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Microwave sintering of CeO_2 and Y_2O_3 co-stabilised ZrO_2 from stabiliser-coated nanopowders

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Abstract

Tetragonal ZrO_2 polycrystalline (TZP) composites with 2 wt.% Al_2O_3 and co-stabilised with 1 mol% Y_2O_3 and (4, 6 or 8) mol% CeO_2 were sintered at 1450 °C for 20 min in a single mode 2.45 GHz microwave furnace. For comparison, conventional sintering was performed in air at 1450 °C for 20 min. The starting powder mixture was obtained by a suspension coating technique using yttrium nitrate, cerium nitrate and pure m-ZrO_2 nanopowder. Fully dense material grades were obtained by both sintering methods. The influence of the composition and the sintering methods on the final phase composition and microstructure were investigated by X-ray diffraction and scanning electron microscopy. Finer and more uniform microstructures were observed in the microwave sintered ceramics when compared to the conventionally sintered samples. The fracture toughness increases with decreasing stabiliser content, whereas a reverse relation was found for the Vickers hardness. Comparable toughness and hardness values were obtained for the microwave and conventionally sintered samples.

Keywords: ZrO_2; Microwave processing; Sintering; Grain size; Mechanical properties

1. Introduction

Microwave sintering (MS) of ceramics is a novel technique that gained much attention because of the rapid heating, enhanced densification rate, and improved microstructure. In MS, electromagnetic waves interact with ceramics, leading to volumetric heating by dielectric loss. When conventional sintering (CS), heat is transformed to the surface of the ceramic component and reaches the core by thermal conduction, producing high temperature gradients and stresses. Such a volumetric heating of MS may result in ceramics with a more uniform and finer microstructure when compared to conventional sintering.

Over the years, various structural ceramics and composites such as CeO_2–ZrO_2, Y_2O_3–ZrO_2, and Al_2O_3 have been successfully microwave sintered.[1–5] Recently, work by Zhao et al.[1] showed that full density of 12 mol% CeO_2–ZrO_2 and 3 mol% Y_2O_3–ZrO_2 ceramics could be obtained by MS resulting in a high toughness of 10 MPa m$^{1/2}$ for Ce-TZP and a high hardness of 12.4 GPa for Y-TZP when sintered at 1450 °C for 20 min. Travitzky et al.[2,3] found that 3 mol% Y-TZP and 2 mol% Y-TZP/20 wt.% Al_2O_3 composites fabricated by MS exhibited a higher density, superior mechanical properties, and a smaller grain size compared to CS. Using a multimode microwave furnace with 2.45 GHz radiation, Xie et al.[4,5] revealed that 99.5% theoretical density and a fracture toughness of 13.7 MPa m$^{1/2}$ were obtained for 5 wt.% CeO_2 + 3 wt.% Y_2O_3 doped ZrO_2 ceramics sintered at 1500 °C for 15 min.

To improve the low strength of Ce-TZP and enhance the thermal stability of Y-TZP, co-stabilised ZrO_2 with different CeO_2 and Y_2O_3 content are fabricated. According to the reports by Huang and Li[6,7] and Lin[8,9] the ratio of CeO_2 and Y_2O_3 strongly influences the tetragonal ZrO_2 (t) and cubic ZrO_2 (c) phase content, leading to the significant difference in microstructure and mechanical properties. The presence of c-ZrO_2 largely decreases the mechanical properties of ZrO_2 ceramics. The fracture toughness of 12 mol% CeO_2–3 mol% Y_2O_3 co-stabilised ZrO_2 obtained by pressureless sintering at 1450 °C for 1–4 h is reported to be only 2.02–2.42 MPa m$^{1/2}$.[6] The large amount of cubic phase, thermodynamically calculated to be 37 mol%, explains the very modest fracture toughness.[6]

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The present work aims to investigate the influence of the mixed $CeO_2 + Y_2O_3$ stabiliser content on the microstructure and mechanical properties of Ce–Y-ZrO_2 ceramics consolidated by microwave sintering. A series of ZrO_2 ceramics co-doped with different amounts of CeO_2 and Y_2O_3 were prepared by a suspension coating method and sintered in a single mode microwave furnace and a conventional furnace. The density, microstructure, grain size distribution and mechanical properties are compared and discussed.

2. Experimental procedures

In the present experiments, a powder coating technique was applied to produce samples with 1 mol% Y_2O_3 + 4, 6 or 8 mol% CeO_2 co-stabilised ZrO_2. In addition, 2 wt.% Al_2O_3 was added as grain growth inhibitor for ZrO_2. Pure Y_2O_3 (grade YT-603, Atlantic equipment Engineers), $Ce(NO_3)_3\cdot 6H_2O$ (Aldrich Chemical Company), fine Al_2O_3 (grade SM8, Baikowski, 0.6 μm) and m-ZrO_2 nanopowder (Tosoh grade TZ-0) were used as starting materials. Hereafter, the name of the nomenclature of the samples is simplified as 1YxCe2Al (with $x = 4$, 6, 8), indicating a starting composition with 1 mol% Y_2O_3, x mol% CeO_2 and 2 wt.% Al_2O_3. A detailed description of the colloidal coating technique and green compact shaping are described elsewhere.[10,11]

The cold isostatically pressed cylinder shaped green compacts (size: 8 mm in diameter and 8 mm in length) were sintered in air using a 2.45 GHz microwave furnace (Ceralab II, MEAC, Leuven, Belgium) with a continuously adjustable power output from 0 to 1 kW, a cylindrical single mode tuneable applicator and a computer controlled system. A SiC tube susceptor was used to initially heat the low dielectric loss ZrO_2. The position of the samples in the microwave cavity was adjusted to diminish the influence of a non-uniform microwave field on the sintering properties. Furthermore, three samples of each composition were sintered for assessing the mechanical properties. The temperature in the microwave furnace was controlled by a pyrometer directly focussed on the sample surface. For comparison, samples were conventionally sintered at 1450 °C for 20 min using the same sintering cycle but with a cooling rate 20 °C/min.

The density of the sintered samples was measured by the Archimedes technique. Phase identification (XRD) on the surface of as-sintered samples was conducted on a θ–θ diffractometer (3003-TT, Seifert, Ahrensburg, Germany) using Cu Kα radiation (40 kV, 40 mA). Polished cross-sectioned and thermally etched samples in air at 1350 °C for 30 min, were examined by scanning electron microscopy (SEM, XL30-FEG, FEI, The Netherlands). The grain size was determined by Image-pro plus software according to the linear intercept method. The Vickers hardness, HV_{30}, was measured with an indentation load of 30 kg on a Zwick hardness tester (Model 3202, Zwick, Ulm, Germany). The indentation fracture toughness, K_{IC}, was obtained from the radial crack pattern of the 30 kg indentations and was calculated by formula Anstis et al.[12] using an elastic modulus of 200 GPa. The mechanical properties reported are the average and standard deviation of five indentations along the cross-sectioned surface on each of the three samples for each material grade.

3. Results and discussion

3.1. Sintering behaviour

Fully dense ceramic grades were obtained by MS and CS sintering for 20 min at 1450 °C. The advantage of microwave sintering has been revealed by Xie et al.[5] Microwave sintered samples exhibited an enhanced densification compared to the conventionally sintered samples, especially at lower sintering temperatures. The same density could be reached at a 100 °C lower temperature when using microwave sintering when compared to CS. It is known that microwave absorption strongly depends on the dielectric loss factor of the material of interest.[1] At low temperature, ZrO_2 with the dielectric loss factor 0.0034 cannot effectively absorb microwaves. However, with the help of hybrid heating by a SiC tube, heat is transferred to the ZrO_2 sample in the lower temperature region. After reaching the critical temperature (T_c), ZrO_2 strongly couples with the electromagnetic field and a higher heating rate is obtained due to the increased dielectric loss factor up to 0.531.

This change is consistent with the sintering curve shown in Fig. 1. When the temperature reaches the critical point, T_c,

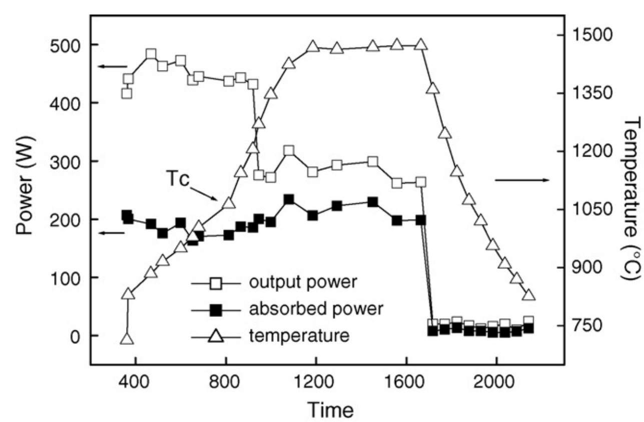

Fig. 1. Sintering cycle and power variation during microwave sintering of ZrO_2 ceramics.

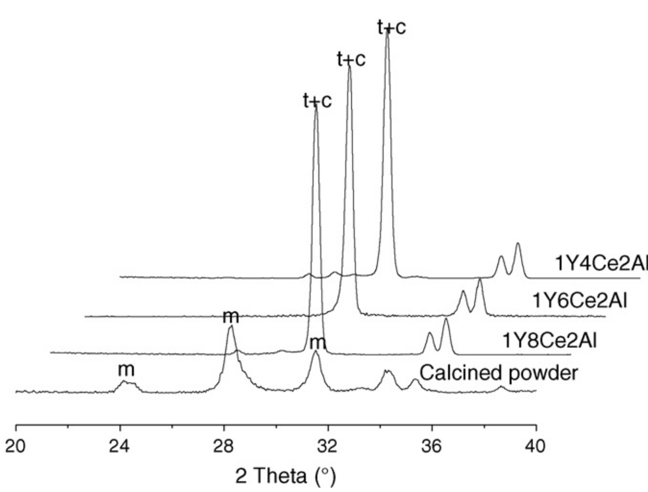

Fig. 2. XRD patterns of the 1YxCe2Al ceramics, microwave sintered at 1450 °C for 20 min, and the calcined 1Y8Ce2Al starting powder at 800 °C for 60 min.

around 1000 °C, the heating rate increases rapidly although the absorbed power is the same whereas the output power of the system concomitantly decreases. The cooling rate after sintering, established by switching of the power supply, is much faster than during conventional sintering, shortening the total sintering cycle.

3.2. Phase constitution

Fig. 2 compares the X-ray diffraction data of the calcined 1Y8Ce2Al ZrO_2 powder and polished surface of the microwave sintered 1Y*x*Ce2Al ceramics. After calcination at 800 °C for 60 min, the 1Y8Ce2Al powder exhibited the same crystal structure as that of the m-ZrO_2 starting powder. The XRD patterns of the sintered ceramics reveal that all CeO_2 and Y_2O_3 dissolved into the ZrO_2, with the formation of tetragonal and/or cubic ZrO_2. It should be mentioned that it is almost impossible to differentiate the t- and c-ZrO_2 phase by means of XRD, implying that the fully tetragonal samples might contain a minor amount of c-ZrO_2, especially with higher stabiliser contents. According to the thermodynamic simulation, the 1Y4Ce2Al and 1Y6Ce2Al grades are fully tetragonal at 1450 °C, whereas the 1Y8Ce2Al grade contains 5 mol% c-ZrO_2.[6,7] A relatively small amount of m-ZrO_2 is measured in the 1Y4Ce2Al sample. The m-phase however can also be a result of the stress-induced transformation during polishing. For the conventionally sintered 1Y*x*Ce2Al samples, the similar phase constitutions were observed.

3.3. Microstructure

The representative microstructures of the microwave and conventionally sintered 1Y*x*Ce2Al ceramics, sintered at 1450 °C

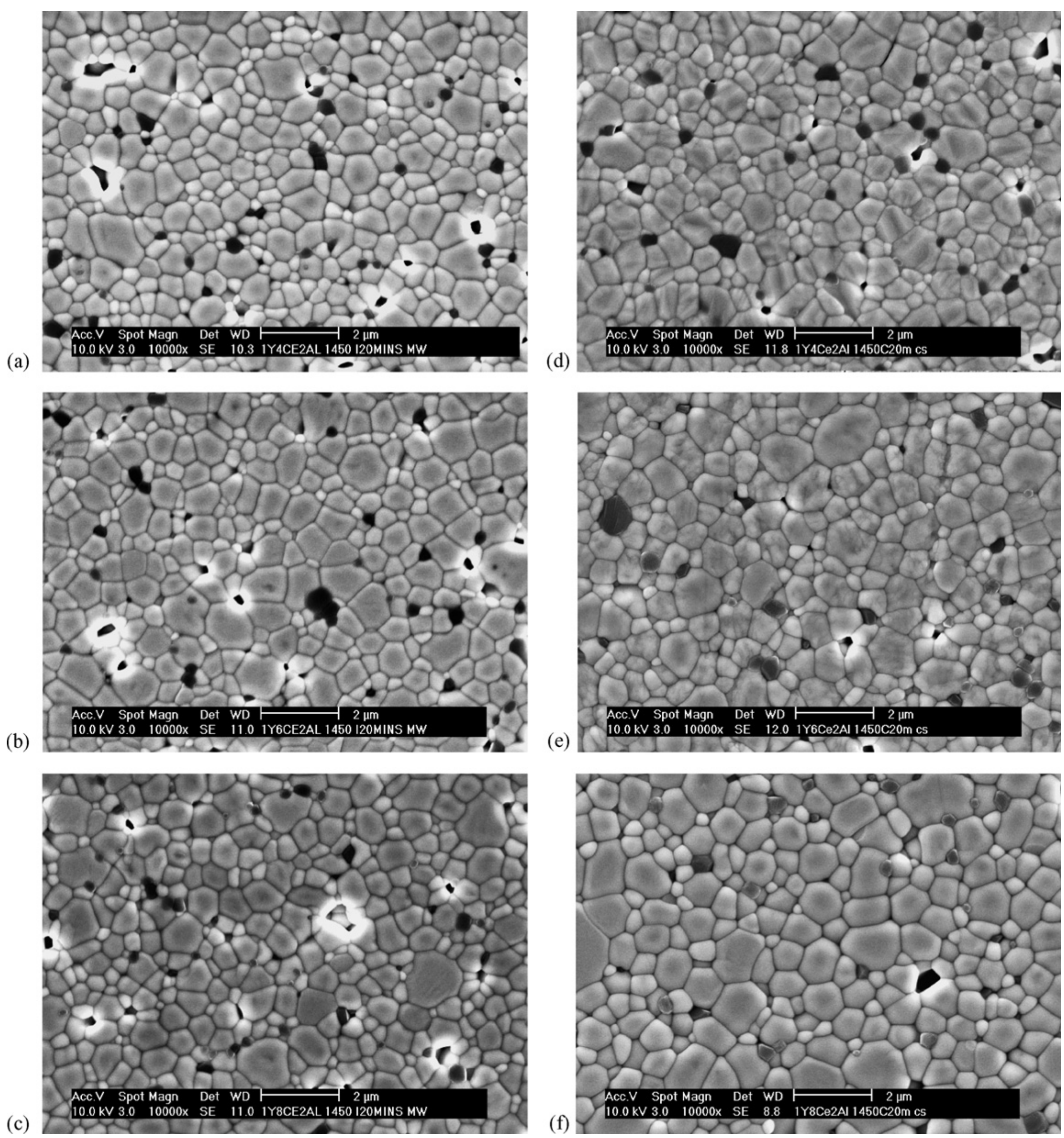

Fig. 3. Microstructures of the microwave (MS) and conventionally (CS) sintered ceramic grades: MS (a) and CS (d) 1Y4Ce2Al, MS (b) and CS (e) 1Y6Ce2Al, and MS (c) and CS (f) 1Y8Ce2Al, sintered for 20 min at 1450 °C.

Table 1
Properties of the 1YxCe2Al ceramics, densified by microwave (MS) and conventional (CS) sintering

Samples	Sintering method	Grain size (μm)	K_{IC} (MPa m$^{1/2}$)	HV_{30} (kg/mm^2)
1Y4Ce2Al	CS	0.58	13.96 ± 0.75	1044 ± 16
1Y6Ce2Al	CS	0.64	9.12 ± 0.70	1049 ± 15
1Y8Ce2Al	CS	0.68	5.17 ± 0.42	1056 ± 20
1Y4Ce2Al	MS	0.48	12.77 ± 1.05	1024 ± 12
1Y6Ce2Al	MS	0.57	8.13 ± 0.44	1045 ± 10
1Y8Ce2Al	MS	0.58	5.41 ± 0.82	1055 ± 19

for 20 min, are compared in Fig. 3. The dispersed black contrast Al_2O_3 grains are found to be pinned at the triple junctions of the ZrO_2 matrix, effectively limiting ZrO_2 grain growth by the elimination of grain boundary migration. The measured mean ZrO_2 intercept length is listed in Table 1. It is clear the mean ZrO_2 grain size of the MS samples is smaller than that of the corresponding conventionally sintered grade. For example, the grain size of 1Y4Ce2Al is 0.48 and 0.58 μm for MS and CS, respectively. A similar trend was also found for Y-TZP composites,[2] where the average ZrO_2 grain size in Y-TZP/20 wt.% Al_2O_3 composites was found to be 0.33 and 0.45 μm for MS and CS, respectively.

Moreover, the grain size increased with increasing CeO_2 content, i.e. from 0.48 μm for 1Y4Ce2Al to 0.58 μm for 1Y8Ce2Al. The cumulative ZrO_2 grain size intercept distribution of MS and CS ceramics is presented in Fig. 4. A more narrow size distribution is found for the MS samples. Based on statistical analysis, around 90% of the grains of the 1Y4Ce2Al, 1Y6Ce2Al and 1Y8Ce2Al ceramic grades are in the 0.2–0.9, 0.3–1.0, and 0.3–1.1 μm range when microwave sintering, whereas only 80% of the grains are in the same range in the conventionally sintered materials. The difference in grain size for the 1YxCe2Al grades implies that microwave sintering has the potential to limit the grain growth and homogenize the microstructure due to a volumetric heating mode and an enhanced vacancy diffusion. Though the similar sintering cycles were applied to the samples of MS and CS, a different microstructure was distinguished. As mentioned above, the MS is a volumetric heating, resulting a homogeneous temperature distribution, both on the surface and core position. As to the CS, the temperature is measured on the sample surface. There exists a high temperature gradient between surface and core positions when using high heating rate and short dwelling time. Present sintering was conducted at 1450 °C, with heating rate 50 °C/min and dwell of 20 min. Therefore, the different microstructure can be expected from this aspect.

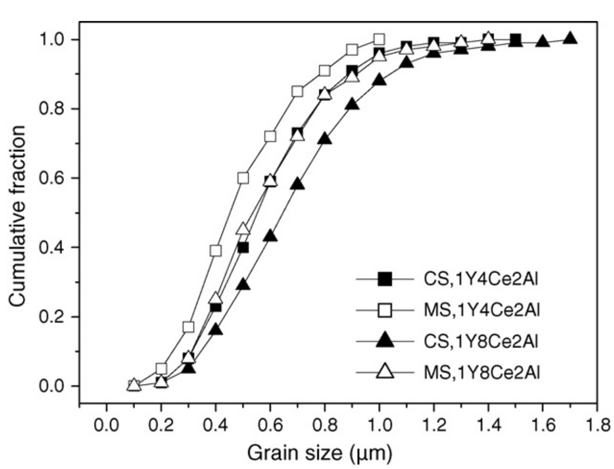

Fig. 4. Cumulative grain size distribution of the microwave (MS) and conventionally (CS) sintered 1Y4Ce2Al and 1Y8Ce2Al grades, sintered for 20 min at 1450 °C.

3.4. Mechanical properties

A comparable hardness and fracture toughness was measured for the MS and CS 1YxCe2Al (x = 4, 6, 8) ceramics, as indicated in Table 1. For instance, the MS and CS processed 1Y8Ce2Al have a fracture toughness of 5.41 and 5.17 MPa m$^{1/2}$ and a hardness of 1056 and 1046 kg/mm^2, respectively. Decreasing the CeO_2 stabiliser content from 8 to 4 mol% increases the fracture toughness to 12.77 and 13.96 MPa m$^{1/2}$ for MS and CS, respectively, whereas the hardness is hardly influenced. This observation is in agreement with that of Upadhyaya et al.[13] and Nightingale et al.,[14] who found a similar toughness trend for 3 and 8 mol% Y_2O_3–ZrO_2 ceramics obtained by microwave and conventional sintering. It is known that the fracture toughness of TZP is highly related to the transformability of the tetragonal ZrO_2 phase. According to the calculated isothermal section of the ZrO_2–CeO_2–Y_2O_3 system at 1450 °C, these compositions are almost 100% tetragonal.[7,15] Nevertheless, the A_s and M_s temperature, which reflects the transformability of the tetragonal ZrO_2 phase, are composition dependent. The 1Y4Ce2Al ceramic has the highest A_s and M_s temperature,[15] and is therefore most susceptible to transformation toughening, explaining the higher fracture toughness.

4. Conclusions

1 mol% Y_2O_3 + 4–8 mol% CeO_2 co-stabilised ZrO_2 ceramic grades with 2 wt.% Al_2O_3 addition were fully densified by means of microwave and conventional sintering. A finer grain size and more uniform microstructure were obtained by microwave sintering due to the shorter sintering cycle because of the faster cooling rate and the establishment of a more uniform temperature distribution within the short sintering time, respectively. The grain size increases with increasing CeO_2 co-stabiliser content. The hardness was hardly influenced by the CeO_2 content, whereas the fracture toughness strongly increases with decreasing CeO_2 content. An excellent toughness of 14 MPa m$^{1/2}$ in combination with a hardness of 1050 kg/mm^2 was obtained for the microwave sintered 2 wt.% Al_2O_3 doped 1 mol% Y_2O_3 + 4 mol% CeO_2 co-stabilised ceramic.

Despite the smaller grain size in the microwave sintered materials, comparable mechanical properties were measured for the conventional and microwave sintered samples.

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