدعمة بـ 3 مول % يتريا تتميز بخصائص ميكانيكية عالية وحجم حبيبات صغير وبنية ميكروسكوبية متجانسة تم تطويرها باستخدام هذا التكنيك ومن خلال هذا البحث.