Monitoring of Binder Removal from Injection Molded Ceramics Using Air-Coupled Ultrasound at High Temperature

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Abstract—A pair of capacitance-type air-coupled ultrasonic transducers have been constructed that were capable of operating in air at temperatures of 500 to 600°C. These devices were then used to monitor the pyrolytic removal of organic binder from injection molded silicon nitride ceramic components using air-coupled ultrasound inside a furnace at elevated temperatures. Through-thickness waveforms were obtained in the ceramic and compared with simultaneous measurements of the mass of the sample. Both the ultrasonic velocity and signal amplitudes could be used to monitor the change in mass of the injection molded ceramic, and other phenomena (such as softening and redistribution of the binder) were observed.

I. INTRODUCTION

BEFORE BEING sintered or fired, ceramic components are usually preformed into the required shape using any one of a number of different processes. These include slip casting [1], in which an aqueous suspension of ceramic particles (the "slip") is poured into an absorbent mold, which then removes the liquid and leaves behind a fragile porous component. This is known as the "green" state, and the ceramic particles are loosely held together by mechanical interlocking. Other techniques include dry pressing [2], [3] and injection molding [4], [5], in which a polymer binder is mixed with the ceramic powder prior to forming the shape of the required component. This binder then must be gradually removed by burning away the polymer (pyrolysis) until only the green state ceramic remains, which is then sintered at very high temperature (typically > 1,200°C) to produce the finished component.

The ceramic in its green state may be tested prior to sintering using a variety of different ultrasonic techniques, provided that contamination of the porous material by conventional fluid couplants is prevented. Several "dry" coupling techniques have been developed, including the use of an adhesive tape [6] or sealed polymer membrane [7] to prevent moisture ingress, a nonwetting silicone gel [8], direct pressure transducers [9], and laser-generated ultrasound [10].

For components formed by injection molding, the pyrolysis of the polymer binder is an additional process during which sample damage may occur [11]–[14]. Defects caused by the injection molding process itself, or due to the choice of polymer binder, already have been investigated [15], [16], and prior to binder removal the component is relatively easy to test. The pyrolysis of ceramic components traditionally is monitored by measuring the change in mass as the binder burns away. This crude technique, however, does not give any information about defects such as cracks or delaminations that may occur during binder removal in the furnace.

Ultrasonic measurements have been made during dry pressing [17], but there does not appear to have been any attempt to monitor the components during pyrolysis using ultrasound, and this is due to the lack of a suitable transduction technique at elevated temperatures. Entirely laser-based techniques [18] have been used to monitor the sintering of green state ceramics, but laser generation of ultrasound in injection molded ceramics may not be feasible due to the low melting point of the polymer binder, and localized melting may occur that may damage the component. Other well established noncontact transduction techniques such as EMATs [19], which are capable of operating at high temperatures, are inapplicable as the ceramic samples are not electrically conducting.

There have been recent advances in air-coupled ultrasonic transducers, particularly those based on electrostatic technologies [20]–[24]. Typically these consist of a contoured conducting backplate, over which a metallized polymer membrane is placed, forming the two electrodes of a capacitor. When a D.C. bias voltage is applied between membrane and backplate, a charge builds up between these two electrodes. When acting as ultrasonic transmitters, a transient voltage superimposed on the bias voltage varies the charge between the electrodes and causes the membrane to move, producing a sound wave in the surrounding air. Similarly, when acting as receivers, an ultrasonic wave striking the membrane causes it to move and vary the charge between the two electrodes, which then may be detected using a suitable charge-sensitive amplifier.

In the work to be described, a pair of electrostatic air-coupled ultrasonic transducers were constructed using a membrane capable of withstanding high temperatures. These devices then were used to monitor the burn out of a polymer binder from an injection molded silicon nitride ceramic component inside a furnace at elevated temper-
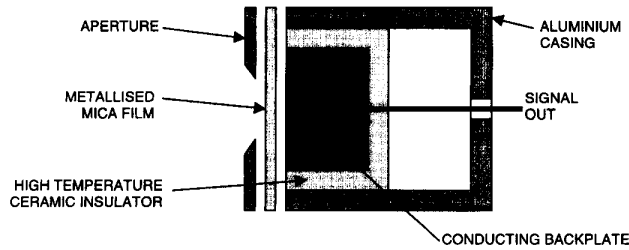
Fig. 1. Schematic diagram of the high temperature air-coupled transducers.

Fig. 2. The high temperature testing apparatus.

ature. The ultrasonic readings were made in conjunction with measurements of the mass of the sample as a comparison.

II. EQUIPMENT

A pair of air-coupled ultrasonic transducers were constructed as shown schematically in Fig. 1. The conducting backplates were made from brass, mechanically roughened to a surface finish R_a of 0.14 μm, and insulated from the earthed casing by a ceramic insulator capable of withstanding temperatures in excess of 800°C. The high temperature membrane consisted of a 10 μm thick Mica film coated on one side with Ni and Au, and it had a continuous upper operating temperature of 500 to 600°C. The apparatus used in the experiments is shown schematically in Fig. 2. The ceramic component to be tested was placed inside a Severn Furnaces "Eurotherm" cylindrical furnace, with a maximum temperature of 1,200°C. The sample was mounted on the end of a lightweight hollow stainless steel arm fixed onto a Precisa 310M mass balance, which had an accuracy of 0.001 g. The arm was counterweighted to reduce the effect of bending moments on the mass measurement. The ceramic sample was placed between the pair of high temperature air-coupled transducers, which were 20 mm apart. A bias voltage of 200 V D.C. was applied between the electrodes of the transmitter, which was connected to an Avtech AVRH-1-C high voltage pulser capable of delivering a variable width square pulse with a rise time of 50 ns and amplitudes up to 1,000 V. The receiver was connected to a Cooknell CA6/C charge sensitive amplifier with a sensitivity of 250 mV/pC, and its own integral D.C. bias supply of 100 V. Waveforms were captured on a Tektronix 2430A digitizing oscilloscope, and transferred to an IBM PS/2 Model 70 386 via an IEEE-488/GPIB interface. The PC also was used to simultaneously monitor the temperature inside the furnace using a digital thermocouple connected to an IEEE-controlled Keithley digital multimeter, and the mass of the sample from the Precisa balance via an RS232 connection. The temperature of the furnace was regulated by its own PID controller and thermocouple, which allowed the heating rate of the ceramic to be precisely controlled.
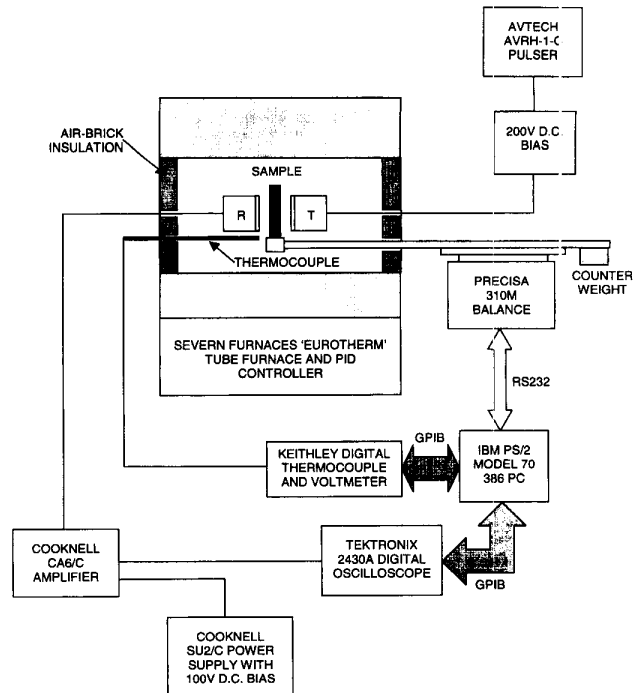
III. THE INJECTION MOLDED CERAMIC

The samples to be tested were supplied by Ceram Research, Stoke-on-Trent, England, and consisted of disks of injection-molded silicon nitride ceramic, with a nominal diameter of 40 mm and 3 mm thick. The organic binder used was based on paraffin wax but also included a range of other compounds to widen the temperature range over which the binder was removed. Typically, the disks were approximately 9% binder, but the exact quantities were unknown as the manufacturer considered this information proprietary. The recommended heating rate to facilitate binder removal was between 2 and 10°C per hour up to a temperature of approximately 500°C, although nearly 100% of binder will have been removed when the temperature reaches 350°C according to information supplied by the manufacturers.

IV. EXPERIMENTAL PROCEDURE

The ceramic sample used weighed 8.049 g at room temperature (27°) and was situated in the furnace between the ultrasonic devices as shown in Fig. 2. The furnace was preheated to 60°C, then set to heat the sample at a constant rate of 10°C/hour. Every 15 minutes (i.e., every 2.5°C), the mass of the ceramic sample was measured on the Precisa balance and transferred to the PC across the RS232 interface. At the same time, an ultrasonic signal was acquired through the ceramic on the oscilloscope and transferred to the PC as a digitized waveform across the GPIB
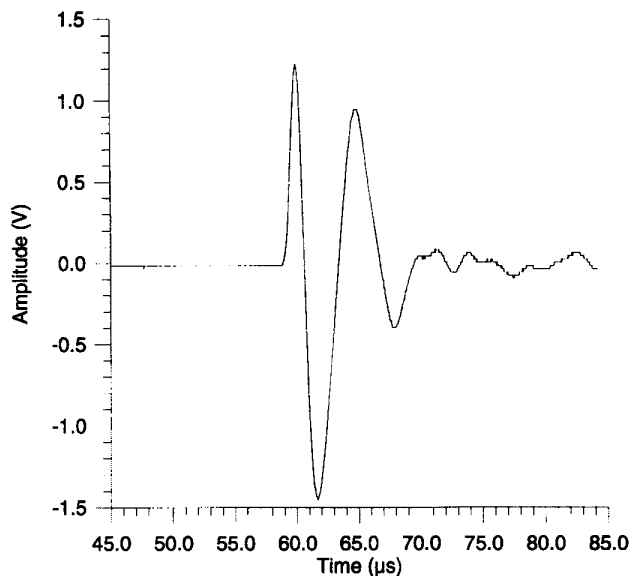
(a)
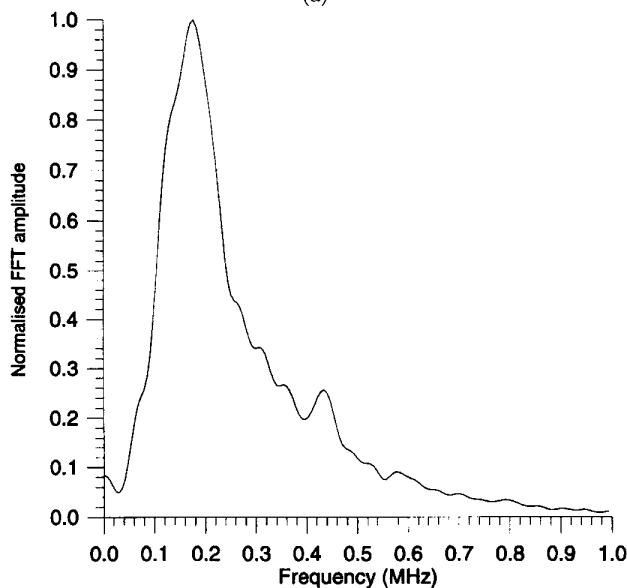
(b)

Fig. 3. (a) Received waveform and (b) FFT showing the sensitivity and bandwidth of the transducer pair.

Fig. 4. Graph of sample temperature against time.

Fig. 5. Plot of mass removed against time.

interface. Similarly, the temperature of the air inside the furnace was simultaneously recorded using the thermocouple and the Keithley voltmeter under GPIB control.

V. RESULTS AND DISCUSSION

A typical waveform transmitted and received through an air gap of 20 mm at room temperature is shown in Fig. 3(a), with the corresponding fast Fourier transform (FFT) in Fig. 3(b), to show the bandwidth and sensitivity of the system. The transducer pair worked well at frequen-
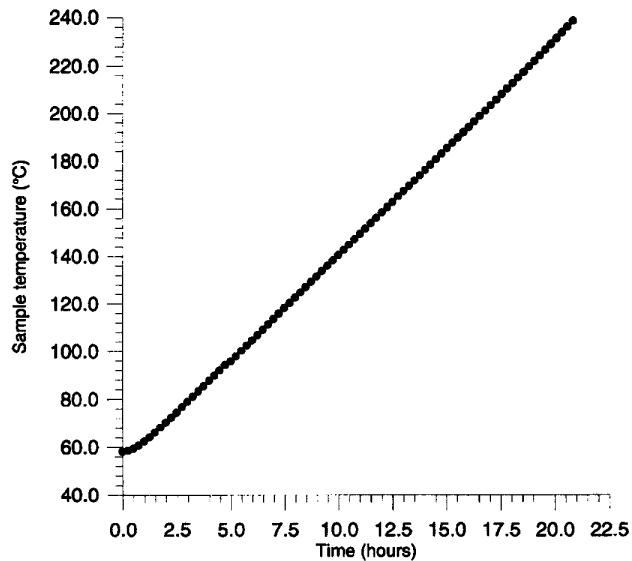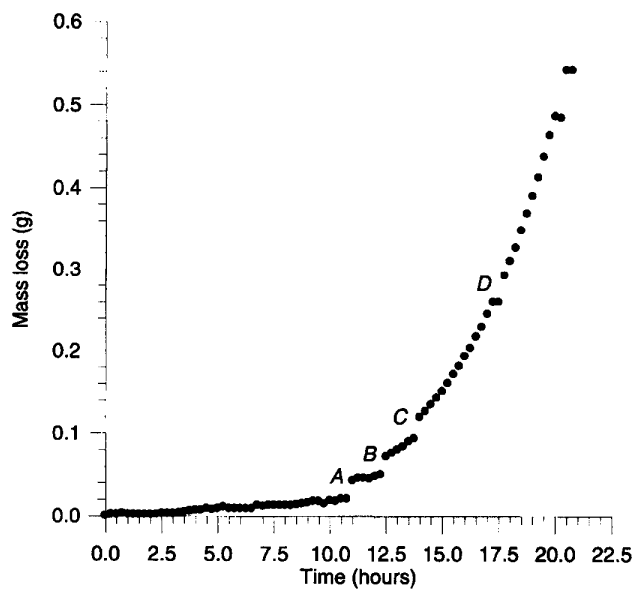
cies up to about 500 kHz with a 3 dB bandwidth of about 200 kHz, which was adequate for the current study.

Fig. 4 shows a plot of sample temperature against time and indicates that the heating rate was tightly controlled by the furnace with a constant heating rate of 10°C per hour. Fig. 5 shows a graph of mass removed against time. For the first 10 hours, very little mass is lost, and during this period any water absorbed by the sample is removed and the polymer binder starts to soften. From the data supplied by the sample manufacturers, very little of the binder will burn out below a temperature of 170° (i.e., before 11 hours have elapsed), and most of this is due to
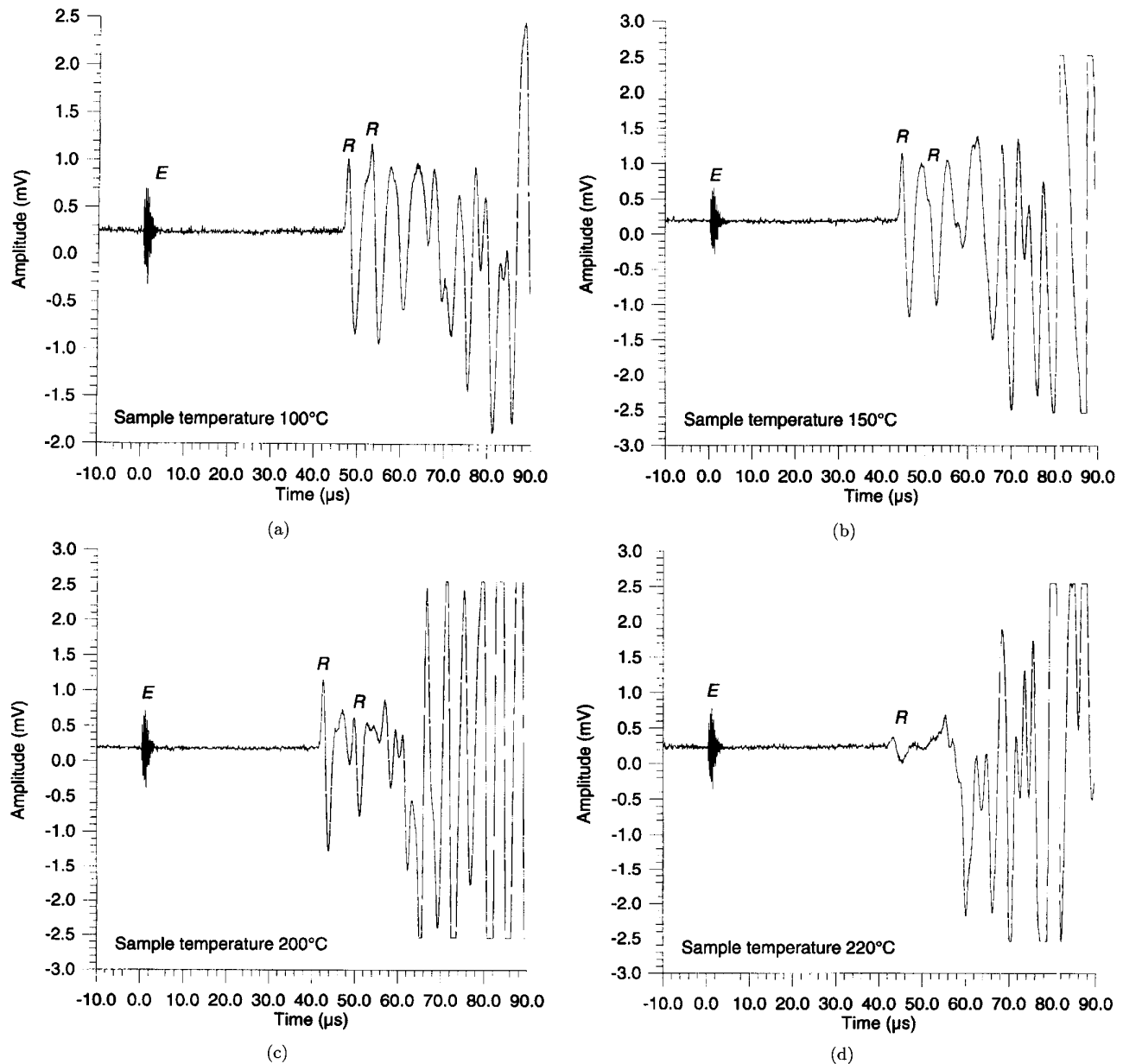
Fig. 6. Typical air-coupled ultrasonic waveforms at temperatures of (a) 100°C, (b) 150°C, (c) 200°C, and (d) 220°C.

the removal of organic compounds with a low molecular weight. Fig. 5 also shows some interesting features—some discrete steps in the curve at A, B, and C after approximately 11 hours, 12.5 hours, and 14 hours where there is a sudden decrease in mass. This was attributed to organic compounds melting and dripping off the end of the sample holder in the interval between readings. When the experiments were completed, this was confirmed by visual inspection of the arm, which was covered in a residue, as was the floor of the furnace directly beneath the sample. At point D, a serious delamination occurred in the sample, preventing the collection of further ultrasonic information.

Ultrasonic signals received through the injection-

molded sample in the furnace are shown in Figs. 6(a) to (d) for different temperatures. The signal at E is electrical noise at the trigger. The waveform in Fig. 6(a) was taken at a sample temperature of 100°C, and it is possible to distinguish individual echoes R within the sample as they arrive close together. At 150°C, the reflections are starting to separate out and individual signals are starting to become more obvious, as can be seen in Fig. 6(b). This becomes even more apparent at a temperature of 200°C, where discrete reflections may be clearly seen in Fig. 6(c). Note that the arrival time of the first reflection R is decreasing as the temperature (and hence the acoustic velocity) of the air between ultrasonic transmitter and receiver

increases. At a temperature of 220°C, the amplitude of the received signal in Fig. 6(d) has been drastically reduced, indicating that a delamination has occurred in the sample.

By extracting the separation of the echoes R within the sample from the ultrasonic data, it was possible to calculate the ultrasonic velocity within the sample as the temperature increased. The effects of thermal expansion over the temperature range of the experiments was assumed to be negligible, as the coefficients of thermal expansion of silicon nitride and typical polymer binders are 3.3×10^{-6} K^{-1} and 70×10^{-6} K^{-1}, respectively. A plot of both ultrasonic velocity and mass removed (as a percentage of the initial total mass) against temperature is shown in Fig. 7, where the velocity decreases at a fairly constant rate as the sample temperature rises. It is interesting to note that there are no steps in the velocity curve corresponding to the sudden decreases in mass at points A, B, and C attributed to dripping of the polymer binder, which further supports this hypothesis.

Fig. 8 shows a graph of ultrasonic velocity against mass removed which may be interpreted as follows. In the initial part of the curve there is a rapid decrease in the acoustic velocity of the sample with a very small decrease in sample mass. This is attributed to softening of the binder, and binder migration within the component—at low temperatures the binder will melt, without burning away, and collect at the base of the sample. Any initial mass loss is attributed to the removal of moisture and very low weight organic compounds. At points A, B, and C there is a sudden loss of mass due to a drop of molten binder falling from the sample, without a sudden change in velocity. The polymer binder begins to burn and the velocity decreases very gradually as the mass is slowly removed.

Fig. 9 shows how the received peak-to-peak signal amplitude varies with Fig. 9(a) temperature and Fig. 9(b) mass of binder removed. Up to about 75°C (a signal amplitude of 1.8 mV), virtually no mass is removed, and the increase in signal amplitude is attributed to softening of the binder material. This reduces the acoustic velocity, and hence the acoustic impedance of the sample, decreasing the reflection coefficient between the ceramic and air. Between 75°C and about 135°C, some of heavier weight binder compounds started to melt and move to the base of the sample, and some of the lighter polymers started to burn away causing a reduction in sample mass. At 140°C and above, the majority of the binding material was removed at a uniform rate, and the signal amplitude remained fairly constant.

VI. CONCLUSIONS

The experiments have shown that it is possible to monitor the burn-out of polymer binders from injection molded ceramic samples using air-coupled ultrasound at temperatures in excess of 200°C. More information about the binder removal process may be gathered from ultrasonic data that is unavailable from the conventional mass mea-
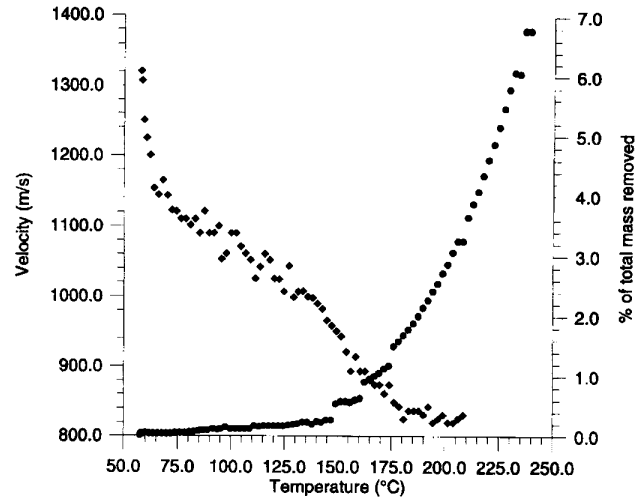

Fig. 7. Graphs of ultrasonic velocity and mass removed plotted against sample temperature.
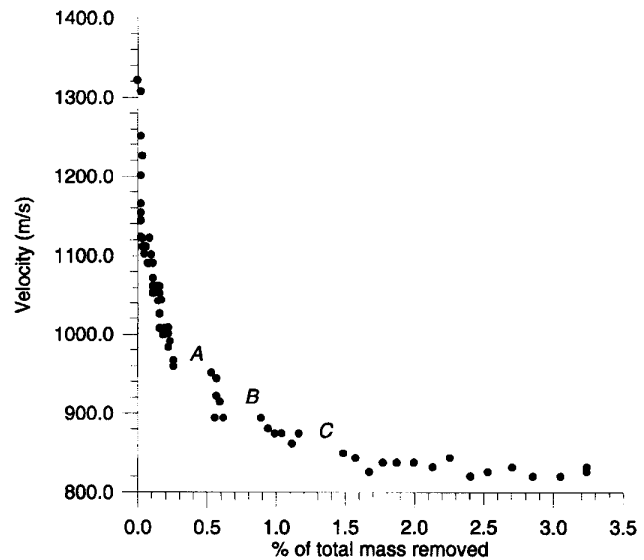

Fig. 8. Plot of ultrasonic velocity against mass of binder removed.

surements, including the point at which softening and migration of molten polymer binder occurs, and whether or not a crack or delamination has occurred during the heating process. Given that the upper operating temperature of the transducers is of the order of 500°C, this high temperature, noncontact technique may be used in a wide variety of similar applications where ultrasonic data may complement existing measurement techniques, and merits further investigation.

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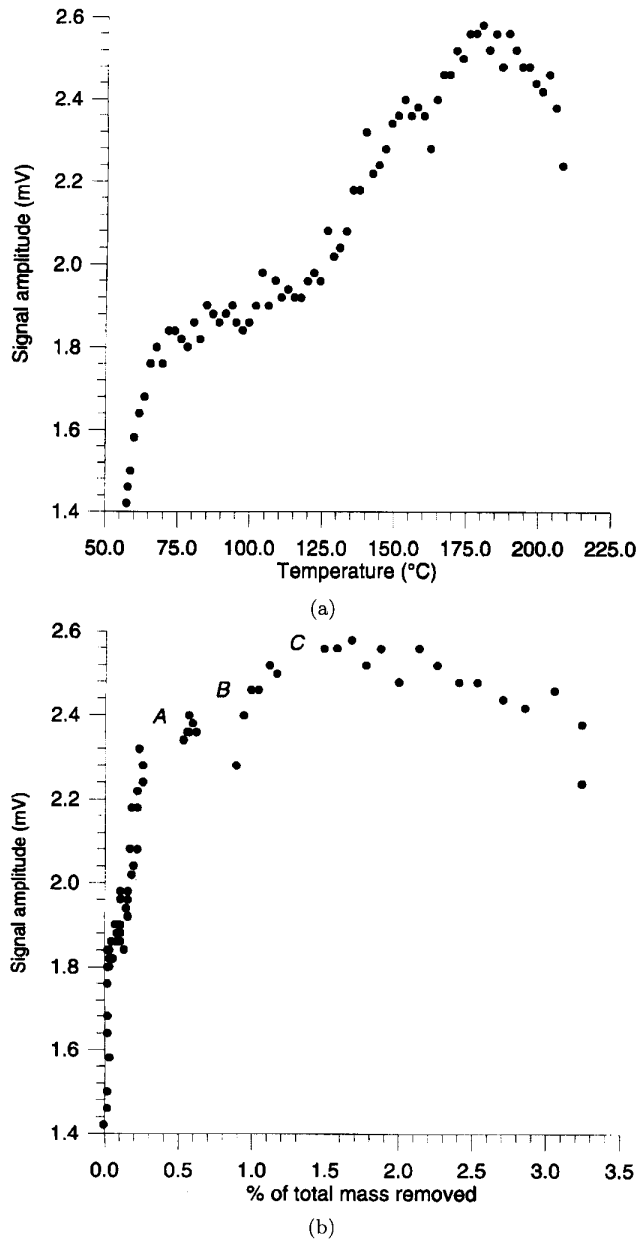
Fig. 9. Graph of received signal amplitude against (a) temperature and (b) mass of organic binder removed.

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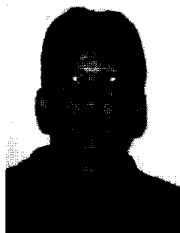
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Dr. Hutchins is an author on over 240 publications, over 100 of which are in refereed journals. His main areas of research interest have been ultrasonic transducers, ultrasonic instrumentation, and applications in materials evaluation. Recent work has investigated a new design of capacitive device, which has other applications, including medical imaging and flow measurement. In particular, such devices could be made to work in gases at high temperature, and they are increasingly being fabricated in silicon to enhance application to a wide variety of industrial measurements.