Structural evaluation of phosphate bonded ceramic composite materials from non-destructive ultrasonic velocity and attenuation measurements

B. BRIDGE*, R. ROUND‡, A. GREEN§
Department of Electrical and Electronic Engineering, South Bank Polytechnic, 103 Borough Road, London SE1 0AA, UK

The fabrication of a ceramic consisting of a matrix of newberyite and aluminium orthophosphate filled with alumina and lesser amounts of carbon and glass fibre, is described. This material, whilst combining excellent insulation properties with forgiving fracture, is easy to produce by moulding without sintering. The ceramic has been characterized by a number of complementary ultrasonic techniques in the frequency range 24 kHz to 5 MHz.

Dynamic elastic moduli measurements have been found to agree well with elastic constants calculated theoretically by treating the matrix and filler as end members of a two-phase material whose properties obey the lower Hashin and Shtrikman bound. In addition the bulk modulus of the matrix computed theoretically from crystallographic data and making an allowance for porosity agreed closely with the experimental modulus. Thus ultrasound velocity (moduli) measurements combined with theory can be used for non-destructive monitoring and quality control of the ceramic composition which is subject to variation with the parameters governing the chemical reaction during preparation. The theoretical bulk modulus of the ideal (pore-free) matrix is 10.4 GPa. This matrix modulus is far less than that of the moduli of the constituent oxides in the starting mixture. The reason for this is the large expansion in the sizes of closed rings of cation-oxygen network bonds that takes place in the reaction, rather than structural weakening (breaking of rings of network bonds) by hydration.

The frequency dependence of ultrasonic attenuation has been used to identify scattering regimes and thus determine the dimensions of the major scattering particles. Grain sizes determined ultrasonically for the three compositions showed excellent agreement with values determined by optical microscopy.

The high frequency dependent absorption and scattering in this material, mean that good ultrasound propagation is obtained only at low frequencies. The lowest frequency at which the ultrasonic propagation and properties are dependent on the material structure alone, i.e. independent of sample size, has been established to be 2 MHz with conveniently sized test pieces of dimensions 1.5 x 1.5 x 6 cm$^3$.

1. Introduction
When $\text{Al}_2\text{O}_3$ and $\text{MgO}$ powders react chemically with a solution of $\text{Al}(\text{H}_2\text{PO}_4)_3$, a multiphase ceramic, consisting of several polycrystalline magnesium and aluminium phosphates with water of crystallization in specific crystalline planes, is produced. This material which is almost as easy to mould as a polymer, and needs no sintering, has excellent refractoriness and thermal and electrical insulation properties. Carbon or glass fibres can be incorporated to impart stiffness, fracture toughness and forgiving fracture.

For many years similar ceramic materials have been used for refractory lining bricks and gunned furnace repairs. Dental ceramics have also been based on these reactions. By virtue of its unusual combination of thermal and mechanical properties this ceramic has been envisaged, amongst other uses, for stealth technology applications, e.g. the minimization of infrared

*Previous address: Department of Physics, Brunel University, Kingston Lane, Uxbridge, Middlesex, UK.
‡Previous address: Department of Physics, Brunel University. Now at the Department of Ceramics, North Staffordshire Polytechnic, Stoke on Trent, ST4 2DE, UK.
§Previous address: Thorn EMI Central Research Laboratories, Dawley Road, Hayes, Middlesex, the Mechanics Group, Department of Engineering, University of Reading. Now at Fison's Scientific Instruments, Manor Industrial Estate, Gatwick Road, Crawley, Surrey, UK.
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signatures when used in aeroengine casings. It also has a large potential impact on the mass marketing of domestic appliances if used, for instance, as lightweight oven casings and venturi, with simple one-piece units replacing the complex fabrications currently required to achieve the desired physical requirements.

In the composites discussed here the dimensions of the alumina and magnesia powder particles were 0.5 to 10 μm and 3 to 40 μm, whilst the milled fibres were short, 150 μm × 10 μm diameter. The prototype material suffers from serious void defects which can be several mm in diameter.

The purpose of the current research programme is to investigate the feasibility of non-destructively evaluating the structure of this and other ceramic materials by ultrasonic methods for quality control and process control applications. Measurement problems arose at low frequencies where the wavelength was greater than the sample dimensions and therefore one of the research objectives was to understand the nature of the wave propagation under such circumstances. This approach was taken in preference to preparing larger samples since in an industrial NDT application the ultrasonic technique must be tailored to the artifact to be examined and not the converse.

This communication is concerned with the frequency dependence of velocity at kHz frequencies, the reliable quantitative determination of grain size and elastic constants from attenuation and velocity data, and comparison of elastic data with theoretical expectations.

2. Preparation of samples
Aluminium orthophosphate bonded alumina-magnesia ceramics, as described in previous reports [1, 2], were prepared with various chopped fibre contents.

When MgO powder reacts chemically with a solution of Al(H₃PO₄)₃ [3, 4], in the presence of Al₂O₃, a multiphase ceramic, consisting of several polycrystalline magnesium and aluminium phosphates with water of crystallization in specific crystalline planes, is produced. The reaction sequence is complex and the main reactions are essentially as follows.

Gibbsite and phosphoric acid react to produce aluminium orthophosphoric acid:

\[
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 6\text{H}_3\text{PO}_4 \approx 2\text{Al(H}_2\text{PO}_4)_3 + 6\text{H}_2\text{O}
\]

Gibbsite Phosphoric aluminium orthophosphoric acid

The aluminium orthophosphoric acid is allowed to retain water, and more is added, to produce a 48% by weight solution which reacts with magnesia in the presence of alumina thus

\[
2\text{MgO} + \text{Al(H}_2\text{PO}_4)_3 \xrightarrow{\text{H}_2\text{O}} 2\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} + \text{AlPO}_4 \cdot x\text{H}_2\text{O}
\]

crystalline amorphous newberyite

In the composites discussed here the dimensions of the alumina and magnesia powder particles were 0.5 to 10 μm and 3 to 40 μm, whilst the milled fibres were approximately 150 μm in length and 10 μm in diameter. The final phase assemblage for the reaction bonded material would be a matrix consisting ideally of about 70% crystalline newberyite, and 30% aluminium phosphate by weight with corresponding values of 79% and 21% by volume, assuming x to be 2. Whilst the prevalent reaction is as stated, others do occur leading to the formation of other magnesium phosphates, so that in practice small amounts of MgO, (Mg(PO₄)₂ and MgH₂P₂O₇ will be present. The filler, alumina and any fibre, 55 to 60% by weight, is dispersed throughout the matrix. In subsequent discussion the matrix should be understood to refer to all the reaction products whilst the particulate or fibrous fillers remain chemically inert although they may influence the end point of the matrix reactions and the amount of porosity in the matrix. Taking the alumina content to be 55% by weight there would be 31.3% newberyite and 13.5% aluminium phosphate by weight ignoring minor phases.

We shall consider three samples with starting compositions in wt % as in Table I. Test pieces of dimensions 1.5 × 1.5 × 6 cm³ were produced using a co-rotary extruder as a compounding mixer. The mixture was extruded under vacuum, vibrated into moulds and set off at 100 or 20 °C.

3. Material structure
Simple observation of the surface shows that the prototype material suffers from serious void defects which can be several millimetres in diameter in extreme cases, and arise from gaseous reaction products and air incorporated during mixing and moulding. Hand lens observation of fracture surfaces reveals a coarse texture, with grain dimensions on a millimetre scale. Therefore another possible defect is poor intergranular bonding (which may be related to grain dimensions) due to departures from the intended chemical reaction route. This may stem from local variations in proportions and/or conditions. Such inhomogeneities are more likely with these multiphase composites than with simpler two-phase composites.

Samples were polished and examined under oblique illumination adjusted to give the greatest possible contrast between the two major phases observable. The photomicrographs are shown in Figs 1, 2 and 3. There are differences in the microstructures of the samples with grains of up to 2 mm in the 5% fibre samples (Fig. 1), grains up to 1 mm in the 1.5% fibre sample (Fig. 2), and grains up to 0.7 mm in the fibre-free samples. In all samples there are two main matrix phases visible, the softer phase containing the majority of the porosity. In the case of the no-fibre sample there is little contrast between the two matrix