Tribological and wear behaviour of alumina toughened zirconia nanocomposites obtained by pressureless rapid microwave sintering

L. Gil-Flores^{1*}, M. D. Salvador¹, F. L. Penaranda-Foix², A. Dalmau³, A. Fernández⁴,
A. Borrell¹

¹Instituto de Tecnología de Materiales, Universitat Politècnica de València, Camino de Vera S/N 46022, Valencia, Spain

²Instituto de Aplicaciones de las Tecnologías de la Información y de las Comunicaciones Avanzadas (ITACA), Universitat Politècnica de València, Camino de Vera S/N 46022, Valencia, Spain

³Instituto Universitario de Seguridad Industrial, Radiofísica y Medioambiental (ISIRYM) Universitat Politècnica de València, Camino de Vera S/N 46022, Valencia, Spain

⁴Centro de Investigación en Nanomateriales y Nanotecnología (CINN) (CSIC-UO-PA), Avenida de la Vega 4-6, 33940 El Entrego (Asturias), Spain

*Corresponding author: Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València, Camino de Vera s/n, 46022, Valencia, Spain. Tel.: +34963877007; Fax: +34963877629. E-mail address: *logiflo@upv.es*

Abstract

Dense alumina toughened zirconia nanocomposites (ATZ, 3Y-TZP with 20 wt.% Al₂O₃) were densified by non-conventional microwave sintering technology at relatively low temperatures (1200 and 1300 °C). The sintering method and its effect on densification, microstructure, mechanical properties and tribological behaviour were investigated. The outcomes demonstrated that the density rose as the sintering temperature was higher, and therefore the mechanical properties were enhanced, reaching a maximum hardness (18.4 ± 0.4 GPa) and fracture toughness (5.7 ± 0.3 MPa·m^{1/2}). In addition, the samples were subjected to a tribological test in dry and wet conditions, using artificial saliva. In both cases, the coefficient of friction and wear volume for samples obtained by microwave sintering are lower than conventional samples, with the wear volume being two times higher in dry conditions than in wet conditions.

Keywords: Zirconia-Alumina, Microwave sintering, Bioceramics, Mechanical properties, Tribology, Wear

1. Introduction

In recent years, zirconia and alumina have been considered the most important ceramic materials due to their excellent intrinsic properties, including hardness, fracture toughness, Young's modulus, chemical stability, wear and mechanical resistance. Thanks to these properties, zirconia and alumina are suitable for a wide variety of applications, including sensors, fuel cells, thermal barriers, implants and structural applications [1–3].

This study is focused on biomedical applications, in particular, orthopaedic implants, as the excellent biocompatibility of alumina and zirconia has been demonstrated [4]. The medical market is continuously improving, which relies heavily on the advancement of new nanocomposites and leading-edge sintering technologies. Therefore, ceramic nanocomposites have been extensively investigated in recent years, especially those containing alumina and zirconia in their composition.

Recent studies claim that the incorporation of alumina into the zirconia's matrix, alumina toughened zirconia (ATZ) materials, improves mechanical properties (i.e. hardness, toughness and wear resistance) [5,6], since these composites combine the best properties of alumina and zirconia. These qualities enable zirconia and alumina to be promising composites for dental implant applications.

There are several studies about the sintering of ATZ composites in the literature. Li et al. [5] sintered a composite of ZrO_2 (3YTZP) + 20 wt% Al_2O_3 using another non-conventional sintering technique: spark plasma sintering (SPS). The samples which were sintered at 1400 °C by SPS reached values of 12.6 GPa and 5.27 $\text{MPa m}^{1/2}$ of hardness and fracture toughness, respectively. Meena and Karunakar [6] also studied an ATZ composite (ZrO_2 (3YTZP) + 10 vol.% Al_2O_3) which obtained a maximum value of 19.9 GPa of hardness for a sample sintered at 1300 °C by SPS. In short, regarding the densification of materials, sintering mechanisms and methods influence the final properties and microstructure of the obtained material [7–13].

Current sintering of ceramics is based on the conventional heat transfer mechanisms: conduction, convection and radiation. This method requires a long processing time and

high energy expenditure to achieve such elevated temperatures and keep it for hours (around 2-4 hours or more) if highly dense materials are required [13]. This causes a microstructure typically of approximately ten microns and, consequently, lower mechanical properties. Through just a size reduction, a proper microstructural approach and the absence of changes in the substance, nanocomposites can present new properties reduction in size, an adequate microstructural design and no change in substance, nanocomposites can exhibit new characteristics, including wear resistance, fatigue resistance, greater strength and durability – properties that the same materials do not present in the micro or macro scales [14].

Nowadays, non-conventional sintering methods are under study to alter densification mechanisms that can enhance the mechanical properties and microstructure of sintering samples [15,16]. In this study, a microwave technique has been suggested, which uses a different heating mechanism based on the material's inherent dielectric properties. Generally, microwave sintering achieves higher material densification at lower dwelling temperatures compared to conventional sintering, using less time and energy [17–19].

For biomedical applications, dental restorations and implants, it is of paramount importance to study the wear resistance, as one of the main causes of implant failures is due to wear and debris generation. It is proven that wear debris induces a severe inflammation as a response that damages the healthy bones that support the implant [20,21]. Therefore, a tribological study in various conditions has been carried out in this study.

The purpose of this study was to obtain highly dense ATZ materials by non-conventional microwave sintering technology and compare their microstructure and mechanical properties, such as fracture toughness and hardness, with conventional-densified materials. In addition, the samples of each sintering method that exhibits the higher mechanical performance have been selected to assess the wear resistance studies in both dry and wet conditions. Tribological parameters such as the coefficient of friction (COF) and wear volume loss have been investigated along with a quantitative and qualitative analysis of the wear tracks.

2. Materials and methods

2.1. Materials

A commercial composite 3YTZP Zirconia-Alumina powder (TZ-3Y20A, Tosoh, Tokyo, Japan) was employed as raw material in this study. This composite has the following proportion: 80 wt.% of 3YTZP and 20 wt.% Al_2O_3 . In this study, this material will be called ATZ.

2.2. Forming and sintering conditions

Ceramic powders were uniaxially pressed at 80 MPa (Shidmazu AG-X Plus) in order to obtain green samples of 10 mm in diameter and 3 mm in height.

Green bodies of ATZ were sintered through two different methods of densification: conventional sintering (CS) and microwave technique (MW). Conventional sintering was performed in an electric furnace (Thermolyne type 46100, Thermo Fischer Scientific) under atmospheric conditions at 1400 and 1500 °C, a heating rate of 10 °C/min and a 2 h of dwell time. Regarding microwave sintering, this was carried out in an experimental microwave system manufactured and designed by ITACA (Institute of Information and Communication Technologies, Spain). Samples were introduced in a mono-mode circular cavity performing in the TE_{111} mode at 2.45 GHz of resonant frequency, which was tuned to maximize material microwave absorption at a controlled heating rate of 50 °C/min. Two final temperatures were selected, 1200 and 1300 °C and a dwell time of 10 and 30 min at the sintering temperature. The cavity had one 30-mm-diameter hole on the top that allowed access to a quartz tube holding the specimen (10 mm in radius and 3 mm in height) and a 12-mm-diameter hole in the lateral wall for a temperature sensor. A pre-calibrated infrared radiation thermometer (Optris CT-Laser GH, 5 μm) was used to monitor the sample temperatures. Hybrid heating, also known as bi-directional heating, was used to facilitate heating of the sample inside the microwave cavity, employing silicon carbide as susceptor. [22–24].

2.3. Mechanical and microstructural characterisation

Bulk densities of the sintered specimens were determined by Archimedes' method, dipping the samples into a water-based liquid, according to the ASTM-C-373 standard

[25]. Mechanical properties were evaluated on surfaces polished down to 1 μm with diamond paste. Hardness, H , and elastic modulus, E , were assessed using the nanoindentation technique. This test was also employed to assess the change of mechanical properties inside the footprint after the tribological tests. The system used in this study consists of a nanoindenter (Model G200, MTS Company, USA) with a Berkovich diamond tip. Tests were carried out under maximum depth control of the 1500 nm. The contact stiffness (S) was determined by the Continuous Stiffness Measurement technique (CSM) to determine the profiles of hardness and Young's modulus [26]. Amplitude was programmed to 2 nm with 45 Hz of frequency. A matrix with 16 indentations was performed for each sample.

Indentation-fracture method was used to estimate the fracture toughness, K_{IC} , according to according to the following Evans equation [27]:

$$K_{IC} = 0.16 \cdot \left(\frac{c}{a}\right)^{-1.5} \cdot H_V \cdot a^{0.5}$$

where H_V is the Vickers hardness; c and a is the palmqvist crack and the half length of the Vickers indentation, respectively. K_{IC} was determined by applying loads of 2 Kg for 15 s with a Shidmazu HMV-20 micro-indenter. 5 indentations were performed in each sample.

Microstructures of the studied samples were characterised using a Field Emission-Scanning Electron Microscopy (FE-SEM, Gemini Ultra 55 model, Zeiss). Grain boundaries were revealed after a heat treatment at 100 $^{\circ}\text{C}$ under the dwell temperature for 30 min. The average grain sizes were measured using the linear interception from FE-SEM micrographs [28]. Approximately 100 grains for each phase were studied. Wear tracks were observed by FE-SEM in order to analyse the wear morphology.

2.4. Tribological tests

Tribological tests were conducted using a reciprocating tribometer in samples, which have high mechanical properties. The different ceramic samples were rubbed against an alumina ball of 3 mm in diameter (G28), provided by Aparicio S.L (Spain). Alumina has been chosen as the counterpart due to its high hardness (1970 HV_{30}); in this way it is the sample that wears out and not the ball. The stroke length was $L = 2$ mm and the applied normal load of $F_N = 8$ N. Taking into account the mechanical properties of the Al_2O_3 ball

($\nu = 0.21$ and $E = 300$ MPa) and those of the studied samples, the maximum initial Hertzian contact pressure is $p_0 = 2354$ MPa. Figure 1 shows the conditions of the tribological test.

Figure 1. Conditions of the tribological test.

Two different test conditions were tested: (1) dry conditions and (2) wet conditions using artificial saliva (AS), the composition of which is shown in Table 1. Tests were carried out at room temperature.

Table 1. Chemical composition of the artificial saliva.

Compound	Concentration (g/L)
NaCl	0.40
KCl	0.40
CaCl ₂	0.60
Na ₂ HPO ₄	1.46
Urea	1.00

After the tribological tests, all samples were observed using an optical microscope coupled with a confocal laser. The experimental profiles of the different wear tracks were measured. For wear quantification, a Matlab routine was employed to fit a circle to the experimental profile and a line to the baseline of the experimental profile. The wear area (A_{wear}) was obtained by integrating the area of the circle that is below the base of the line. Finally, the wear volume (V_T) was obtained by multiplying this area by the length of the wear track (Figure 2).

Raman spectroscopy was carried out by means of a Raman emission spectrometer, Horiba-MTB Xplora, in order to analyse if the material had been degraded through the formation of monoclinic zirconia after the tribological tests [29]. Spectra inside and outside the wear track were assessed to verify this transformation.

Figure 2. Calculation of wear volume from the length of the wear track

3. Results and discussion

3.1 Densification and microstructural characterization

Table 2 summarises the sintering conditions and the final density of ATZ composites sintered by conventional sintering (CS) and microwave (MW).

Table 2. Overview of the sintering parameters and relative density for ATZ samples sintered by conventional and microwave.

Sintering method	Sintering temperature (°C)	Holding time (min)	Nomenclature	Relative density (%)
MW	1200	10	MW1200_10	98.5
	1200	30	MW1200_30	99.0
	1300	10	MW1300_10	99.8
	1300	30	MW1300_30	99.8
CS	1400	120	CS1400_120	98.3
	1500	120	CS1500_120	99.2

The relative density was calculated from the accurate theoretical density of the studied composite ATZ; 4.89 g/cm³. The results indicated that all specimens reached a high degree of densification, since most relative densities were above 99.0%. Relative densities increased with the rise of sintering temperatures, both in microwave and conventional sintering.

A significant outcome is that MW sintered samples showed a higher relative density than those sintered by CS, reaching 99.8% for MW1300_10. It should be noted that sintering temperatures and dwell times used in microwave sintering are significantly lower than in a conventional process. In short, whereas the sintering time required to reach relative densities higher than 99.0% using CS is 350 min and 1500 °C, the MW produces denser samples in only 35 min and 1300 °C. It should be noted that the final financial cost is reduced considerably due to the decrease in time processing and energy consumption and, consequently, the environmental impact is also lower. Therefore, microwave technology is considered an eco-friendlier technique than conventional sintering.

The FE-SEM micrographs of the ATZ composites densified by MW and CS are shown in Figure 3. The samples are highly dense and have a great homogeneity, as the alumina grains (the darkest ones) are uniformly dispersed in zirconia matrix. These results are consistent with the relative density values provided in Table 2.

Table 3 shows the final grain sizes of zirconia and alumina, which were measured from their micrographs. Average grain sizes increased with the holding time and final temperature in both sintering methods, as can be seen in the micrographs. Regarding MW densified specimens, the average grain sizes of ZrO₂ and Al₂O₃ in MW1200_10 reached approximately 210 and 270 nm, while in MW1300_10 the values of grain size were 280 and 400 nm for ZrO₂ and Al₂O₃ respectively.

For conventional sintered samples, the evolution of average grain sizes was similar to the MW ones; the higher the sintering temperature, the greater the grain size. The average grain sizes of ZrO₂ and Al₂O₃ were 240 and 350 nm respectively in CS1400_120, and 330 and 450 nm respectively in CS1500_120. The latter reached the highest value for both ZrO₂ and Al₂O₃ grain size.

Figure 3. FE-SEM micrographs for ATZ composite under different conditions: (a) MW1200_10, (b) MW1200_30, (c) MW1300_10, (d) MW1300_30, (e) CS1400_120 and (f) CS1500_120.

Wu et al. [30] investigated the effects of the Al_2O_3 addition into 3Y-TZP on the mechanical properties and microstructure of the composite. The increase of the content of alumina slightly promoted the grain growth during densification. Therefore, the average grain size of ZrO_2 is slightly bigger than that found in the literature [18].

Table 3. Average grain size of zirconia and alumina for ATZ composites sintered by microwave and conventional methods.

Sample	Grain size (nm)	
	Zirconia	Alumina

MW1200_10	210 ± 64	270 ± 84
MW1200_30	240 ± 67	300 ± 100
MW1300_10	280 ± 75	400 ± 157
MW1300_30	280 ± 70	380 ± 146
CS1400_120	240 ± 41	350 ± 98
CS1500_120	330 ± 56	450 ± 100

3.2 Mechanical properties after sintering

Regarding mechanical properties, the hardness and fracture toughness values for MW and CS are shown in Figure 4 and Figure 5, respectively. H_v values of MW sintered samples were between 17.3 and 18.4 GPa. As relative density (Table 2), hardness increases with the sintering temperature. However, except for MW1200_10, which reaches 17.3 GPa, the other samples had similar H_v values. For CS sintered samples, hardness did not change significantly after increasing sintering temperature, as both CS1400_120 and CS1500_120 reached 18.4 and 18.5 GPa, respectively.

Figure 4. Hardness as a function of indenter penetration depth profile for ATZ samples sintered by MW and CS.

Figure 5. Fracture toughness values for ATZ composites after microwave and conventional sintering at several temperatures.

The hardness of the materials was strongly influenced by their relative density and grain size. The increase of the hardness of ATZ composites with the final sintering temperature was consistent with the relative density increase.

Regarding Young's modulus, E did not undergo an abrupt change with the temperature or sintering method. All E values, for both MW and CS samples, were very similar (between 265-280 GPa). This is similar to the results of alumina toughened zirconia composites studied by Kern and Gadow [31].

Fracture toughness values for MW sintered samples were slightly greater than those densified by CS. The lowest K_{IC} value was 4.9 MPa·m^{1/2} in CS1400_120, while MW1300_10 was the highest at 5.7 MPa·m^{1/2}. There was an increase in the K_{IC} values of 15%, even when the samples sintered by MW required lower temperatures and shorter dwell times than those sintered by CS. The samples sintered by MW at 1300 °C show relative densities nearly 99.8% and similar grain size of zirconia but with a small difference in alumina grain size, which show a morphology slightly elongate in MW1300_10. This small difference of grain size makes that the fracture toughness values are higher. The samples sintered by conventional process show important differences in final relative density and grain size, CS1500_120 composite achieved the highest K_{IC} value at 5.5 MPa·m^{1/2}.

In the literature, the found K_{IC} values of ATZ samples are quite higher than those obtained in this study. Nevertheless, the achieved values were more than sufficient for dental joint applications [32].

Table 4 shows some mechanical properties which were found in the literature about the studied ATZ composite. The obtained hardness values in this study were higher than those in the bibliography, as there was an increase of 20% in hardness.

To summarise, the hardness of ATZ composites was improved. In addition, the use of a non-conventional technique such as microwave technology makes it possible to obtain highly dense samples with excellent mechanical properties at lower temperature and in shorter time.

Table 4. Overview of the hardness, Young modulus and fracture toughness values for ATZ investigated by different authors and in this study.

Material	Authors	H _v (GPa)	E (GPa)	K _{IC} (MPa·m ^{1/2})
Conventional sintering				
80 vol% 3Y-TZP + 20 vol% Al ₂ O ₃ (1500°C/2h)	Zhang et al. [33]	12.5 ^a	-	6.2 ^c
80 vol% 2.5Y-TZP + 20 vol% Al ₂ O ₃ (1500°C/1h)	Kern and Gadow [31]	14.2 ^a	278	5.9 ^c
80 wt% 3Y-TZP + 20 wt% Al ₂ O ₃ (1400°C/3h)	Sequeira et al. [34]	14.6 ^a	-	4.9 ^c
80 wt% 3Y-TZP + 20 wt% Al ₂ O ₃ (1500°C/2h)	Present study	18.5 ^b	276	5.5 ^c
Microwave sintering				

80 wt% 3Y-TZP +

20 wt% Al₂O₃

Present study

18.4^b

268

5.7^c

(1300°C/10 min)

Hardness was estimated by (a) microhardness, and (b) nanohardness. Fracture toughness was estimated by (c) the indentation-fracture method.

3.3 Tribological behaviour

ATZ samples with the highest mechanical performance were selected to carry out the tribological tests: MW1300_10 and CS1500_120.

The COF evolution over time for the CS1500_120 sample is shown in Figure 6. It increased just after the rubbing started and remained constant over time after 100,000 cycles. All samples presented the same frictional behaviour.

Table 5. COF values for MW1300_10 and CS1500_120 in wet and dry conditions.

Sample	Test conditions	COF
MW1300_10	WET	0.23 ± 0.02
	DRY	0.37 ± 0.03
CS1500_120	WET	0.35 ± 0.02
	DRY	0.38 ± 0.01

Figure 6. COF evolution with time for the sample CS1500_120.

Table 5 summarises the average values of the COF obtained in the tribological tests. They ranged from 0.23 to 0.38. The COF values for the samples tested in dry conditions were slightly higher than those which were tested under wet conditions. Samples obtained by microwaves presented a lower COF when compared to those sintered by CS. This effect was more pronounced in wet conditions.

The wear volume of material lost during the tribological tests was quantified and the average of the wear volume values are shown in Figure 7. The wear volume was two times higher in dry conditions than in wet conditions. These values were $2.9 \cdot 10^{-3}$ and $3.0 \cdot 10^{-3} \text{ mm}^3$ for MW1300_10 and CS1500_120 respectively. In contrast, the samples tested with artificial saliva reached $1.5 \cdot 10^{-3}$ and $1.6 \cdot 10^{-3} \text{ mm}^3$ for MW1300_10 and CS1500_120 respectively.

Figure 7. Wear volume of MW1300_10 and CS1500_120 samples in wet (AS) and dry conditions.

However, if the MW and CS samples are compared in the same condition (wet and dry), they do not present great differences in their measured wear volume, although MW samples showed a slight lower wear volume than those obtained by CS. These results are consistent with their mechanical properties, since there are no significant variations between them.

Figure 8 shows the hardness values of the two selected samples for the tribological test both in the matrix and inside the wear track. Few differences in hardness were obtained, except for CS1500_120 in dry conditions, whose hardness decreased by 12%.

Figure 8. Hardness of MW1300_10 and CS1500_120 samples both inside and outside the wear track in wet (AS) and dry conditions.

These results are consistent with the track's micrographs (Figure 9), as the wear was not very pronounced, except for CS1500_120, whose micrograph showed the greatest wear. The reduction of hardness for this sample is because the measurement was made on the adhered material, which was removed and adhered again in the wear track. Therefore, hardness was partially measured between the new adhered material and the sintered material, which caused the reduction in the hardness value.

After the tribological tests, the obtained wear tracks were assessed. In order to ascertain if zirconia had been transformed from tetragonal to monoclinic phase inside the wear track, the samples were subjected to Raman analysis. No peaks of monoclinic zirconia were found in any of the tracks, and therefore no transformation of zirconia tetragonal phase occurred [35,36].

Figure 9 presents the FE-SEM micrographs of the wear tracks of the different samples after the tribological tests. All samples present the same wear mechanisms: ploughing, plastic deformation and surface cracking. Therefore, according to Erikson et al. [37], mild wear regime is achieved after the tribological tests.

Figure 9. Micrographs of the wear track for MW1300_10 in (a) wet(AS) and (b) dry conditions; and CS1500_120 (c) in wet(AS) and (d) dry conditions.

Single debris particles of around 50 – 100 nm in diameter and agglomerations of debris ranging from 500 nm to 1 μm were observed inside and outside the wear tracks. This debris was powder-like and flake-like. The latter is known to be a consequence of the brittle fracture within the wear test [38]. Cracks were also found around the worn contact zone as a consequence of the wear induced by friction.

5. Conclusions

The results obtained suggest that ATZ composites can be highly densified by a microwave technique, producing materials with mechanical properties and microstructure similar to or even superior than by conventional sintering when the sintering temperatures and dwell times are fairly low in microwaves.

It should be noted that the hardness and fracture toughness properties of the sample MW1300_10 were 18.1 GPa and $5.7 \text{ MPa}\cdot\text{m}^{1/2}$ respectively, whereas CS1500_120 reached 18.3 GPa and $5.5 \text{ MPa}\cdot\text{m}^{1/2}$.

Concerning the tribology tests, there were no significant differences between MW and CS, although both the COF and wear volume of MW samples were slightly lower than CS samples. In addition, the test conditions had a strong influence on the wear of the material, with the most worn samples being those tested in dry conditions. Specifically, the wear volume was two times higher in dry conditions than in wet conditions.

Therefore, microwave sintering is a new technique that could replace conventional sintering to obtain dense ATZ composites with improved mechanical properties and finer microstructure. In addition, densification is achieved at shorter dwell times and lower sintering temperatures in comparison to conventional methods, meaning that microwave technology manages to reduce processing times and energy consumption, and, consequently, produces a lower environmental impact.

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