REAL-TIME MONITORING OF CERAMIC SINTERING WITH LASER ULTRASONICS

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SUMMARY

A Fabry-Perot Doppler interferometer that directly measures elastic waves from rough, optically diffuse, surfaces of materials has been constructed at the Idaho National Engineering Laboratory (INEL). This apparatus, coupled with a pulsed laser for elastic wave generation, is currently being used for real-time monitoring of the sintering of zinc oxide. From the ultrasonic propagation measurements, actual densities and shrinkage values can be calculated as the material sinters; the algorithm requires previous knowledge of the ultrasonic velocity dependence on density and assumptions concerning the method of shrinkage in the material.

INTRODUCTION

The properties of ceramic components are often determined by residual porosity in the material. Increased production efficiency and improvements in the consistency of properties of ceramics could be achieved if the porosity could be monitored during the sintering stage. In a material with porosity, the effective compliance is increased due to the presence of voids, with an attendant decrease in the elastic modulus and the velocity of ultrasonic wave propagation with increasing porosity. Therefore, ultrasonic measurements can be used to monitor the sintering process; however, to be most effective, a noncontacting technique is needed. This paper describes the successful application of laser ultrasonic techniques, which require only optical access to the sample surface, to the monitoring of sintering of zinc oxide at temperatures from 850 to 1050°C. The basic measurement process has been previously described.[1,2] This paper focusses on some of the complications of ultrasonic measurements at high temperatures in ceramics and on an algorithm that allows real-time determination of the sample density and shrinkage during the sintering process.

CERAMIC MATERIAL

The material used was commercial zinc oxide (Fisher Z52-500) with a very small particle size of around 1 μm. The green state samples were pressed into disks 25 mm in diameter and 8 to 10 mm thick with a theoretical density of approximately 47%. They were particularly soft with roughly the

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consistency of chalk. Sintering was done in a tube furnace at temperatures from 850 to 1050°C; the ultrasonic measurements were performed in a through transmission geometry.

ULTRASONIC LASER GENERATION AND DETECTION

A pulsed Nd:YAG laser with a 10 ns pulse width and pulse energies of 100 to 150 mJ was used as the ultrasound source. The laser beam was focused to a diameter of approximately 3 to 4 mm. The generation mechanism for ultrasound in ceramics generally includes both thermoelastic and ablation sources. Most ceramics exhibit a significant optical penetration depth, which alters the thermoelastic generation mechanism and can be used to advantage. Thermoelastic generation alone at the surface produces elastic wave radiation that is largely directed away from the surface normal, whereas ablation produces its largest wave motion in the direction of the surface normal.[3] In ceramics that exhibit a sizeable optical penetration depth, however, the thermoelastic mechanism itself produces a significant ultrasonic wave in the direction of the surface normal because the optical penetration extends the thermoelastic expansion into the material. This subsurface expansion produces a precursor waveform normal to the surface and a significant normal surface motion.[3-5]

Fig. 1 shows the ultrasonic displacement waveforms recorded with a capacitive detector from a sintered 6.3 mm thick sample of zinc oxide. The source was on the top of the sample and the detector on the bottom. To illustrate that this material absorbs green light more than infrared light, more pulse energy was needed with the infrared than with the green. This wavelength dependence of optical properties needs to be considered carefully when adapting a particular laser source to a given material.

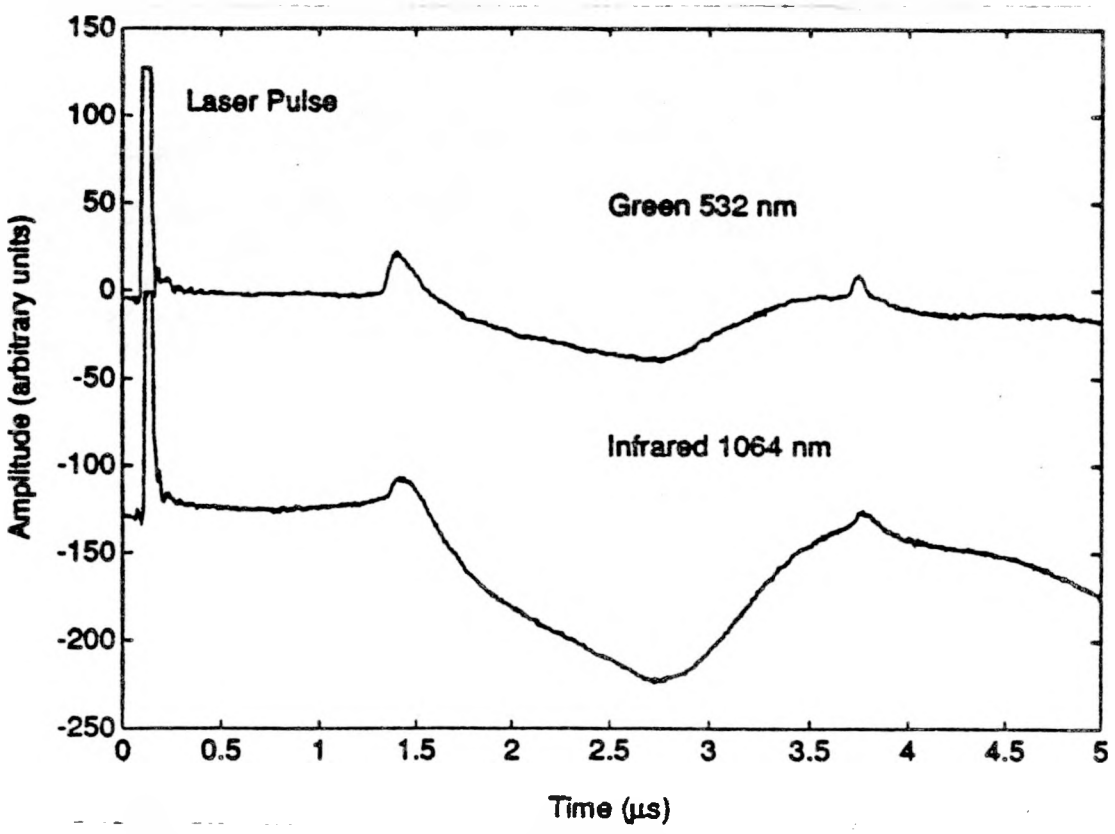

Fig. 1. Pulsed laser generated ultrasonic waveforms recorded with a capacitive detector through a fully sintered zinc oxide sample using the frequency doubled pulse at 532 nm, 40 mJ/pulse and the infrared pulse at 1064 nm, 145 mJ/pulse.

The initial spike displacement seen in the waveforms of Fig. 1 is the precursor waveform due primarily to optical penetration into the sample and was used for the waveform time of flight measurements. It was observed that the optical properties of the zinc oxide change with temperature, which can markedly alter both the generation and detection of ultrasonic motion at the surface. Fig. 2 shows a time series of waveforms, again detected with the capacitive detector, as a function of the number of laser pulses absorbed in the material. The waveform at t=0 s is that recorded after the first laser pulse. Subsequent waveforms show the cumulative effect of the laser pulses. The repetition rate is 10 Hz, so the waveform at t=1.1 s is after 11 pulses, etc. Clearly, the precursor waveform grows significantly during the first 32 laser pulses, after which it remains constant. This is because the optical absorption coefficient for zinc oxide increases with temperature, which was confirmed by direct reflection measurements from the sample surface at different temperatures (Fig. 3). The increased absorption at high temperatures was both a help and hindrance. It helped by increasing the efficiency of the ultrasonic generation process, but it hindered the optical detection process since it reduced the light scattered back to the detector. Quite different effects could pertain to other ceramics.

The laser beam was absorbed to a depth of about a millimeter at 532 nm and produced a strong longitudinal precursor waveform due to the optical penetration and some ablation of material from the surface, as was evident from minor pitting and discoloration. However, the sintering measurements could be completed without ablation of the ceramic of more than about 25 to 50 μm. The green state samples were more susceptible to ablation than those sintered to a density greater than 50%.

A confocal Fabry-Perot interferometer, modeled after that described by Monchalin and Heron,[6] was used to detect the ultrasonic waves on the surface of the samples. The detector is sensitive to the Doppler shift of light reflected from the sample surface, which is proportional to the velocity of the sample surface. This is confirmed by the comparison in Fig. 4, which shows the same ultrasonic waveform recorded with the capacitive displacement detector and the optical detector. The optical detector waveform is essentially the time derivative of the capacitive detector waveform. This response is maintained for frequencies up to approximately 8 MHz for this interferometer. Note that the major distinguishing feature in the optical detector waveform is that part due to the precursor, which can be generated by optical penetration, ablation or by using special coatings.

An argon ion continuous laser (1.0 W maximum at 514 nm) was used to illuminate the sample surface. This unit is sensitive to the frequency of the reflected light and not its phase, which allows it to collect light from a relatively large surface area (about 4 mm^2) including many speckles. This gives it the sensitivity needed for detection from rough and/or optically diffuse material surfaces, as encountered in ceramic materials in general and "green" state ceramic materials in particular. No surface damage resulted from using the detection laser at powers up to 900 mW, which were necessary at high temperatures due to the increased sample absorption noted earlier.

The zinc oxide samples used for the sintering study exhibited nearly complete diffuse reflection from their surfaces, even after sintering. The optical collection of scattered light from the sample, the determining factor for the signal to noise ratio, was limited by the opening of the furnace tube.

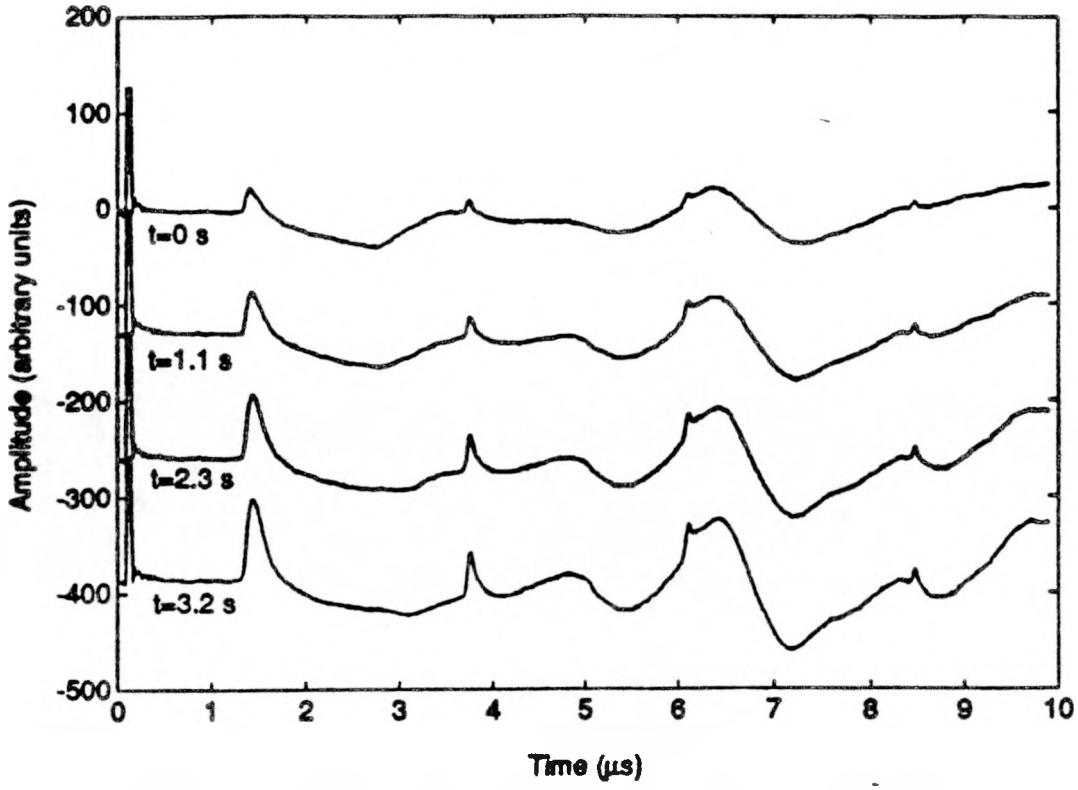

Fig. 2. Time sequence of the displacement waveforms recorded as in Fig. 1 showing the cumulative effect of the laser pulses. The repetition rate is 10 Hz.

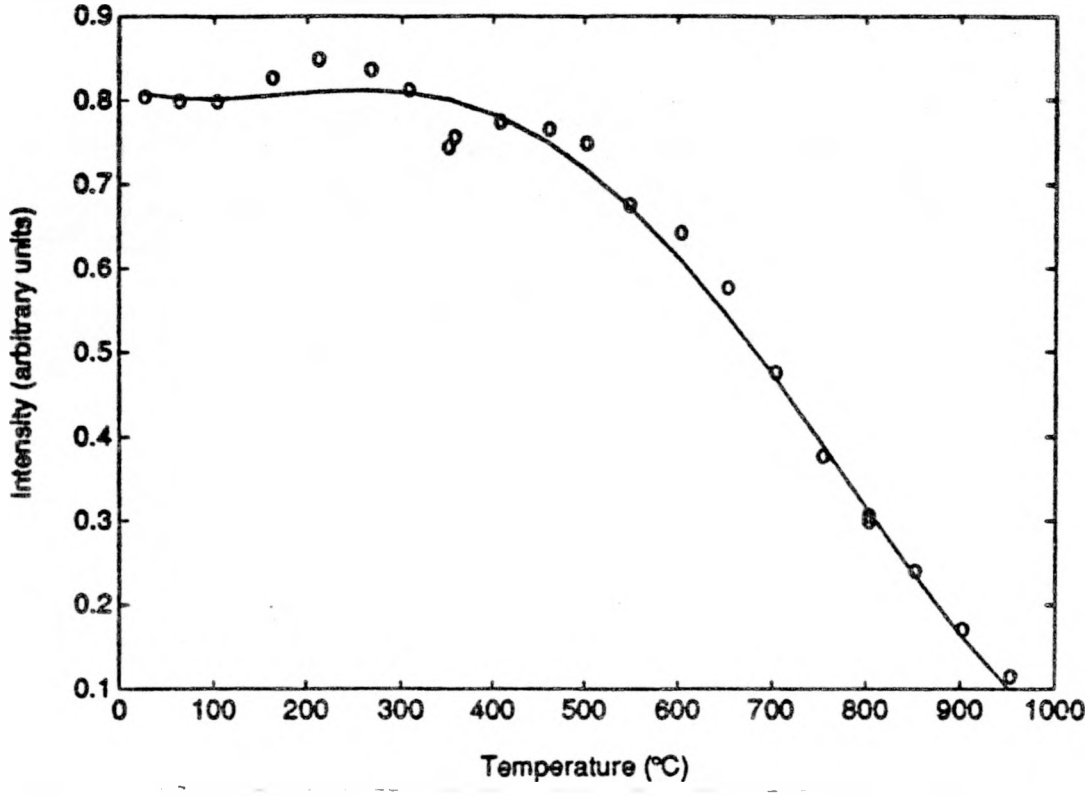

Fig. 3. Reflected optical intensity at 514 nm from a fully sintered sample of zinc oxide as a function of temperature.

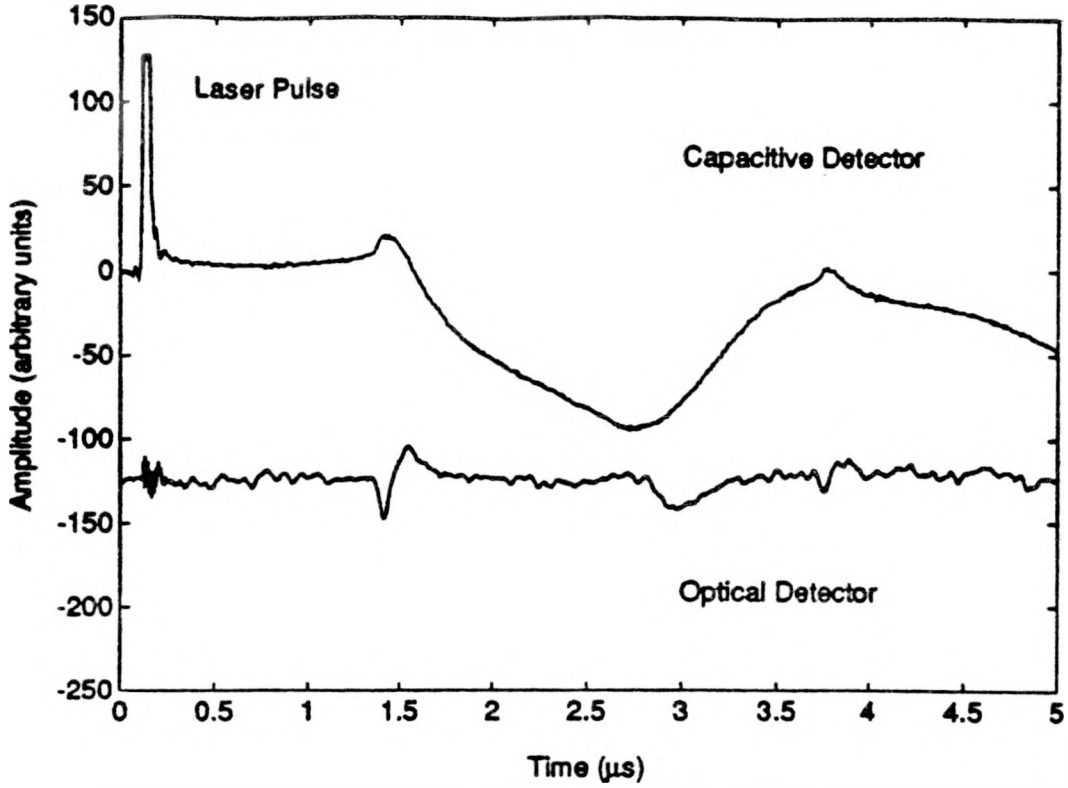

Fig. 4. Comparison of the ultrasonic waveform recorded with the capacitive detector showing surface displacement and the optical detector showing surface velocity for a fully sintered zinc oxide sample with pulsed laser excitation.

REAL-TIME SINTERING MEASUREMENTS AND THE RELATIVE DENSITY ALGORITHM

The procedure for the sintering measurements was to insert a sample into the furnace and preheat it at 700°C for about 1 h. This step was necessary as it was found that initially a large change in elastic constant occurred with very little change in average density, believed to be due to the powder particles beginning to join together. The measurements were of the time of flight of longitudinal ultrasonic waves propagating through the sample, as it sinters. In order to determine the sample average density from these measurements, it is necessary to know the sample thickness and the dependence of the ultrasonic velocity on density and temperature. In addition, there are most likely density and temperature gradients in the material as it sinters, since it is heated from the outside. There is no way to determine these gradients with the through transmission measurements reported here, so only average sample densities are considered in what follows. There is a connection between the sample thickness and density since many ceramics shrink uniformly during sintering if compacted uniformly with little residual stress. It was confirmed that the zinc oxide experiences uniform shrinkage, i.e. the sample diameter shrinks in the same proportion as its thickness. In addition, no mass loss occurred to within a precision of 4%. Densities are reported in percent of the theoretical density (5.6 g/cm^3).

The temperature dependence of the ultrasonic velocity in the zinc oxide compacts during sintering is unknown. For fully sintered samples the longitudinal wave velocity was found to be essentially temperature independent (to within 5%) over the range of temperatures from ambient to 1100°C. Therefore no correction for temperature dependence has been considered for the data presented here.

During sintering, the ultrasonic time of flight decreases significantly as the material's density increases and its thickness decreases. To complete the density determination algorithm, the dependence of the ultrasonic wave velocity on density must be known for the material. Several samples of zinc oxide were prepared in the "green" state and then sintered at various temperatures and times to produce a set of partially sintered samples with relative densities from 52% to 97%. Longitudinal ultrasonic wave velocities were recorded for this sample set to provide basic information on the effects of sample density. Measurements were taken with a 5 MHz contact piezoelectric transducer, using a vacuum coupled polymer film[7] with gel couplant and pulse echo overlap, and the laser ultrasonic method. In the green state the measured velocities were low, around 0.7 mm/μs, and not very dependent on the sample density. However, the velocity rises abruptly after a small amount of sintering, up to 52% density, probably due to bonding between the powder particles in the initial sintering. This results in a large change in elastic constant for the sample but very little densification. Further sintering produces an approximately linear change in velocity with relative density up to values approaching that of the bulk material as full densification is achieved.

The assumptions of conservation of mass and uniform shrinkage yield the following relation between density and thickness (applicable before, during and after, sintering): $\rho_i L_i^3 = \rho L^3 = \rho_f L_f^3$ where (i,f) refer to (before, after) sintering. This, coupled with the longitudinal velocity dependence on porosity, $C(\rho)$, determined previously, yields a relation between density and ultrasonic wave time of flight of the following form: $\rho^{1/3} C(\rho) T = \rho_m^{1/3} C_m T_m$. Here (m) can refer to either before or after sintering values. This equation can be inverted to obtain the density as a function of time of flight through a given sample. The size of different samples is taken into account by the normalization values, determined either before or after the sample is sintered. The range of applicability for this algorithm is determined by the range over which the velocity as a function of density is reliably known. For the zinc oxide samples described here, only the data recorded for samples of density greater than 50% of theoretical density were used.

Fig. 5 shows typical results obtained for zinc oxide sample #49 with starting density around 47% and presintered by heat treating at 700°C for about 1 h to 50% density and 8.62 mm thickness. At the time indicated in the graph the temperature is raised quickly to a final temperature of 975°C and the longitudinal wave time of flight recorded as a function of time. Both the sample relative density and shrinkage can be calculated as a function of time using the above algorithm. These values are also shown in Fig. 5. Several samples with roughly the same starting density and size were monitored and sintered in this way to a variety of final temperatures ranging from 850 to 1050°C. Similar results to that shown in Fig. 5 were obtained in all cases; the speed at which the sample sintered and the final density reached were monotonic functions of the final sample temperature. The slope of the densification and shrinkage curves becomes small after times of about 1.5 to 2.0 h for all the samples tested. The final density of the sample after sintering was predictable from this procedure to a precision of about 2-3% of theoretical density, which is about the precision to which the various parameters used in the algorithm are known. That the final sample density seems to level off after some time, or at least continues to increase very slowly, indicates that the furnace temperature is the most important parameter in determining the final density for zinc oxide.

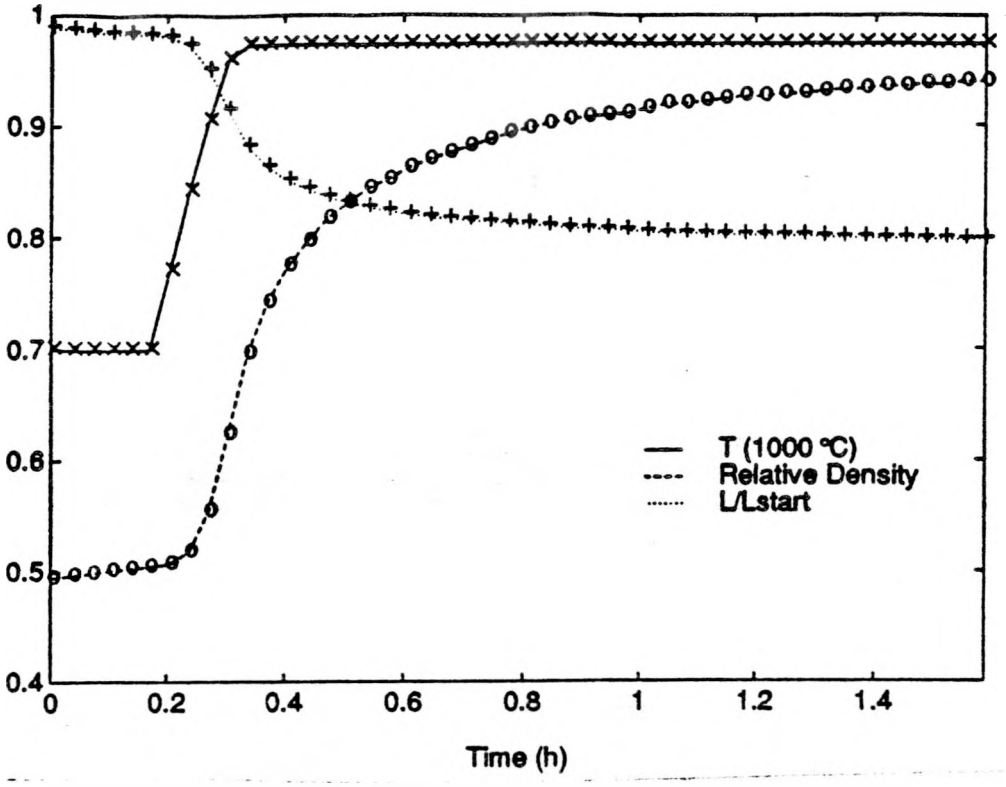

Fig. 5. Sintering plot for sample #49, with initial density of 50% and thickness 8.62 mm, showing the relative density, shrinkage ratio, and sintering temperature history with time.

CONCLUSIONS

These results show that laser ultrasonic techniques, which allow measurements on samples with rough and unpolished surfaces, can be used for noncontacting *in situ* measurements of elastic properties and, with an appropriate algorithm, sample density and shrinkage at high temperatures. The technique has been successfully applied to the sintering of zinc oxide. It can be concluded that the ultrasonic velocity provides a direct measure of the densification of the material during sintering. Several different factors in the sintering process are still unknown, such as the temperature uniformity of the material during heat up and the effects of powder size, compaction pressure, and composition. These factors can now be easily and quickly explored by using noncontacting laser ultrasonics to measure densification, which allows the direct monitoring of the sintering process as a function of both time and temperature. This technique should also be applicable to other materials and processing environments, such as heat treatment of metals.

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REFERENCES

1. K. L. Telschow, J. B. Walter, G. V. Garcia and D. C. Kunerth, "Process Monitoring using Optical Ultrasonic Wave Detection," Review of

Quantitative Nondestructive Evaluation, Vol. 9, D. O. Thompson and D. C. Chimenti eds., Plenum Press, New York, (1990), to be published.
2. K. L. Telschow, J. B. Walter, and G. V. Garcia, "Laser Ultrasonic Monitoring of Ceramic Sintering," in preparation.
3. D. A. Hutchins, "Ultrasonic Generation by Pulsed Lasers," Physical Acoustics, vol.XVIII, W. P. Mason editor (Academic Press, N.Y.,1988), 21-123.
4. K. L. Telschow and R. J. Conant, "Optical Parameter Effects on Laser Generated Ultrasound for Microstructure Characterization," Nondestructive Materials Characterization, P. Holler, V. Hauk, G. Dobmann, C. O. Ruud and R. E. Green eds., (Springer-Verlag, N.Y., 1989), 799-806.
5. K. L. Telschow and R. J. Conant, "Optical and Thermal Parameter Effects on Laser Generated Ultrasound," To be published in J. Acoust. Soc. Am. (1990).
6. J.-P.Monchalin and R.Heron, "Laser Ultrasonic Generation and Detection with a Confocal Fabry-Perot Interferometer," Materials Evaluation, 44, 1231 (1986).
7. R. A. Roberts, "Ultrasonic NDE of Green-State Ceramics by Focused Through-Transmission, "Review of Quantitative Nondestructive Evaluation, Vol. 6B, D. O. Thompson and D. C. Chimenti eds., Plenum Press, New York, 1443 (1987).