Sintering of Zirconia Nanopowder by Microwave-Laser Hybrid Process

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A new hybrid sintering process has been developed by replacing all but one laser by microwaves in the existing simultaneous multiple laser process (SIMPLE). Microwave energy has been used to preheat the material before laser radiation, and the synergism between microwave and laser energies could effectively heat the material to temperatures of 1700°C and beyond in just a few minutes. Using this process, rapid sintering of 3Y–ZrO₂ (3Y–TZP) pellets has been achieved in a few minutes. Microstructural investigations reveal that the microwave–laser hybrid sintered pellets of 3Y–ZrO₂ have nanograins averaging about 20 nm. The microwave–laser hybrid sintering process can clearly be a new approach for fabrication of nanoceramics and nanocomposites.

I. Introduction

Sintering of materials in a microwave field has demonstrated advantages such as the rapidity in processing and improvement in physical, chemical, and mechanical properties with significant differences in their microstructure.¹⁻³ Multimode cavities are widely used for the purpose of sintering, in which the interference among microwaves results in regions of field concentrations with the maximum field located at the center of the cavity. Non-uniform field distribution, in general, leads to inhomogeneous heating patterns that usually result in a non-uniformly sintered material. Use of mode stirrers and rotating tables can effectively reduce this problem. On the other hand, microwave field distribution can either be altered or concentrated to a particular zone by the use of highly absorbing susceptors such as SiC rods. Modeling studies conducted by Iskander⁴ suggested that room-temperature susceptors (such as SiC rods) confine the field efficiently around the sample, thus enhancing the heating ability of the specimen. This procedure is highly effective in sintering various low dielectric loss ceramics such as ZrO₂, Al₂O₃, SiO₂, and mullite, etc. In addition to the above-described thermal effects, reports also exist on non-thermal effect playing a significant role in promoting sintering.⁵

Mixing of different wavelengths of electromagnetic radiations is, in general, beneficial for the enhancement of radiation effects. At the Pennsylvania State University, we have been involved, in cooperation with QQC, Inc., Dearborn, MI, in evaluation of their products obtained by simultaneous multiple laser process (SIMPLE).⁶⁻⁷ QQC, Inc. exploited a combination of excimer, Nd:YAG, and CO₂ lasers for a variety of surface modifications. Such a combination was used, for example, in the case of surface hardening of zirconia balls used in ball milling. After the treatment, it was found that a subsurface layer of 20 μm thick tetragonal zirconia transformed to cubic zirconia.⁷ The combined laser process was able to displace the atoms in tetragonal ZrO₂ lattice, thus inducing a phase transformation. The QQC process was also used in cladding steel with ceramic coatings. To our knowledge, not many deposition processes were able to fabricate thick coatings of such an outstanding quality with respect to toughness and adhesion. Also, a single laser coating process very similar to this has been reported by Krell and co-workers.⁸

Combining our experience in microwave sintering and laser processing, we attempt to explore the hybridization of these two energies. By hybridizing pulsed Nd:YAG (1.06-μm) laser and 2.45-GHz microwave radiation, we anticipate synergism between these two energies leading to an improvement in sintering. In this paper, we report the cooperative effects of these radiations during sintering of yttria-stabilized tetragonal zirconia polycrystals (3Y–TZP).

In the ceramics literature, a somewhat different process has been reported. Recently, laser-assisted microwave plasma (LAMP) has been demonstrated as a new tool for ceramics processing.⁹ The occurrence of plasma using centimeter waves or laser radiation happens because of vaporization of the target material and excitation of gas species. The combination of microwaves and laser allows controlling gas break down and avoiding a thermal run away.

In this paper, we report design of the microwave–laser hybrid system, cooperative effects between microwave and laser energies, sintering of 3Y–TZP ceramics, and microstructural and hardness characterization.

A kitchen oven (2.45 GHz, 1100 W) was modified by drilling two 2.5-cm holes on top, one for the laser beam and the other one for the infrared pyrometer. Power to the microwave facility was provided through a variac attached to the power meter. An optional thermocouple hole was also made at the bottom of the furnace. However, the temperatures reported in this paper were recorded using an infrared pyrometer (Model MA2SC, Raytek Co., Santa Cruz, CA). The IR pyrometer used in these experiments was capable of measuring temperatures from 350° to 2000°C. By using a data converter, the temperature data could be digitized and recorded in a computer for a span of every 1 s. The block diagram of the experimental setup is shown in Fig. 1. The Nd:YAG laser (Lumonics Model IK-701) used in the sintering experiments was defocused to have a laser beam diameter of ~15 mm. The average

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agglomerate size of zirconia powder (TZ-3Y, Tosoh Corp., Yamaguchi, Japan) was 210 nm, measured using a Malvern nanoparticle analyzer. Each agglomerate comprises a number of crystallites with an average crystallite size of 23 nm. Measured quantities of the powder were uniaxially pressed in a steel die, and the size of the pressed pellet was \( \frac{12}{10} \text{mm diameter and 5-mm thickness.} \) Before sintering, these pellets were cold isostatically pressed (CIP) resulting in \( \frac{10}{15} \%-15\% \) reduction of volume. During every experiment, it was ensured that the pellet top surface was completely enclosed by the laser beam. The sintered samples were characterized for density by the Archimedes procedure, for crystallinity by X-ray diffraction (XRD) (Scintag, Inc., Cupertino, CA), and for microstructure by field emission scanning electron microscope (FESEM; S-3500N Hitachi, Ltd., Tokyo, Japan).

Thermal equilibrium can be achieved by preventing thermal losses occurring from the sample. Detailed experimental studies established that the radiation losses are domimative only after \( 800^\circ C \). In the present case, a \( \text{ZrO}_2 \) pellet was surrounded by thin SiC plates and the temperature difference between them did not allow the \( \text{ZrO}_2 \) temperature to drop rapidly. The SiC plate and \( \text{ZrO}_2 \) pellet arrangement was placed inside a Fiberfrax high-alumina package with all the slits and holes completely closed using a 1-in. thick ceramic blanket. During laser–microwave hybrid sintering the only aperture kept open was the 1-in. hole on the Fiberfrax package right above the pellet for laser penetration.

The cooperative effects between laser and microwave energies for zirconia have been noticed during the sintering trials. Microwaves alone can heat the \( \text{ZrO}_2 \) pellet with the help of SiC preheating plates barely reaching close to sintering temperatures (1450°C). The kitchen oven used, however, has to be operated at its highest power limit to achieve this temperature. Also, the initial high heating rates can heat the pellet up to 1100°C; beyond this, the heating rates drop due to the thermal balance between absorbed heat and heat loss from the sample, and the sample needs a prolonged microwave exposure to heat the sample to sintering temperatures.

On the other hand, laser heating has the disadvantage connected with evaporation caused by the ablation of illuminated material. At high powers, namely, 1000 W and above, the top surface of the zirconia pellet gets intensively heated with melting. Power levels of 300 W and higher are still not good because of surface evaporation and non-uniform heating. Hence, further dropping of power is necessary to avoid any adverse effects of laser heating.

Ablation associated with laser illumination creates gas species. The excitation of these species by microwave irradiation leads to cooperative effects of heating in the hybrid process. The interaction of visible light and microwaves leads to plasma generation in addition to the bulk heating, and cooperative effects occurring between laser and microwaves are depicted in graphs of Figs. 2(a) and (b).

Our experiments established the fact that the laser radiation with a power of 90 W alone was not sufficient to heat the material to sintering temperatures. Higher laser power levels produce ablation of \( \text{ZrO}_2 \), making sintering unpractical. Hence, it was decided to preheat the sample by microwave energy to a certain temperature level, before irradiating with laser energy. The pulse energies and frequencies used were, namely, 1 J/(94 Hz) and 10 J/(10 Hz), and the microwave preheating temperatures varied between 450° and 1100°C. Lines in Figs. 2(a) and (b) mark the temperatures attained by initial microwave heating. The heating trends after these lines are predominantly laser-induced. In all the cases, the laser was irradiated for about 4 min after the line temperature. For example, at 90-W laser power, a microwave preheating temperature of 450°C was not sufficient enough to raise the temperature to sintering temperatures. From Fig. 2(a), it can be observed that the cooperative interactions become increasingly stronger with the increase in microwave preheat temperatures. The maximum temperature recorded was higher than 1700°C, in which the plasma interference factor had not been excluded. Figure 2(b) corresponds to an identical study with the doubling of laser power from 90 to 180 W.

Despite the fact that the laser–microwave hybridization can heat the 3Y–ZrO₂ samples to 1700°C and above, for sintering, the
temperature is just one criterion and factors such as volumetrical uniformity, crack-free samples, and minimal ablation are equally important ones. For example, higher laser power has resulted in raising the sample temperature to sintering temperatures in a few seconds, while the intense power has shattered the pellet into pieces, however. So, adequate conditions for sintering were achieved only after a number of trial and error procedures. The hybrid conditions used in the present sintering experiments were 90-W laser power, 1 J/pulse pulse energy, and 94 Hz (repetition rate) and 90-W laser power, 10 J/pulse pulse energy, and 10 Hz (repetition rate) with a microwave preheating temperature of \( \approx 1150^\circ C \). Microwave preheat temperatures lower than this have resulted in sample break-up due to poor particle–particle binding.

The role of the Nd:YAG laser is just not limited to heating. The laser pulses play an important role in hammering the powder sample because laser energy is delivered in pulses of 0.5 ms. Due to the pulsing effect, pressure waves were generated inside the pellet, which has helped in particle packing.10

Samples sintered by this procedure appear highly uniform. Density measurements, scanning electron microscopy (SEM) studies, and microhardness experiments indicated a well-sintered material. Laser irradiation of the top surface has caused a thermal gradient across the sample, but the smaller sample size precludes...
these samples from negative sintering effects. Also, the heating of SiC rods has diminished the thermal gradients within the sample.

Figure 3(a) shows a density graph only for the crack-free samples. The density points are unconnected in the graph because the sintering temperature used for each point is different. It should be noticed that densities of 90% and above could be achieved in less than 3 min (180 s) of laser heating. Figure 3(b) corresponds to the same sample sintered using only microwaves. Although the density values for microwave and hybrid sintering are nearly the same, the sintering time involved in the microwave process is several times higher than the hybrid-sintered process.

Link and Thumm11 have studied the combination of millimeter waves and conventional resistant heating in detail for YSZ materials. Using a dilatometer setup, in their study, they have established a correlation between density and microstructure. Though we have not conducted a similar study in this work, some interesting microstructural features are worth mentioning. Microstructural comparison studies were conducted between the microwave-sintered and the laser–microwave-sintered 3Y-TZP samples using micrographs obtained from FESEM. The micrographs of these samples are given in Figs. 4(a) and (b). A simple comparison between Figs. 4(a) and (b) highlights the clear differences between their microstructures. The micrographs obtained from top and bottom surfaces of the laser–microwave-sintered sample were identical. The laser–microwave hybrid sintered specimen shows uniform grain size distribution without any observable cracks or pores, whereas the best microwave-sintered sample revealed the existence of nano- and microcracks throughout the microstructure. In spite of the fact that their sample densities lie close to each other, the microstructural differences observed are astounding. Since pulsed laser was used in all our experiments, it is possible that the “hammering effect,” explained previously, could have resulted in better packing, which in turn was responsible for maintaining the sample in a thermal equilibrium. Average grain size was obtained by drawing a straight line that intersects with the X-axis at the 50% value in the cumulative size distribution graph plotted for 400 grains (Fig. 4(c)). The average grain size value derived from the plot was about 20 nm. This grain size is close to the starting crystallite size, indicating that possibly zero grain growth has occurred. The existence of nanopores could very well have hindered grain growth, keeping it to a minimum. Additional experiments are being conducted to understand the generation of nano-microstructure and to find out any microwave or laser involvement in the grain pulverization process.12

Vickers microhardness measurements were conducted on the ZrO₂ samples, and the results for an average of seven measurements are given in Fig. 5. The hardness values depend on laser pulse energies and repetition rates. The highest value of hardness was obtained for 90-W, 10 J/pulse, 10-Hz (repetition rate) treated samples with an irradiation time of 3 min.

In summary, the microwave–laser-hybrid system has successfully been demonstrated for sintering of 3Y–ZrO₂ ceramics that can possibly be extended to other oxide ceramics too. Various laser power levels, namely, 90, 180, and 270 W with different pulse frequencies (10 and 94 Hz) and pulse energies (1 and 10 J/pulse), were used for cooperative interaction studies. Adequate conditions for sintering were achieved only after many trial and error procedures to yield crack-free samples. The laser–microwave hybrid-sintered samples possessed nanograins with an average grain size of 20 nm, suggesting that only minimal grain growth has occurred during the sintering process. The pure-microwave-sintered samples revealed micro- and nanocracks throughout the sample, highlighting the advantage of the laser–microwave-hybrid process. The highest value of microhardness was obtained for a hybrid-sintered sample with the laser conditions 90 W, 10 J/pulse, and 10 Hz (repetition rate) irradiated for about 3 min.

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References