Improvement of mechanical and microstructural properties of 3Y-TZP materials by conventional and non-conventional sintering techniques

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Abstract

3 mol% Y_2O_3-stabilized zirconia nanopowders were fabricated using various sintering techniques; conventional sintering (CS) and non-conventional sintering such as microwave (MW) and spark plasma sintering (SPS) at 1300 ºC and 1400 ºC. A considerable difference in the densification behaviour between conventional and non-conventional sintered specimens was observed. The MW materials attain a bulk density

99.4% theoretical density (t.d.) at 1300 ºC, while the CS materials attain only 92.5% t.d. and SPS 98.7% t.d. Detailed microstructural evaluation indicated that a low temperature densification lead to finer grain sizes (135 nm) could be achieved by SPS followed by MW with an average sintered grain size of 188 nm and CS 225 nm. It is believed that the high heating rate and effective particle packing are responsible for the improvements in these properties. On this basis, it was also demonstrated that the hardness values of the samples increased significantly through the application of microwave sintering (16 GPa).

Keywords: A. Sintering; B. Grain size; C. Mechanical properties; D. ZrO_2

1. Introduction

Recently, much effort has been focused on the synthesis and densification of ceramic nanoparticles. The reason for the interest in nanocrystalline ceramics lies in their unique properties resulting from the small grain size, and the growing significance of grain boundaries in the nanocrystalline structure [1]. Due to the excellent properties of the Yttria-stabilized Tetragonal Zirconia Polycrystalline (Y-TZP) ceramic materials, such as low thermal conductivity, excellent biocompatibility, high fracture toughness and strength, high crack resistance and low wear rates are widely used for many applications [2]. Therefore, a variety of approaches in the field of sintering have arisen due to the widespread demand of ceramics in recent decades. Hence, understanding how the processing variables affect microstructural evolution is the key to initiating a proper sintering procedure. Various sintering methodologies based on diverse mechanisms are currently available to engineer the densification kinetics enabling the realization of above cited objectives. Applying a promising sintering procedure is, therefore, of a great importance for the superior performance of zirconia bodies. Conventional sintering techniques (hot pressing, sinter forging, hot isostatic pressing, etc.) and non-conventional sintering techniques (spark plasma sintering and microwave) represent an alternative approach to the densification of nanoparticles. In ceramic materials, the high temperatures required to fully densify ceramic powders result in large grain sizes due to Ostwald ripening when traditional sintering techniques are used. This makes it extremely difficult to obtain dense materials with nanometric and submicrometric grain sizes [3]. To overcome the problem of grain growth, non-conventional sintering methods has been proposed in this work.

Spark plasma sintering simultaneously applies pulsed electrical current and pressure directly on the sample leading to densification at relatively lower temperatures and short retention times [4-6]. As both the die and sample are directly heated by the Joule effect extremely high heating rates are possible due to which non-densifying mechanisms like surface diffusion can be surpassed. This technique is widely explored for the development of nanostructured ceramics. The mechanisms responsible for high rate densification were identified as grain rotation and sliding, aided by partial melting of the particle surface or plastic deformation in materials with low yield stress [7,8].

Microwave radiation for sintering of ceramic components has recently appeared as a newly focused scientific approach [9-16]. Microwave sintering has several advantages such as rapid end volumetric heating, improved production rate, enhancement in densification and grain growth prohibition of ceramics [17-19]. This technique generally uses a frequency of 2.45 GHz resulting in relatively rapid heating rates with uniform grained microstructures and has been employed for the sintering of a wide variety of ceramics ranging from dielectric materials to transparent ceramics.

Microwave heating of these material results from the absorption by molecular vibration (rotating electric dipole/dipole reorientation) and ionic conduction of a portion of the energy transported by an oscillating electric field [11]. A genuine “microwave effect”, i.e. the acceleration of diffusion mechanisms by the oscillating electric field, was also proposed by some authors to explain the enhancement of the sintering process [11,16,20,21].

The objective of the present study is therefore a comparative evaluation of the densification, microstructure development and mechanical properties in yttria-stabilized zirconia ceramics by the different sintering methodologies: conventional sintering (CS), microwave sintering (MW) and spark plasma sintering (SPS).

2. Experimental procedure

The raw material used in this study was commercial ZrO_2 (3Y-TZP-B) nanopowders (Tosoh Corp., Japan) with average particle size of (50-60) nm. The MW and CS specimens were prepared by uniaxial pressing at 200 MPa of pressure in a steel cylindrical die (2.5 mm thick, 10 mm ϕ). The green density was approximately 2.9 g cm^{-3}, i.e. 49% of theoretical density (6.08 g cm^{-3}). Before MW sintering, the binder of the nanopowders was burnt out under air in an electric furnace by heating at 5 ºC min^{-1} up to 600 ºC and by soaking for 3 h. The weight loss and shrinkage were about 0.5% and 20%, respectively. This preliminary debinding stage is necessary, since we observed cracks development during microwave heating for other specimens. After, all samples were sintered by different methods at 1300 ºC and 1400 ºC of final temperature.

Zirconia exhibit low dielectric losses at room temperature (~0.04) and increases markedly to ~1000 around 1000 ºC. This combined with low thermal conductivity ~2 W m^{-1} K^{-1} and high thermal expansion ($\alpha = 10^{-6}$ K^{-1}) suggest that thermal stresses resulting from non uniform and/or fast heating may cause warpage/cracking. Therefore, SiC crucible with a high dielectric loss must be used as a susceptor in heating by microwave. Green samples were sintered in an experimental microwave oven with 800 W of power and 2.45 GHz of frequency in microwave mono-mode rectangular cavity (Figure 1). This resonant cavity is coupled by an iris which dimensions are optimized for this application. The method to tune and detune the cavity consists of a sliding short circuit that can be moved electronically, depending on the reflected and consumed power and on the material temperature. The temperature was measured with an optical pyrometer (Optris GmbH, Germany) through a circular hole located on the top of the cavity.

(Figure 1)

The microwave sintered samples were heated with a heating rate of 30 ºC min^{-1} and a holding time of 10 minutes. Other non-conventional technique is spark plasma sintering, where the powder was placed into a graphite die with an inner diameter of 20 mm and cold uniaxially pressed at 30 MPa. Then, they were introduced in a pulsed electric-current pressure sintering HP D 25/1 (FCT Systeme GmbH, Germany) under low vacuum (10^{-1} mbar). The holding time was to 1 min at the maximum temperature under an applied pressure of 80 MPa and a heating rate of 100 ºC min^{-1}. The conventional heating process was carried out in an electrical furnace (Thermolyne type 46100) with 5 ºC min^{-1} heating rate and 1 h of holding time.

The density was measured by the Archimedes method (ISO-3369). Vickers hardness and fracture toughness assessments were carried out using the indentation method. Sintered samples were longitudinally cut in half cylinders with a diamond saw. The samples were previously polished (Struers, model RotoPol-31) with diamond to 1 μm roughness. The hardness of the materials was determined using the indentation technique (Buehler, model Micromet 5103) with a conventional diamond pyramid indenter. Measuring conditions for the Vickers hardness, H_{v}, were an applying load of 5 N for 10 s and the standard specification ASTM E92-72. The value of H_v is the relationship between applied load *P* and the surface area of the diagonals of indentation [22]. To estimate the indentation fracture toughness K_{IC}, 306 N Vickers indentations were performed on the surface of the samples, inducing Palmqvist cracks, from which the indentation fracture toughness was obtained by the method of Niihara [23].

In order to investigate sample microstructure, polished sections were thermally etched between 30 min in an electrical furnace under air 100 ºC below their maximum sintering temperature to reveal their microstructure. These sections have been observed using a field emission scanning electron microscope (FE-SEM, S4100 HITACHI). The grain size of the sintered samples was determined by multiplying the average linear intercept by 1.56 [24]. For each specimen, at least 15 lines were taken, and their average was reported.

3. Results and Discussion

Table 1 shows the sintering parameters, relative densities and average grain size of 3Y-TZP powders densified using the sintering methodologies of CS, MW and SPS. It can be observed, a meaningful difference between the relative densities of the conventionally sintered samples and those prepared by MW and SPS.

(Table 1)

At 1300 ºC, the density of the MW sample was significantly higher than that of the CS and SPS samples. At this temperature if we compare the samples sintered by MW with 10 min of dwelling time and CS with 1 h of dwelling time, the MW sample has a density enhancement up to 7% (from 92.5% to 99.4%) in a shorter time.

On increasing the temperature to 1400 ºC a significant improvement in densification is observed in the CS samples. On the other hand, the MW method shows full dense samples compared to the pressed compacts sintered by SPS at equivalent temperatures. Therefore, maximum densification was provided by MW, wherein samples could be sintered to >99.9% at a temperature of 1400 ºC for 10 minutes. According to previous reports [16,19], microwave heating has been recognized as a promising method to improve the densification in the same ceramic systems.

During microwave heating energy is transferred to the material electro-magnetically and not as a thermal heat flux enabling the material to be heated at rapid rates. The higher oxygen vacancies associated with 3 mol% yttria-stabilized zirconia provides higher ionic conductance at elevated temperatures leading to high dielectric losses and enhanced absorption of microwaves. This mechanism could be one possible reason for the shorter sintering times in MW.

The rapid densification of samples by SPS is attributed to the enhanced densification rate due to mechanisms such as particle rearrangement and the breaking up of agglomerates aided by applied pressure and faster heating rates. By rearrangement of particles, the SPS process also impedes the pore size increasing which was generally observed in the first and intermediate stages of sintering. Further, applied electric field also promotes the diffusion of ions and vacancies which enhances the sintering rate.

But this method has a big problem with the sintering of zirconia materials. As can be observed in Figure 2a, the sample sintered by SPS at 1300 ºC shows a full black colour. This is due to carbon diffusion within the zirconia sample by SPS processing, which is linked to the carbon rich atmosphere in which it is performed. As the sintering of the compact is taking place in a graphite die, the carbon diffuses into the sample from the die and this process is promoted by the applied pressure. Eliminating this contamination is possible (Figure 2b), but this implies high temperatures (>800 ºC) and a long time inside a furnace (>2 h), resulting in high economic costs.

(Figure 2)

Figure 3 represents the FE-SEM microstructure of 3Y-TZP samples sintered by SPS, MW and CS at 1400 ºC. All the sintered specimens exhibited equiaxed grain microstructures and the average grain size varied over a wide range from 135 nm to 256 nm. Nanocrystalline 3Y-TZP ceramics with average grain size of 225 nm and a complete elimination of residual porosity were obtained at 1400 ºC for 10 min by MW. The CS samples revealed a slight grain growth with an average grain size of 256 nm, and the SPS of 245 nm. These microstructures show similar values of grain size, but the MW micrograph (Figure 3b) shows a better homogeneous microstructure than the SPS and CS ones. Therefore, application of a heating microwave method has provided traces of improvement for grain growth suppression and densification compared to the other sintering techniques employed.

(Figure 3)

Figure 4 shows the variation of Vickers hardness and indentation fracture toughness with the sintering temperature. It is evident that the hardness improves significantly in MW and CS samples, whereas the fracture toughness slightly decreases with increasing grain size, in contrast to the values of the SPS sample. A maximum hardness of 16.0 GPa was achieved in the MW sample at 1400 ºC, which is an excellent value compared with 13.4 GPa which was achieved in the CS sample at the same temperature. The strong difference of the hardness values between 1300-1400 ºC in CS samples is due to the abrupt change in density (>6%). It can be noted that fracture toughness values of 3-6 MPa $m^{1/2}$ are commonly reported for the Y-TZP ceramics [6,16].

(Figure 4)

Fracture toughness is a property of a material which expresses its susceptibility for unstable crack propagation. In other words, it quantifies catastrophic fracture emanating from an existing crack or flaw. Localized high stresses in front of a crack tip cause plastic deformation, which helps to dissipate part of the fracture energy. As a general rule, increasing plasticity increases fracture resistance. Therefore, a correlation between microhardness (local plasticity) and fracture toughness (affected by localised plastic deformation) is not inconceivable. With this is mind, it is possible to consider that the increase of the fracture toughness in SPS samples could be referred to the plasticity of these samples sintered at high temperatures. A future work in nano-indentation studies is required to clarify this interesting mechanism.

4. Conclusions

The microstructural evolution of the nanometric 3Y-TZP powder subjected to different sintering techniques (MW, SPS and CS), has been carried out in the current investigation. Comparison with conventional sintering shows that microwave sintering has a number of benefits in terms of microstructural design and mechanical properties. Zirconia powders sintered by the microwave technique at the temperature of 1400 ºC shows a full density of 99.9% at an average grain size of 225 nm with a more homogeneous microstructure compared to the specimen conventionally sintered at the same temperature. Microwave sintered 3Y-TZP materials exhibited superior hardness values when compared with the CS and SPS materials. On the contrary, the fracture toughness values of samples sintered by MW and CS decreased compared to SPS samples due to the final plasticity that these materials show.

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Figure Captions:

Figure 1. Microwave system setup.

Figure 2. (a) 3Y-TZP sample sintered by SPS and (b) 3Y-TZP sample sintered by SPS after heating treatment.

Figure 3. FE-SEM micrographs of near full dense specimens sintered by SPS at 1400ºC/1min (a), MW at 1400ºC/10min (b), and CS at 1400ºC/60min (c).

Figure 4. Influence of sintering temperature on Vickers hardness and fracture toughness of the MW, SPS and CS fabricated 3Y-TZP materials.

Figure 1

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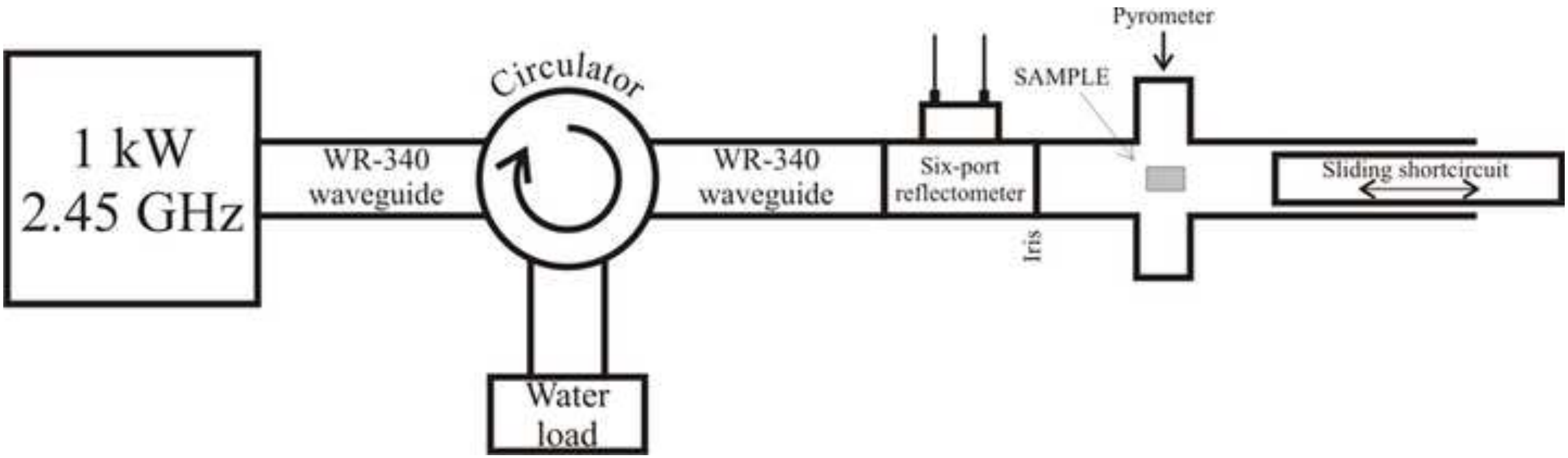

Figure 2
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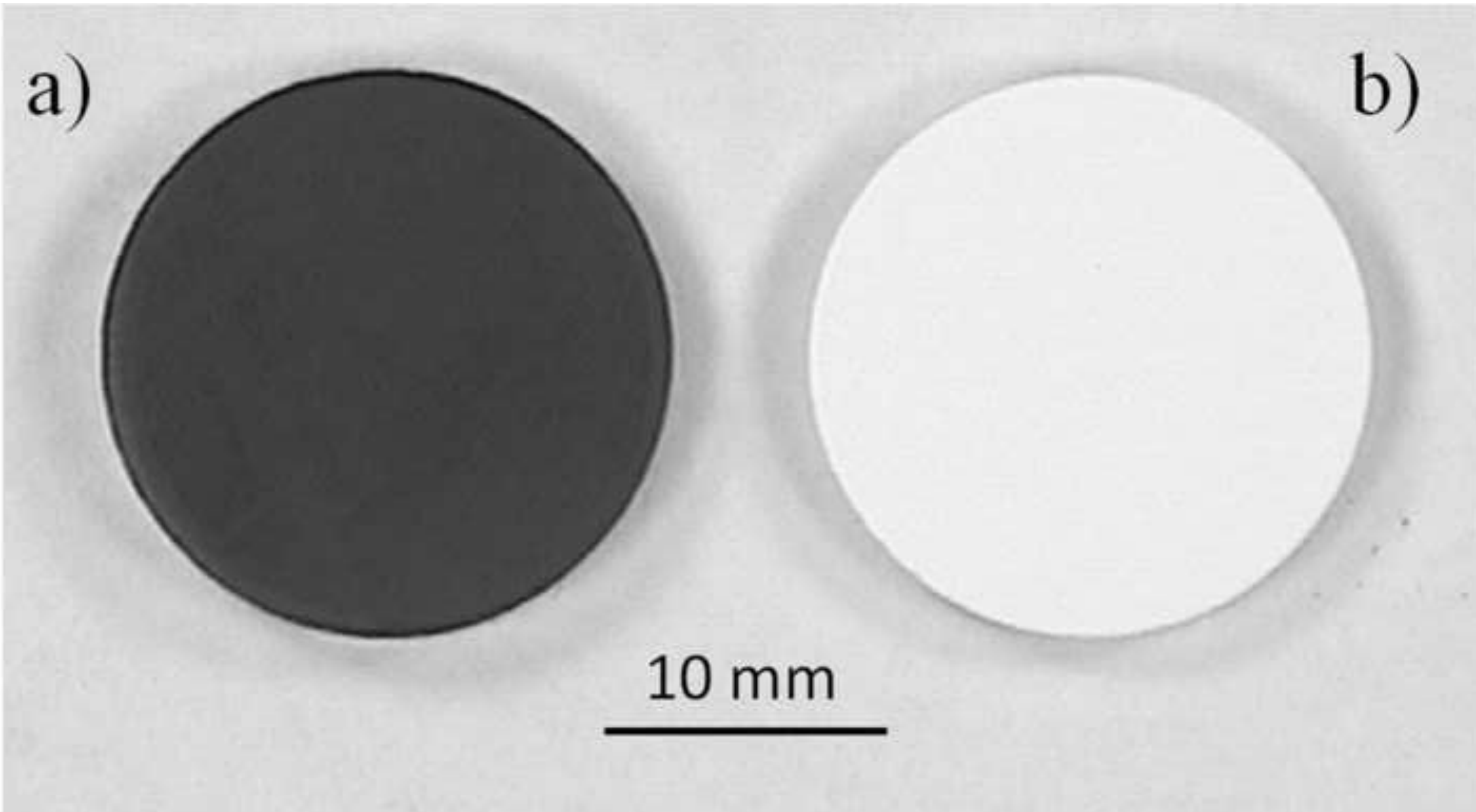

Figure 3

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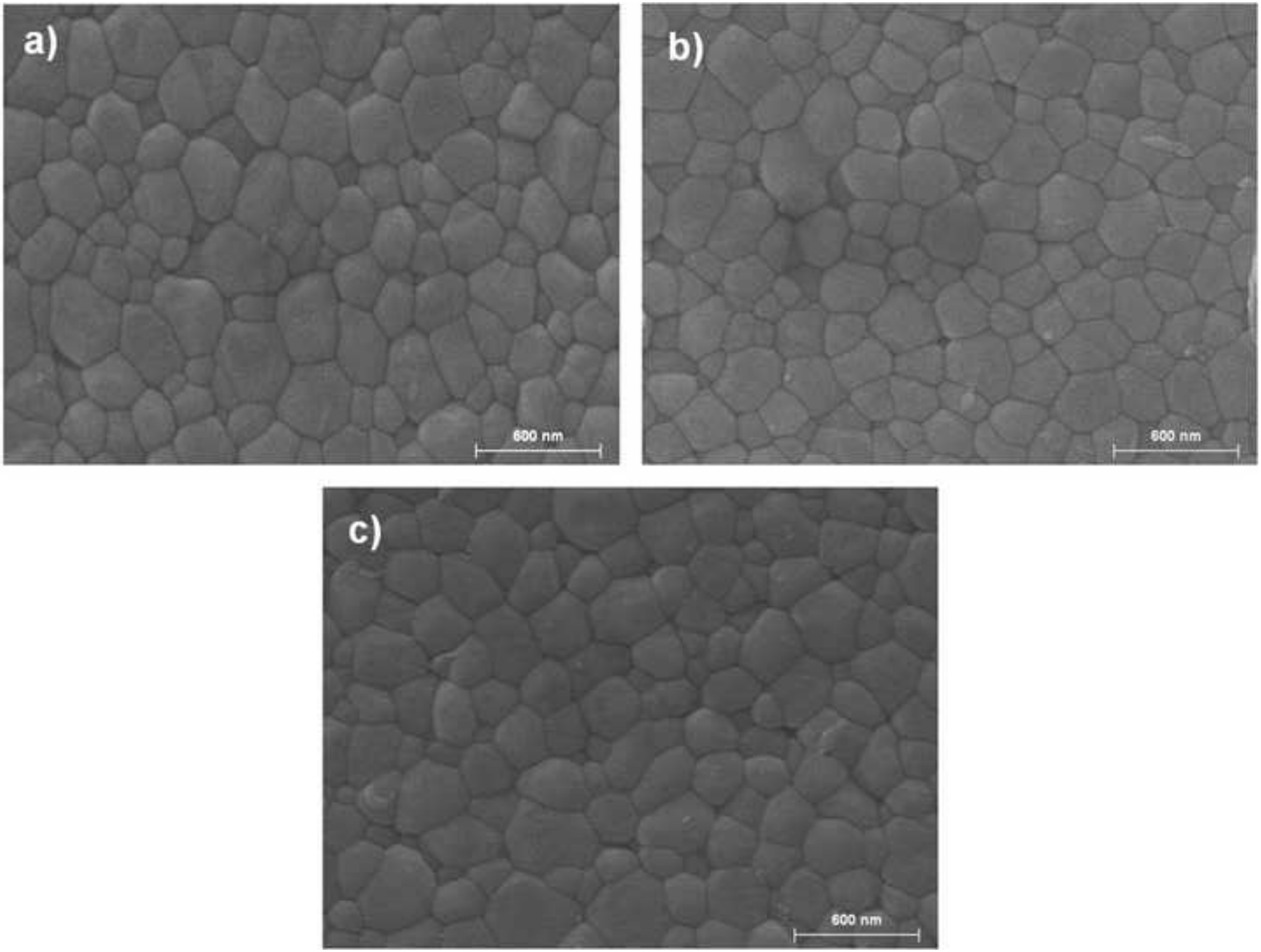

Figure 4
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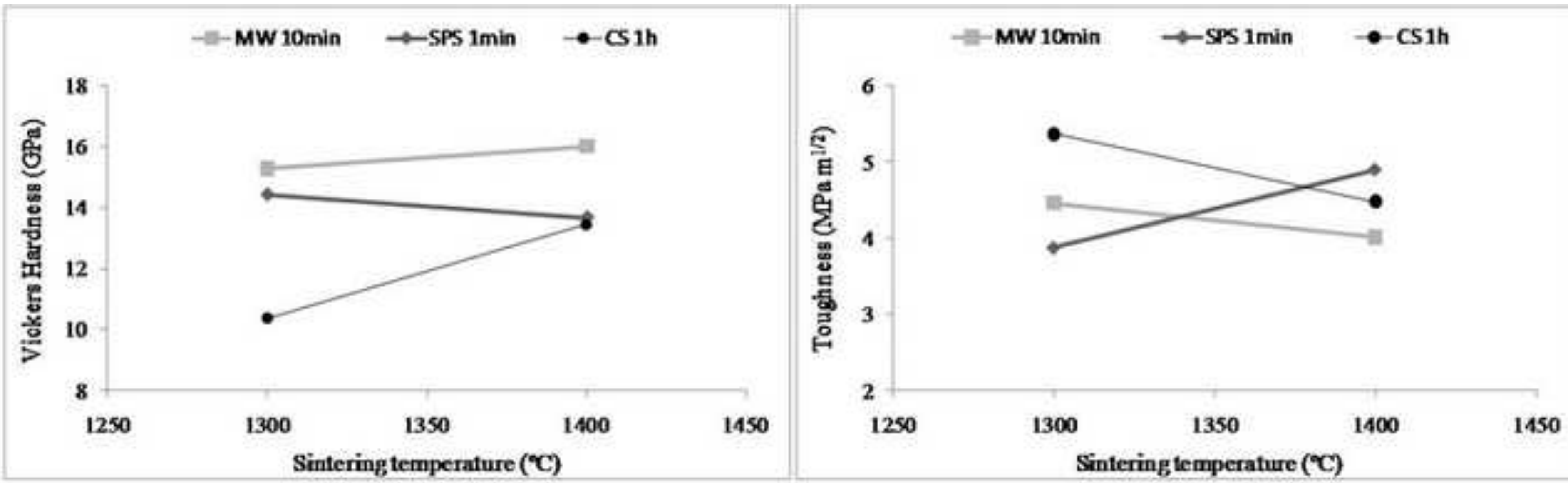

Table 1

Sintering technique	Final temperature (ºC)	Dwell time (min)	Relative density (% t.d)	Average grain size (nm)
CS	1300	60	92.5 ± 0.5	165 ± 5
	1400	60	98.3 ± 0.5	256 ± 3
MW	1300	10	99.4 ± 0.5	188 ± 6
	1400	10	99.9 ± 0.5	225 ± 4
SPS	1300	1	98.7 ± 0.5	135 ± 6
	1400	1	99.0 ± 0.5	245 ± 5

Table 1. Sintering parameters, sintered densities and average grain size of the 3Y-TZP materials.