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Microwave sintering of nanocrystalline Ytzp (3 Mol%)

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Abstract Microwave sintering of nanophase Y_2O_3–ZrO_2 (3 mol%), 3-YTZP, to near theoretical density was achieved using a multimode cavity furnace at 2.45 GHz. Sintering is discussed briefly and compared with the conventional sintering process reported in literature. Different characterization techniques have been performed, showing that a small and uniform nanograin structure was developed in fully dense sintered samples. The average grain size of the microwave-sintered specimens, less than 50 nm, was measured, and the creep behaviour of the samples was studied at temperatures between 1,050 °C and 1,150 °C.

Introduction

Microwaves are electromagnetic radiation with wavelength ranging from 300 MHz to 300 GHz. For industrial and scientific applications, microwave frequencies of 2.45 GHz are commonly used. Although it was conceived over 50 years ago, its use in ceramics processing is relatively new, gaining much attention during last decade, especially for ceramics sintering. Reasons from the growing interest in the use of microwave energy to sinter ceramic compacts include rapid heating, enhanced densification rate decreased sintering activation energy and grain growth inhibition [1–3].

Many ceramic materials have low microwave adsorption ability at lower temperature, whereas an increase in adsorption is produced at higher temperature [4]. Typically, the use of susceptors, to enhance the low temperature coupling, or the use of hybrid heating have been required for successful processing of those materials.

Microwave sintering of zirconia ceramics has been previously studied. Enhanced densification and reduced grain growth have been extensively reported in literature [5–9]. This work is devoted to the study of direct microwave sintering of yttria-stabilized zirconia nanopowders, YTZP (3 mol%), at a frequency equal to 2.45 GHz.

In this paper, we present the experimental procedure to obtain fully dense nano-YTZP, and then its mechanical behaviour at temperature below 1150 °C.

Experimental procedure

Materials

Spray-dried zirconia powders (graded TZ-3YB-E, TOSOH Co., Tokyo, Japan) with an average particle size of 28 nm were used. The powders were compacted by cold isostatic pressing with an applied pressure of 350 MPa and a holding time of 60 s. The density of the green specimens ranged from 48% to 50% of the theoretical density (TD), assuming that it is equal to 6.05 g/cm^3.

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The binder of the green compacts has been burned out by heating to 900 °C in a conventional furnace and holding for 2 h. The resulting compacts had a density of approximately 60% TD. The densities of the specimens were obtained both by Archimedes method and direct measurement of weight and dimensions. Both methods gave similar results.

Microwave furnace

The green samples (60% TD) were sintered in air using a 2.45 GHz microwave furnace (Autowave^{TM} VIS-300-01D). This model is operated through a computer interface that is controlled using a LabVIEW^{TM} executable program, which allows us to generate an adjustable microwave power from 0 kW to 3 kW continuous wave, and to register temperature or supplied power schedules running in the sintering processes. The specimen and two SiC susceptors were placed inside an inner, transparent to microwaves, chamber of alumina fibreboat for heat containment.

The temperature of the specimen inside the microwave furnace was measured by using an infrared fibre optic pyrometer Mikron-M770S/780 positioned directly above the sample at a distance of approximately 50 cm. Temperature measurement starts at 750 °C. The sample was viewed through a tube on top of the furnace cavity and a hole in the roof of the housing.

Sintering process

Sintering processes have been run using two different peak temperatures $T = 1{,}400$ °C and $T = 1{,}500$ °C, with dwell times of 30 min and 20 min, respectively. Thermal runaway has been observed in many microwave-heated materials above a critical temperature [10, 11]. In order to avoid thermal stresses and cracking, heating rate should be carefully controlled by varying the input microwave power. A constant power of about 0.5 kW was applied for an initial few minutes, and then was gradually increased to get the dwell temperature, and held constant during sintering. After the dwell time, the cooling ramp was set up at 20 °C/min until it was reached 1,150 °C to prevent surface damage. Then, control program was switched-off and the natural cooling rate was 80 °C/min.

Characterization

X-Ray diffractometry (XRD) was used to analyse the phase composition and the grain size of the nano-YTZP. Microstructure of fully dense sintered samples was observed by high resolution scanning electron microscopy (HRSEM) performed on specimens, which underwent the standard procedure for ceramics observation. The samples were not thermically treated to avoid grain growth. The average grain size of the polished surface of the sintered compacts was estimated by the Warren–Averbach method [12].

Mechanical tests

High temperature mechanical behaviour of fully dense sintered samples at 1,500 °C (20 min) was characterized by compression creep tests. The samples were cut in parallelepipeds of $4 \times 2 \times 2$ mm^3 and deformed in air at constant load in a prototype machine [13]. The creep tests were performed in the temperature range between 1,050 °C and 1,150 °C and stress range between 50 MPa and 120 MPa. Creep parameters n and Q were obtained, using the standard procedures.

Results and discussion

Sintered samples

Highly dense samples, (density approximately 98% TD), were achieved both at 1,400 °C and 1,500 °C dwell temperatures (thereafter will be labelled MWA-1400 and MWA-1500). It can be seen that the microwave-sintered samples at a given temperature exhibit enhanced densification for shorter holding time compared to the conventional-sintered at that temperature [9]. This result suggests that samples densify faster using microwave radiation.

Fracture surfaces of highly dense samples were observed by HRSEM. There are no significant differences between microstructures of both specimens. A typical fracture surface of MWA-1500 samples is shown in Fig. 1. No cracks have been found in the compacts after sintering, and the observed grains are relatively fine (well below 200 nm). This is a very rough estimation, which must be improved by XRD studies.

These ones have been performed under different temperature conditions (room temperature, 1,150 °C and 1,200 °C), i.e., below and above the martensitic transformation, to see if it could have any effect on phase composition and grain size distribution of microwave-sintered samples or not.

The average grain sizes ($\bar{d}$) of the sintered samples were estimated by the Warren–Averbach method [12]. The average grain size, do not change, within experimental scatter, for the different temperatures, i.e., no significant differences regarding the grain size distribution have been observed. Sintered samples

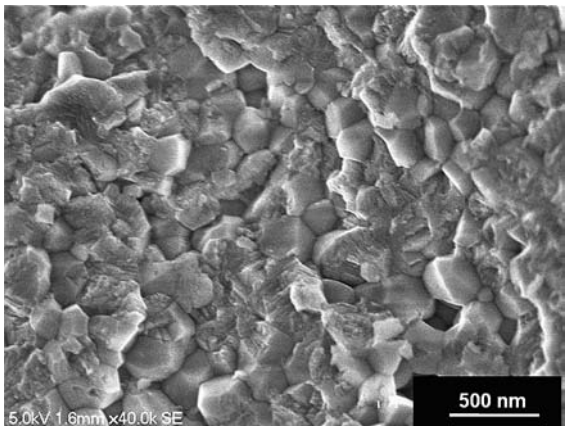

Fig. 1 HRSEM image of the fracture surface of the MWA-1500 microwave-sintered sample. A fine and uniform microstructure was observed

MWA-1400 and MWA-1500 have found to have a grain size of approximately 35 nm and 45 nm, respectively. The log-normal grain size distributions for different temperatures are shown in Fig. 2: (a) MWA-1400, and (b) MWA-1500.

These results reveal that microwave sintering has the potential of suppressed grain growth, since the average sizes obtained were almost equal to that of the initial powders. It is necessary to point out that 15 nm has found to be the average grain size for the MWA-1400 specimens at room temperature. This value cannot be accepted as the real grain size of the material, since it is smaller than the as-received powder size. This ''anomaly'' disappears when the sample is heated inside the diffractometer (the values obtained for 1,150 °C, 1,200 °C and then room temperature again, are almost the same and differ widely of 15 nm), so this fact could be due to the presence of residual stresses that did not relax during cooling period in sintering process. Further investigation must be done.

XRD analysis performed under different temperature conditions showed that microwave sintering produced a high fraction of tetragonal zirconia phase (almost 100%), so the sintered samples were essentially single phase. No evidence of cubic phase material was found in either case. Adjusted X-ray diffraction patterns at room temperature are displayed in Fig. 3.

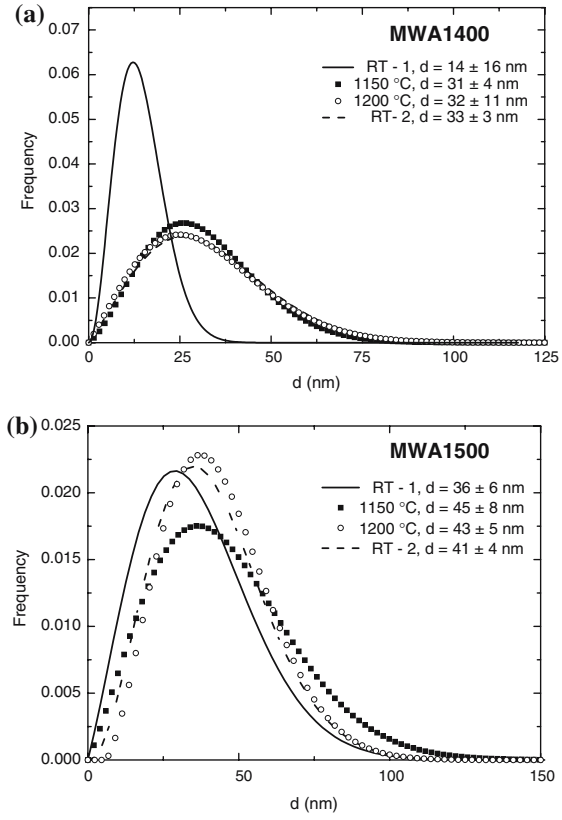

Fig. 2 Log-normal grain size distributions at different temperatures: (**a**) MWA-1400, and (**b**) MWA-1500

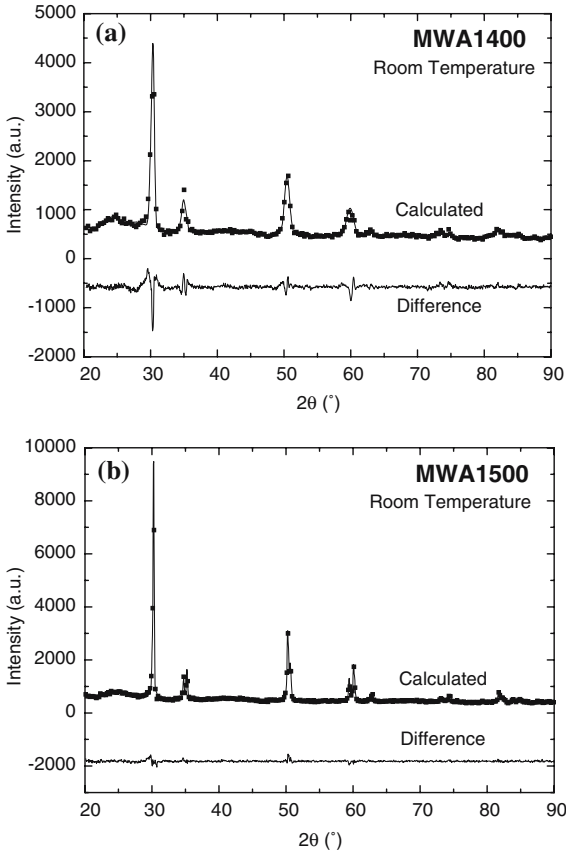

Fig. 3 Adjusted X-ray diffraction patterns performed at room temperature: (**a**) MWA-1400, and (**b**) MWA-1500. The experimental data, calculated through computer simulation and the difference between them have been plotted. All peaks correspond to tetragonal zirconia phase

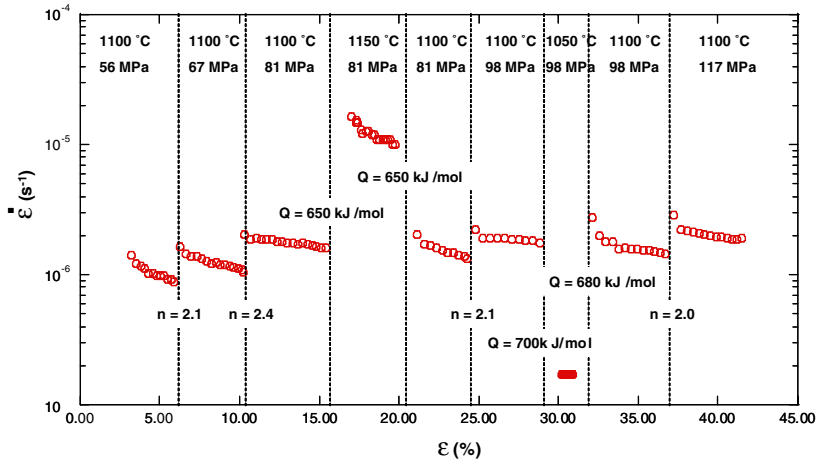

Fig. 4 Creep test at 1,100 °C of a MWA-1500 sample. Different n and Q values are shown

These results are similar to those reported previously [14], where it has been concluded that, in addition to finer grain size and uniform microstructure, microwave sintering achieved a greater fraction of tetragonal phase compared to that obtained by conventional heating; i.e., the small grain size achieved in microwave processing has been proved to avoid the tetragonal-to-monoclinic phase zirconia transformation during cooling.

Mechanical properties

High temperature mechanical behaviour of MWA-1500 specimens was characterized by compression creep tests. The strain rate ranged between 10^{-6} s^{-1} and 10^{-5} s^{-1}, and the direct measurement of the creep parameters n and Q were performed. Typical creep test as a strain rate versus strain plot is shown in Fig. 4.

The stress exponent value was found to be approximately equal to $n = 2$, and an average value of the activation energy for plastic deformation of (670 ± 25) kJ/mol were measured.

This value of the stress exponent has been shown to be typical of a grain-boundary sliding mechanism without the presence of a threshold stress. Further investigation must be conducted in order to explain this fact. The values of the activation energy are similar to those reported in literature for the creep of polycrystalline 1.7 mol% YTZP [15].

Conclusions

Microwave heating has been presented as a powerful technique for sintering nanopowders of 3-YTZP ceramics, promoting grain growth inhibition and uniform microstructure. Highly dense tetragonal samples have been achieved both at 1,400 °C and 1,500 °C sintering temperatures.

Mechanical properties of MWA-1500 samples were studied. The parameters of the constitutive creep equation were found to be $n = 2.2 \pm 0.2$ and $Q = (670 \pm 25)$ kJ/mol. An enhanced plasticity was found in this material.

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