NONDESTRUCTIVE CHARACTERIZATION OF GREEN MATERIALS

M. C. Bhardwaj and Karen Trippett
Ultran Laboratories, Inc.
State College, PA

Manuscript of a paper submitted to the American Ceramic Society - June 1990

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ultran laboratories, inc.
139R north gill street
state college, pa 16801 usa
814.238.9083 *phone*
82.0978 *telex*
814.234.3367 *fax*

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M.C. Bhardwaj** and K.A. Trippett
ULTRAN LABORATORIES, INC.
State College, PA USA

Knowledge of defects and heterogeneity in materials during their early stages of processing can be highly beneficial in establishing parameters of quality and producibility. It is desirable that such information be generated by nondestructive means so that it can be adapted to materials manufacturing functions such as statistical process control, as well as time, energy, and economic benefits.

In order to establish the reliability and reproducibility of data, it is imperative that composition and physical conditions of green materials are not adversely affected during the nondestructive characterization process. In this paper we report the successful achievement of these conditions through the applications of recent developments in ultrasonic science and technology.

INTRODUCTION

Ceramic materials such as refractories, whitewares, and china have been traditionally used for their high temperature resistant and high strength properties for a long time. These materials, in conjunction with powder metals and their composites, provide exciting and more useful electronic, structural, optical, nuclear, magnetic, and energy-related properties. Therefore, interest in such materials is widespread as their applications and development continue in aircraft/aerospace, chemical and petroleum, nuclear, electronic/electrical, domestic, automotive, high speed railroad, and other industries. Not only are different compositions required for different properties, but the final shape and size of components also vary according to the requirements of a given application. Performance and reliability of materials under the constraints of their applications, particularly critical ones, are important to both materials manufacturers and users. Therefore, the significance of understanding modern materials, whether their uses are conventional or advanced, cannot be over-estimated. Here we provide a brief review of materials processing with emphasis on characterization at the green stage.

The Materials Advisory Board, U.S. National Academy of Sciences, in 1968 made important conclusions and recommendations relative to compositional and physical parameters at preconsolidation, consolidation, and final densification stages of ceramic processing, (1). According to this report, ***"ceramic consolidation (green stage) processes present particular problems in character uniformity and reproducibility that are primarily associated with density inhomogeneities resulting from cold-forming operations."*** This report recommends:

**Presented at the 92nd meeting of the American Ceramic Society.*
***Member American Ceramic Society.*

1. Relationships between rheological behavior during consolidation and the fundamental structural and compositional characteristics of particulate systems.

2. Method of characterizing agglomerates and green bodies.

3. Fundamental research into the response of particulate systems to applied pressure and to develeopment of methods to eliminate density gradients during consolidation.

Physical characterization parameters associated with consolidation stage in materials processing are shown in Table I. Knowledge of these parameters is vital for smooth operation of various particulate processing functions. For example, besides chemical composition, and sintering temperature, pressure, and time, factors affecting the final properties of a densified material are: particle size (affects densification and grain-growth rates), bulk density (affects density limit and maximum shrinkage), particle size distribution (affects densification rate, density limit, and secondary grain growth), and bulk density distribution (affects distortion and density limits) while the material is in green stage. The process of material-making and the quality of the final product can be greatly enhanced if certain physical parameters can be controlled in the early consolidation stage of materials processing by nondestructive means. It is interesting to note that while citing the significance of the elimination or control of density gradients during the green stage processing, the Materials Advisory Board on ceramic processing made specific recommendation for *"sound-velocity"* relationships for the characterization of materials in green stage. However, some practical difficulties needed to be overcome before such relationships would become reality.

NDC vs. NDT

For a long time ultrasonic NonDestructive Testing (NDT) has been well-known and practiced in the primary metals (steel and aluminum) industry for defect detection and thickness/corrosion measurements (2). However, its uses for materials characterization began only recently, (3, 4, 5). For example, if ultrasound can be propagated in a given material, then the investigation of its time domain (time of flight and velocities of ultrasonic waves) and frequency domain (frequency-dependence of ultrasonic attenuation) can provide significant information about that material, besides simply the detection of *overt* flaws, Table II. However, compared to compositional and microstructural diversity of ceramics, powder metals, and their composites, primary metals are relatively homogeneous, dense, and impervious. Therefore, nondestructively what is applicable to metals may have limited use in the characterization of non-metallic materials.

Reliability and confidence in the analyzed data are directly proportional to the suitability of the characterization method with respect to test material composition and its microstructure. For example, utilization of liquid couplants between ultrasonic transducers and test materials surfaces - one of the many limitations of *metals-NDT* practice - is unreliable for the characterization of green, partially sintered, porous, and liquid-sensitive materials, (6). In order to facilitate the NDC of these materials, we have formulated an ultrasonic technique that eliminates wet coupling of transducers. Here we describe the time domain applications of this technique for the nondestructive characterization of green materials.

PRINCIPLE OF TIME DOMAIN ANALYSIS

Velocities of longitudinal and shear waves are directly related to the density of the material through which they are propagated, i.e.,

$$E = V_l^2 \times \rho \times f(\sigma) \qquad 1$$

$$G = V_t^2 \times \rho \qquad 2$$

where,

E = Young's modulus, V_l = velocity of longitudinal wave, ρ = material density, $f(\sigma)$ is function of Poisson's ratio = $(1+\sigma) \times (1-2\sigma)/(1+\sigma)$, G = shear modulus, and V_t = velocity of shear wave.

Therefore, measurement of ultrasonic velocities can provide information about test materials' densities and their elastic properties. Velocity, V is determined by measuring the time of flight, t, through a known material thickness d,

$$V = d/t \qquad 3$$

BASIC REQUIREMENT FOR GREEN MATERIALS NDC

Conventional ultrasonic NDT is universally based upon the "wet coupling" of transducers to test material surfaces. Such transducers typically feature a hard material layer in front of the active piezoelectric element. This layer provides suitable acoustic impedance matching and protects the piezoelectric element. For efficient propagation of ultrasound into the test material, liquids such as water, oil, glycerene, or grease are used between the transducer and material interface. However, couplants are liable to change the characteristics of fragile green materials, besides destroying them. Therefore, dry transducer coupling is the only conceivable alternative for reliable ultrasonic measurements of green materials.

The condition for dry coupling can be met by replacing the hard protective layer of conventional transducers by a *"solid compliant"* material. From an acoustical standpoint, it is highly desirable that such a material also exhibit transparency to relatively high frequencies for the evaluation of a wide range of materials - including those characterized by relatively high velocities and thinner materials sections. In 1982 after considerable amount of *"hit-and-trial,"* this task was accomplished in our laboratory through the development of a special polymer layer, implanted on the active piezoelectric element, Fig. 1. This layer acts as a near-perfect *"solid compliant transitional layer"* between the piezoelectric element and test material for efficient transmission of ultrasound in it. Transducers based upon this design have been successfully produced for longitudinal and shear wave propagation from frequencies <100KHz to >20MHz.

MEASUREMENT OF GREEN MATERIALS VELOCITIES

In order to determine ultrasonic velocities in green materials, pulsed ultrasound was used to measure Times-Of-Flight (TOF) by the dry coupling direct transmission method. Excitation of transducers and amplification of transmitted signals were performed by a fully computerized short rise time pulser with a broadband amplifier. Test materials were sandwiched between two dry coupling transducers with "finger pressure." (Dry coupling transducers can also be clamped by ordinary or special spring-loaded mechanism in order to facilitate measurements on a large number of samples.) Time domain rf A-scan signals corresponding to the transmission of ultrasound through test material are directly displayed on the computer monitor. A schematic arrangement of this system*, along with transducer configuration and observed ultrasonic signal is shown in Fig. 2.

**Ultran system NDC 7010.*

The mechanism of the TOF measurement included the establishment of a reference signal corresponding to the "zero" position on the rf A-scan trace. This is sequentially shown in figures 3, 4, and 5. Fig. 3 is the triggered time domain trace, i.e., without the connection of cables and transducers. Determination of the "zero" reference point is important so that the TOF corresponding to the transducer matching/ protective layers (irrespective of transducer type) is eliminated, lest an error be introduced in test sample TOF. This is shown in Fig. 4. Here, the two transducers - transmitter and receiver - were placed together with their active regions touching each other. The ensuing transmitted signal in this case corresponds to the TOF through the matching/ protective layers of two transducers. A cursor was placed at the trailing edge of this signal to indicate the zero or the reference point from which TOFs corresponding to test sample travel distance were measured. For example, Fig. 5 shows the appearance of a transmitted signal through a test sample. The right hand cursor in Fig. 5 is placed at the trailing edge of the transmitted signal. The difference between the two cursors is the true TOF of ultrasound through the test material.

It is important to note that beyond certain "finger pressure," - sufficient for optimum amplification of the transmitted signal - no significant changes in TOF are noticed. For example, at a given point, the accuracy of TOF measurement by this method is typically better than +/-1%. By manipulating the location of the right hand cursor with respect to sample TOF, the velocity of ultrasound is automatically calculated and displayed on the computer monitor from the programmed thickness of a given test material. As an example, figures 6 and 7, respectively show longitudinal and shear waves A-scans of a green alumina substrate.

OBSERVATIONS AND RESULTS

The following observations were made by applying the ultrasonic technique described in the previous section. Salient characteristics of transducers used for this investigation are described in Table III.

Velocity, density, and elastic properties relationships

In order to establish reference velocity-density relationships, several batches of green Al_2O_3 and steatite were investigated by longitudinal and shear wave ultrasound. Density of control samples was varied through the application of different compaction pressures to submicron ceramic powder mixed and homogenized with PVA (polyvinyl alcohol) binder.* The final dimensions of samples were 22.0mm diameter and 1.6mm thick. Bulk density of each sample was determined by dividing its weight into its volume.

Fig. 8 shows the relationships of longitudinal and shear wave velocities with predetermined density of green Al_2O_3. Simple straight line curve fitting method produced the best correlation, yielding regression co-efficient, R, equal to 0.99 for both longitudinal and shear wave velocities. Fig. 9 shows the relationships between Young and shear moduli of elasticity - determined from equations 1 and 2 - for green Al_2O_3.

Figures 10 and 11 exhibit longitudinal velocity and Young's modulus of elasticity, respectively, as functions of green steatite density, yielding R factors of 0.99 for both straight line curves.

*ALSIMAG Technical Ceramics, Laurens, SC.

Determination of unknown densities when velocity-density relationships are established

In order to check the reliability of ultrasonic observations as well as to determine the unknown densities, several green Al_2O_3 samples were evaluated by using the relationship shown in Fig. 8. A comparison of ultrasonically determined and measured values of green density is shown in Fig. 12. This correlation generated an R factor of 1.0, suggesting high reliability of the ultrasonic method for the determination of green material density. By using a similar approach, densities of several samples of an Al_2O_3 substrate at various points - cooresponding to 6mm diameter - were determined. Results of this investigation are shown in Fig. 13.

Similarly, densities at a number of locations in a green steatite were determined by using the relationship shown in Fig. 10. This data is shown in Fig. 14.

Estimation of unknown densities when velocity-density relationships are not available

In the foregoing sections we have demonstrated that as the density of a green material increases, so do its ultrasonic velocities. In order to determine exact density of a given green material, it is desirable that its velocity-density reference curve be generated as shown for green Al_2O_3 and steatite. However, if such data is not available, it is possible to obtain significant information about green material density in terms of ultrasonic velocities at various points. This is shown in Figures 15,16, and 17. Figures 15 and 16 exhibit velocity variations in two green ferrite components, indicating relatively lower density at lower velocity, and vice versa.

A similar example for a green WC component is shown in Fig. 17. Here, a number of samples prepared at varying compaction pressures were examined to evaluate heterogeneous conditions within the bulk of this material at discrete points. Once again we conclude that lower velocity values are indicative of lower densities, and vice versa. However, in this particular case it is feasible that velocity - thus density - variations might also be due to heterogeneity in powder-binder content.

OTHER USES OF ULTRASONIC NDC OF GREEN MATERIALS

Whereas in this paper we have described the significance of simple velocity-density relationships for green material characterization, similar methodology can also be applied for the evaluation of process and quality related parameters, such as:

1. Investigation of anisotropic grain orientation, elastic behavior (spring back), and other parameters described in Table I, by relating ultrasonic velocity to them.

2. Investigation of reflected and transmitted ultrasound through green materials can be used for defect/pore detection. This task can be accomplished by applying direct reflection or separate transmit-receive (T-R transducers, placed side-by-side) dry coupling transducers. For example, if 10MHz frequency can be successfully transmitted into a green material, it is then feasible to detect pores as small as 50μm. However, this practice is restricted by the upper limit of frequency applicable for the analysis of such materials. Since green materials - particularly coarse grain refractories and porous ceramics and composites - have been found to be highly attenuative, higher frequencies and short pulse widths - requirements for high resolution and detectability - are not as readily applicable as they are to their (green materials') sintered counterparts, (7). Significance of wavelength and attenuation in ultrasonic NDC has been described elsewhere (8).

3. Direct transmission technique can be used to detect cracks in green bodies by comparing the strength of transmitted signals as functions of "cracked" and "uncracked" regions. The former condition should exhibit higher transmitted signal amplitude compared to the latter.

LIMITATIONS OF GREEN NDC

It should be noted that green materials, prepared by a variety of materials processing techniques - tapes, slip cast, isostatically and rigid die pressed, injection molded, multi-layerd and thick film forming - of simple shapes can be relatively easily examined by the methodology described in this paper. Similarly, by applying suitable frequencies and transducer excitation and amplification systems, coarse grained and large ceramic bodies, including refractories, can be successfully analyzed nondestructively. However, NDC of complex shapes may require special attenation from the standpoint of suitable transducer designs.

CONCLUSIONS

In accordance with the objective of this paper we have described simple, yet significant mechanism for the NDC of green materials. From the foregoing discussion we conclude:

1. Ultrasonic NDC is an important discipline for the advancement of the materials industry.

2. It is feasible to transmit longitudinal and shear waves in green materials for the measurement of their velocities.

3. Measured ultrasonic velocities - at discrete points - can be related to green material density, elastic moduli, compositional, and other parameters, prior to sintering process.

4. While overt defects, such as large pores and internal cracks can be relatively easily detected by ultrasound in green materials, to a degree it is also possible to detect small pores.

5. Nondestructive characterization obviously benefits in establishing the quality of final products, besides saving the cost of their manufacturing process through materials and energy conservation.

ACKNOWLEDGEMENTS

We are indebted to Parke W. Wright, ALSIMAG Technical Ceramics, Laurens, SC, for supplying a wide variety of well-characterized green samples of Al_2O_3 and steatite, as well as for his thoughtful suggestions and observations. We gratefully acknowledge the assistance of Amy Dietz and P.B. Trippett in the data acquisition portion of this study. This work was supported by the on-going ultrasonic NDC projects at Ultran Laboratories, Inc.

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TABLE I. **Significant physical characterization parameters in particulate consolidation processing, (1).**

CONSOLIDATION SOLID PROCESSING	PHYSICAL CHARACTERIZATION PARAMETERS IN PROCESSING
MODIFIED-PARTICULATE SYSTEM Cold-forming operations Die filling Assists to die filling; vibration, ultrasonics, vacuum pressure. Forming by: 1. Pressure compaction a. Rigid die b. Isostatic 2. Plastic a. Extrusion b. Jiggering, etc. 3. Slip casting a. Normal b. Vacuum c. Pressure 4. Injection molding 5. Vibratory packing 6. High-energy imapct 7. Film-forming 8. Other	Flow; applied pressure - absolute, pressure/density relationships; microstructure as formed. Homogeneity: density, orientations, micro-stresses; strength for mold release, elastic behavior (spring back), stresses imposed, cracks, contact area between grain surfaces.
GREEN BODY Green-body modifications Drying (100°C) Expulsion of organics (200 - 800°C) Presintering (1,000 - 1,400°C) Development of porous body Sometimes shaping, turning, fettling, etc.	Dimensional changes, density-porosity, strength, flaws, micro-structure.

TABLE II. **Significance of ultrasonic measurements for nondestructive characterization of materials.**

MEASUREMENT CATEGORY	MEASURED PARAMETERS	INFORMATION REVEALED & APPLICATIONS
Time Domain	Velocities of longitudinal, shear, and surface waves	Direct correlation with density, porosity, defect detection, elastic and mechanical properties. Ultrasonic imaging.
Frequency Domain	Frequency dependence of ultrasonic attenuation (Ultrasonic Spectroscopy)	Direct correlation with microstructure: grain size and grain boundary relationships, porosity, and study of any process/compositional parameter that results in microstructural or phase changes.

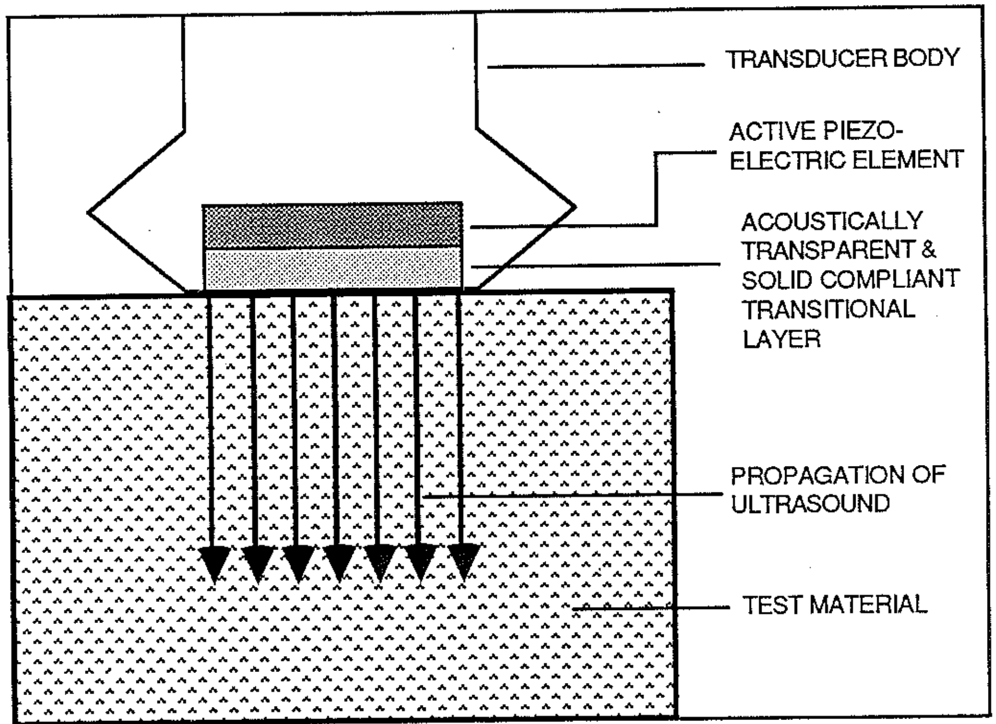


Fig. 1. A schematic cross-section of a dry coupling ultrasonic transdsucer showing the propagation of ultrasound into a test material.

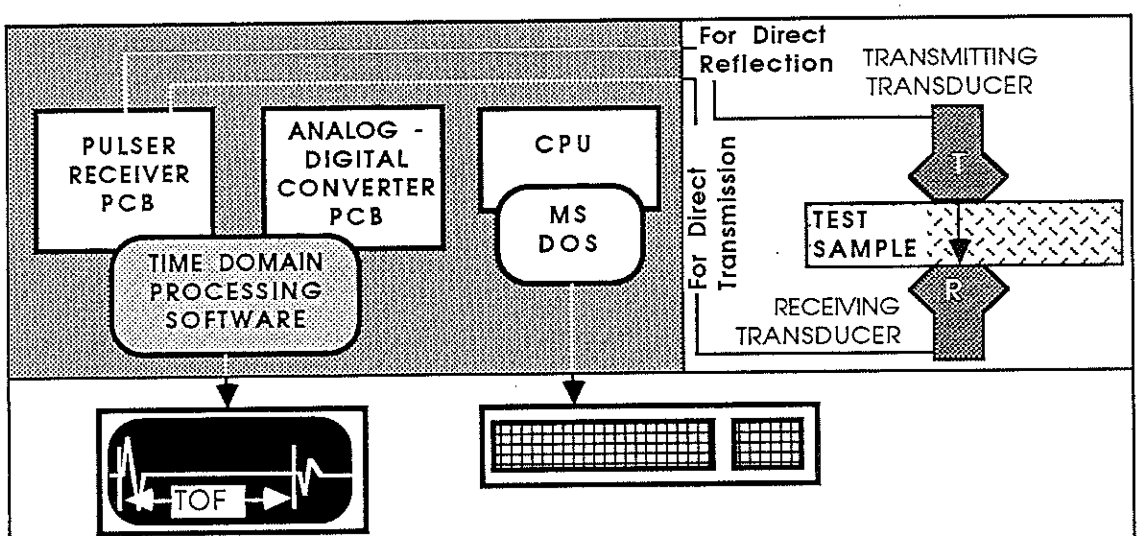


Fig. 2. A schematic layout of pulsed ultrasonic set up and transducers configuration used for nondestructive characterization of green materials.

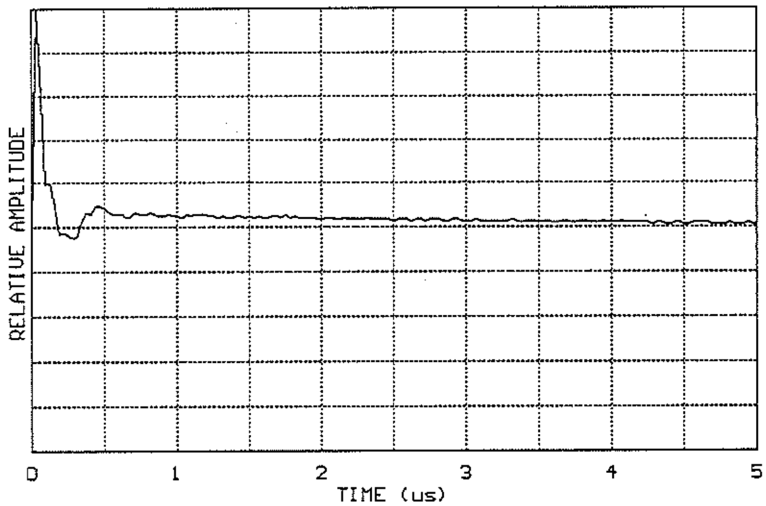


Fig. 3. RF trace without transducers.

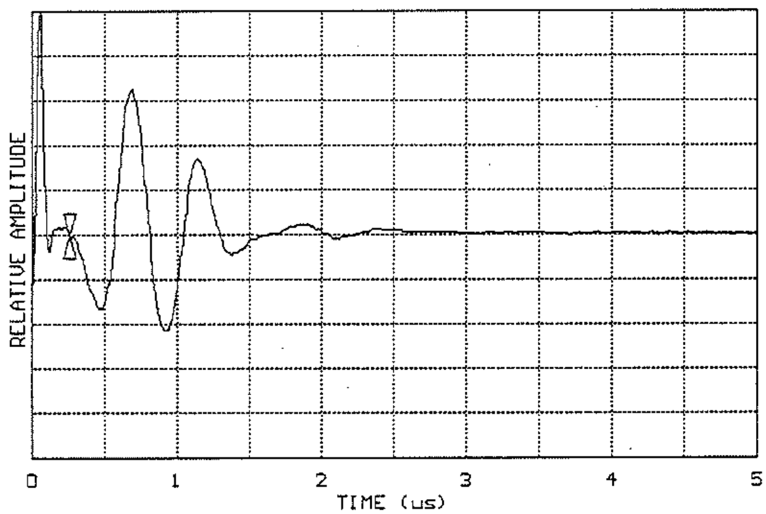


Fig. 4. RF trace with transmit and receive transducers touching each other. Note the position of left hand cursor, indicating "zero" reference point.

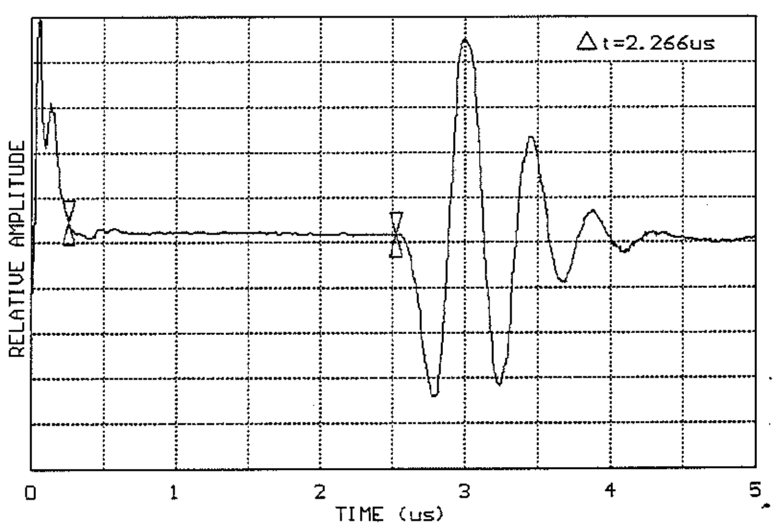


Fig. 5. RF trace with example material (6mm) sandwiched between the transducers. Note the position of right hand cursor, indicating the transmitted signal through material.

Δt, TOF (time of flight between two cursors) = 2.266μs.
V_t = 2,650m/s

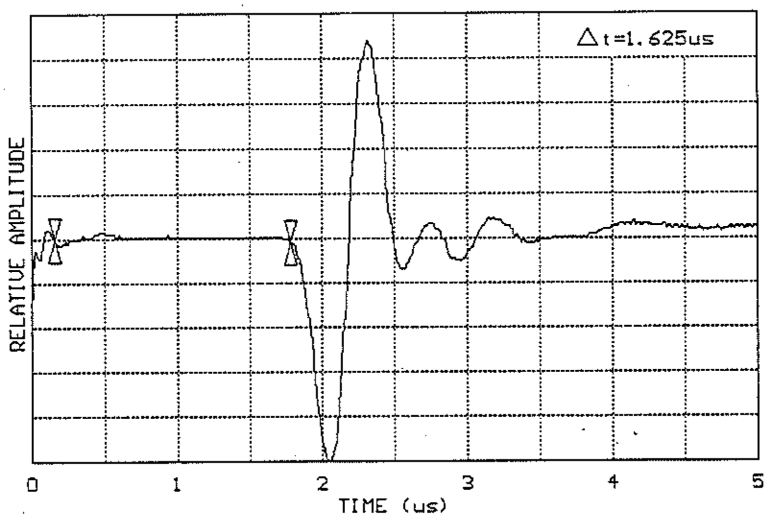


Fig. 6. Propagation of longitudinal ultrasound through green Al_2O_3 (2.4mm).

Δt = 1.625μs.
V_l = 1480m/s

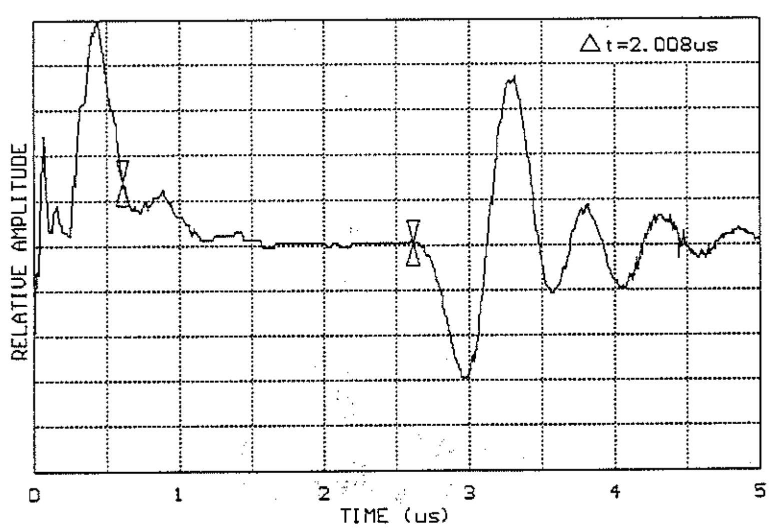


Fig. 7. Propagation of shear ultrasound through green Al_2O_3 (2.4mm).

Δt = 2.008μs.
V_t = 1190m/s

TABLE III. Salient characteristics of longitudinal and shear wave dry coupling transducers as functions of green sample thickness.

TRANSDUCER TYPE	COUPLING MECHANISM	ACTIVE AREA DIAMETER (mm)	NOMINAL FREQUENCY (MHz)	BANDWIDTH (% at -6dB)*	GREEN SAMPLE THICKNESS (mm)
LONGITUDINAL	DRY	12.5	2.0	>50	~5 to >10
		6.0	5.0	>50%	<1 to 5
SHEAR	DRY	12.5	1.0	~40	~5 to >10
		6.0	2.0	~40	<1 to 5

**Determined by averaging the -6dB level high and low values of frequency spectrum, and reported as percentage of nominal frequency.*

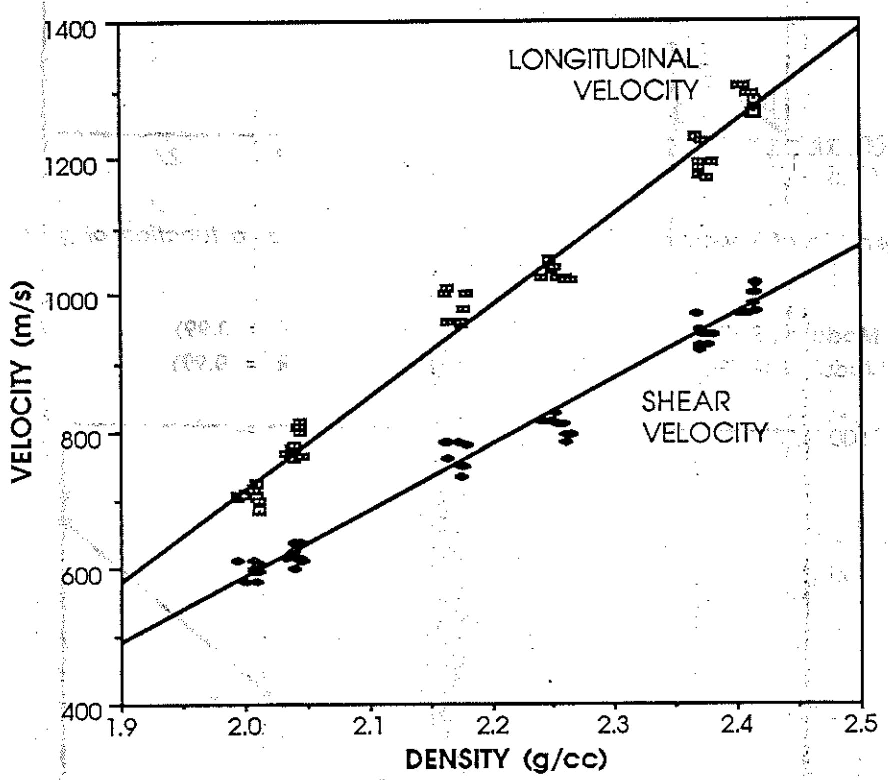
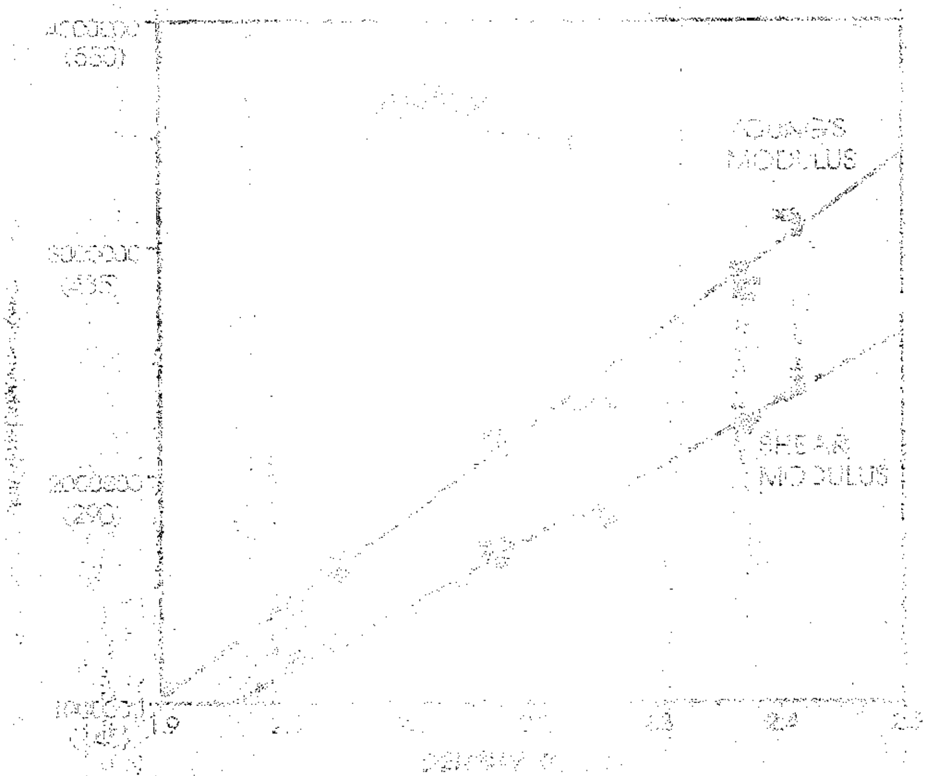


Fig. 8. Relationship of longitudinal and shear wave velocities with green $Al_3 O_3$ density.

Density, ρ g/cc, (from longitudinal velocity, V_l) = $(1938 + V_l)/1328$. (R = 0.99)
Density, ρ g/cc, (from shear velocity, V_t) = $(1322 + V_t)/954$. (R = 0.99)



[illegible]lationship of Young [illegible] a function of green Al_2O_3 [illegible]

[illegible] Modulus, E (Pa) [illegible] (R = 0.99)
[illegible] Modulus, G (Pa) [illegible] (R = 0.99)

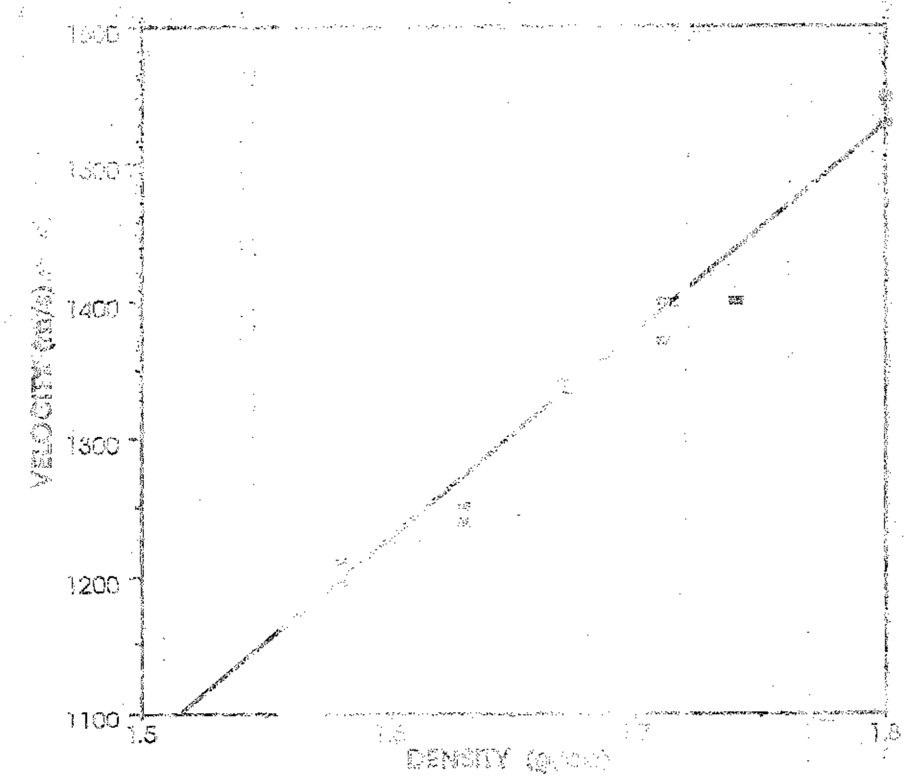


Fig. 10. Relationship [illegible] gitudinal velocity [illegible] green steatite density.

[illegible] sity, ρ (g/cc), (from longitudinal velocity, [illegible] + V_l)/1648. (R = 0.99)

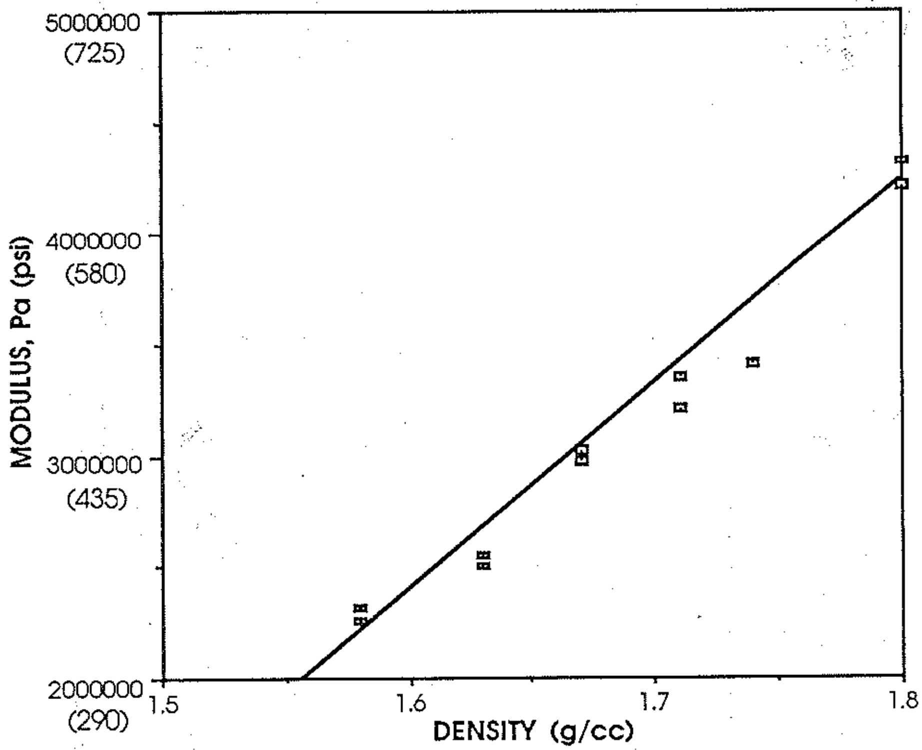


Fig. 11. Relationship of Young's modulus of elasticity as a function of green steatite density.

Elastic modulus, E (Pa) = $1.12 \times 10^7 + 8.95 \times 10^6 \rho$. (R = 0.99)

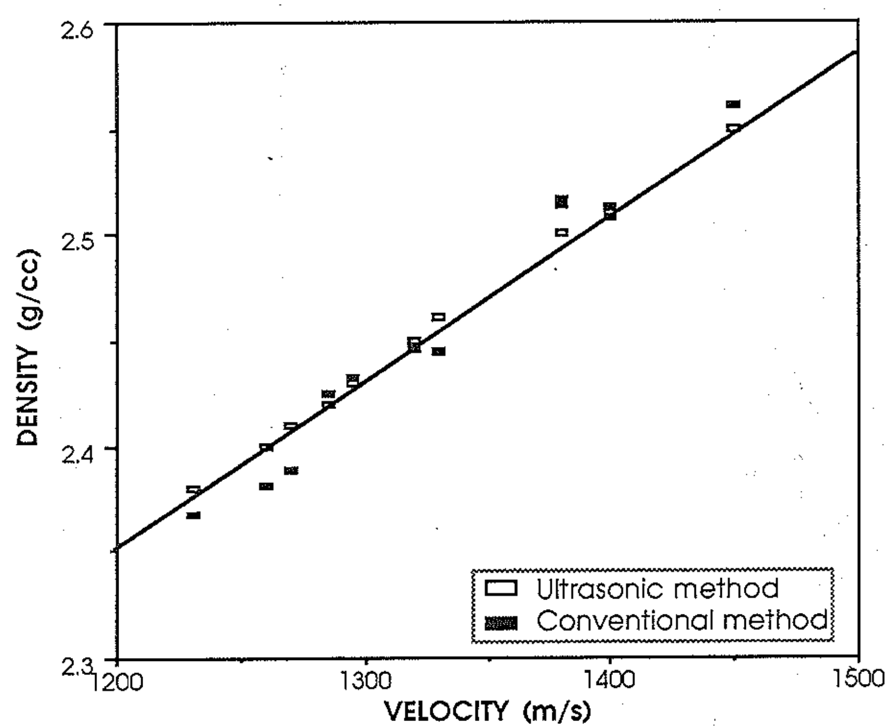
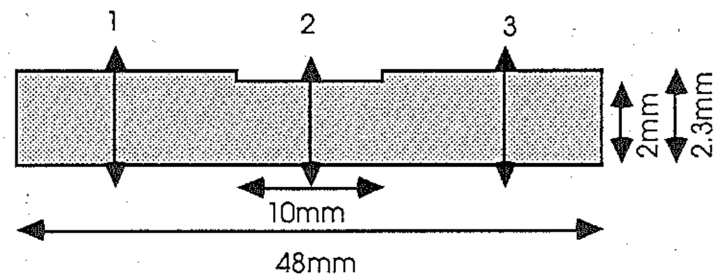
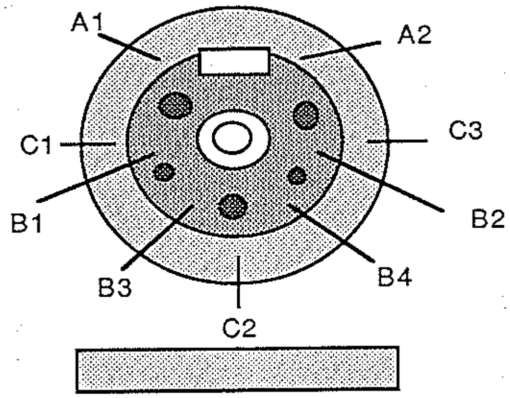


Fig. 12. Comparison of ultrasonically determined and measured density of green Al_2O_3.



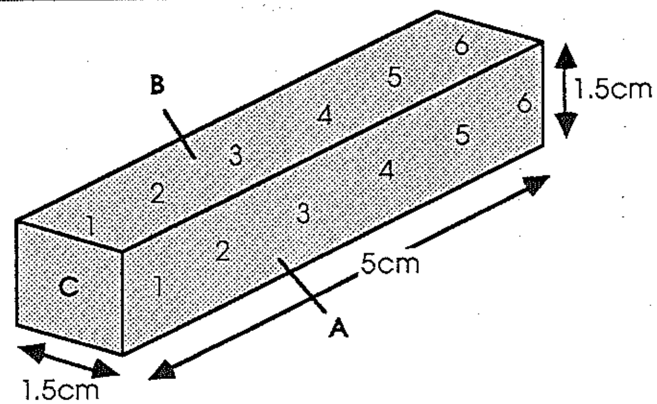
SAMPLE #	LOCATION	VELOCITY (m/s)	DENSITY (g/cc)
1	1	1430	2.53
	2	1370	2.49
	3	1530	2.61
2	1	1435	2.54
	2	1350	2.47
	3	1450	2.55
3	1	1470	2.56
	2	1415	2.52
	3	1490	2.58

Fig. 13. Ultrasonically determined density (from relation in Fig. 9) of green alumina substrates at various locations. Here, each point of measurement corresponds to 6mm diameter.



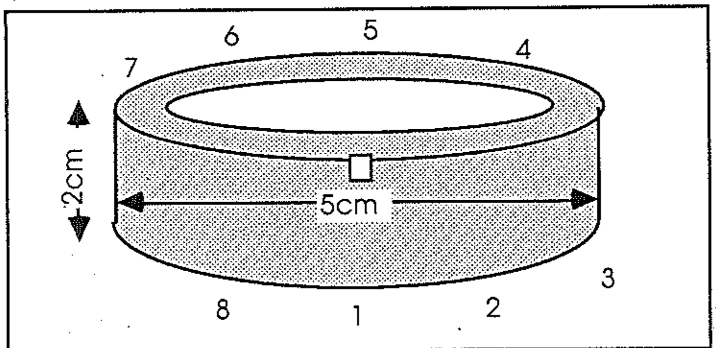
LOCATION #	THICKNESS (mm)	VELOCITY (m/s)	DENSITY
A1	3.0	1610	1.85
A2		1610	1.85
B1	1.75	1650	1.88
B2		1600	1.85
B3		1620	1.86
B4		1650	1.88
C1	3.0	1890	2.03
C2		1650	1.88
C3		1710	1.92

Fig. 14. Ultrasonically determined density (from relation in Fig. 11) of green steatite component at various location. Point of each measurement here corresponds to 3mm diameter.



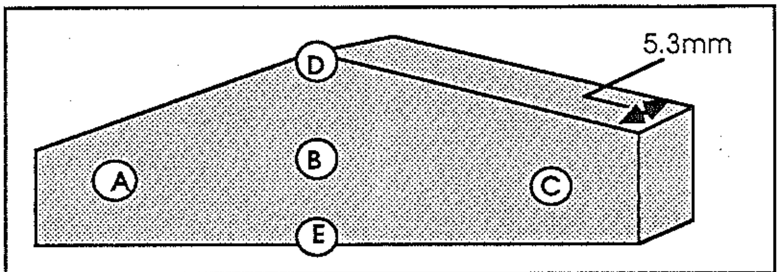
SIDE	LOCATION #	VELOCITY (m/s)	REMARKS
A	1	1150	LOWER VELOCITY : LOWER DENSITY
	2	1130	
	3	1120	
	4	1120	
	5	1120	
	6	1150	
B	1	1010	
	2	1000	
	3	980	
	4	940	
	5	980	
	6	980	
C	1	1260	

Fig. 15. Velocity variations at different points - presumably indicative of density or binder content variations in a green ferrite component (composition, unknown). Here, each test point corresponds to 6mm diameter.



LOCATION #	VELOCITY (m/s)	REMARKS
1	650	Lower velocity : Lower density
2	660	
3	680	
4	680	
5	710	
6	700	
7	680	
8	670	

Fig. 16. Velocity variations at differernt points - presumably indicative of density or binder content variations in another green ferrite component (composition, unknown). Each point of test here corresponds to 3mm diameter.



LOCATION #	VELOCITY (m/s) Increasing Compaction Pressure				
	SN: 1	SN: 2	SN: 3	SN: 4	SN: 5
A	1300	1335	1395	1430	1465
B	1200	1215	1235	1300	1285
C	1240	1325	1340	1430	1430
D	1175	1220	1250	1335	1315
E	1090	1175	1160	1275	1250

Fig. 17. Velocity variations at different points in a green WC component as a function of compaction pressure - at ~ 0.25 ton increments between various samples. Each point of measurement in this case corresponds to 6mm diameter.