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The preparation of laminated ceramic composites using paint technology

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Ceramic paints comprising ceramic powder, dispersant, resin and solvent were prepared by high speed mixing. The powders were alumina and alumina with 20 vol% zirconia. Alternate layers of paint having thicknesses of 20–30 μm were deposited by the random deposition of droplets from a conventional paint spray gun operating on compressed air. Laminates of up to 1 mm were produced. The microstructure of the multilayer ceramic wafers produced by drying, thermolysis and sintering is reported. The method avoids the thermolamination step associated with tape casting and allows laminates to be prepared on contoured fugitive substrates.

1. Introduction

Functional ceramic powders have been incorporated in multilayer devices for decades using a combination of tape casting and screen printing [1]. Recently there has been interest in laminated ceramic composites in structural applications [2]. If planes of relative weakness are incorporated, crack diversion takes place and resistance to catastrophic failure is conferred [3]. Modelling of the fracture process [4, 5] and experimental studies [6, 7] confirm the advantages for brittle materials.

The main manufacturing route involves the preparation of a ceramic suspension in a solvent–resin vehicle which can be cast onto a moving endless belt to produce a film whose thickness is regulated by a "doctor blade". This is the tape casting process which has been developed from the solvent casting of polymers and can produce ceramic plates down to about 100 μm thickness. It is currently the favoured way of preparing ceramic layers which can then be joined before firing by thermolamination [2, 8, 9]. Similar microstructures in $Al_2O_3/Al_2O_3–ZrO_2$ composites have been prepared by slip casting [10]. Electrophoresis in ethanol [11] or an aqueous medium [12] has been described as an alternative method for preparing $Al_2O_3–ZrO_2$ laminates.

Tape casting and the many other ceramic manufacturing procedures derived from polymer technology [13, 14] all involve the incorporation and dispersion of ceramic powder in an organic vehicle. A similar procedure is followed in the paint and printing ink industries and, since in the case of laminated ceramic composites, thin (10–30 μm) alternate layers are sought, these industries offer the possibility of interesting novel fabrication procedures. Many thermoplastic resins are available for incorporation in paint systems. Often these are methacrylate copolymers which incorporate acid or amine groups which make them well suited to enhancing dispersion.

Acrylic polymers are used in ceramic processing, for example by injection moulding, and are considered to leave a low carbon residue on pyrolysis. Such resins confer another advantage in that high-shear melt processing could be used to enhance the dispersion of powder before dilution with solvent.

This paper describes the application of conventional paint deposition as a method of making ceramic multilayers. Large areas of laminate can be prepared. The limitation of having a flat substrate, which applies to tape casting, is not a restriction. The ceramic film will reproduce the profile of the substrate, for example it will follow corrugations or protrusions. No subsequent lamination process is needed.

2. Experimental details

The alumina powder was A16SG (ex Alcoa G.B. Ltd., Worcs., UK) having a particle size in the range 0.3–0.5 μm and a specific surface area of 9.5 $m^2 g^{-1}$. The zirconia was HSY3 (ex Daiichi-Kigenso, Japan) which has 5 wt% Y_2O_3, an average ultimate particle size of 100 nm and a specific surface area of 7 $m^2 g^{-1}$. The density of the alumina was 3987 kg m^{-3} and that of the zirconia 6000 kg m^{-3}.

The resins used were Paraloid B99 (ex Rohm and Haas, Croydon UK, supplied by Chemacryl Ltd., Bishops Stortford, UK) which is an acrylic copolymer with a density 1100 kg m^{-3} and Paraloid B66 (supplied *ibidem*) which is an acrylic homopolymer with a density 1100 kg m^{-3}. The dispersant was Efka polymer 401 (ex Efka Chemicals BV, Hillegom, Holland, supplied by Stort Chemicals Ltd., Bishops Stortford, UK) which is a modified acrylic polymer supplied in solution at 50% wt/wt. The density of the dispersant polymer is 1030 kg m^{-3}. The solvent was grade QT 76 (ex Trimite Paints, Uxbridge, UK) with a density of 830 kg m^{-3}.

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TABLE I Composition of ceramic paints

	Composition (wt %)				
	1	2	3	4	5
Alumina	92.27	91.75	67.32	84.61	62.48
Zirconia	–	–	25.13	–	23.33
Dispersant Efka 401	–	2.75	2.77	2.54	2.57
Resin B99	7.73	5.50	4.78	–	–
Resin B66	–	–	–	12.85	11.62
Ceramic (vol %)	0.75	0.75	0.75	0.60	0.60

The compositions of the paints are given in Table I. The compositions are based on a ratio of ceramic/resin/dispersant designed to give a chosen ceramic volume fraction. The solvent amount was chosen according to suitability for spraying. Composition 1 was mixed by manual stirring followed by ultrasonic treatment. The remaining paints were mixed by dissolving the resin and dispersant in some of the solvent by heating on a hot plate. This solution and the powder were then placed in a high speed stirrer and stirred at 7000 r.p.m. for 5 min stopping occasionally to allow the mixture to cool. The ceramic paints were then assessed for rate of sedimentation.

Spraying was carried out using a professional quality paint spray gun operated by compressed air in a fume cupboard. Coupons of ashless filter paper (Whatman Int. Ltd, Maidstone, UK) were attached to a metal gauze to act as a substrate (Fig. 1). This allowed drying from both sides of the paint film. Laminate was built up with multiple passes of paints consisting of diluted compositions 4 and 5 (Table I) to give a composite and with paint 4 to give a monolith. The films were stacked between filter paper to dry for 100 h.

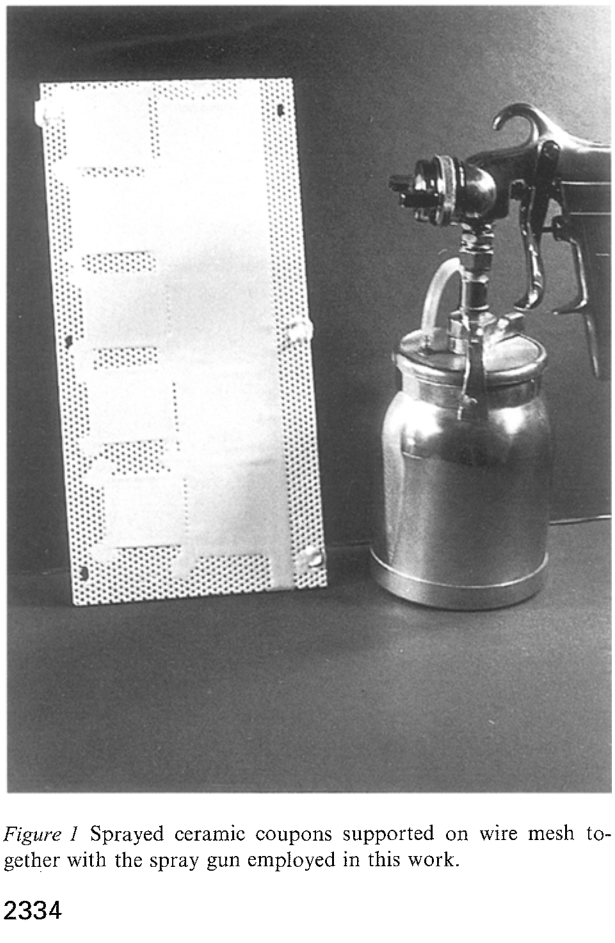

Figure 1 Sprayed ceramic coupons supported on wire mesh together with the spray gun employed in this work.

Pyrolysis was carried out in air using a stainless steel oven controlled by a Eurotherm 818P programmable temperature controller. The coupons were heated at 3 °C h^{-1} to 120 °C and held for 1 h to remove residual solvent. The temperature was then raised at 5 °C h^{-1} to 450 °C followed by furnace cooling. After this treatment, the ceramic coupons separated easily from the filter paper substrate and were sintered at 1650 °C for 2 h in air. Polished sections and fracture surfaces were examined using a Cambridge S250 scanning electron microscope. Shrinkage was measured with a travelling microscope between marks inscribed on a monolithic alumina coupon.

3. Results

The compositions were tested initially for sedimentation. Composition 1, to which no dispersant was added, began to show signs of sedimentation after 24 h. Composition 2 showed remarkable stability; signs of sediment appeared after 168 h. The corresponding composite ceramic paint (composition 3) was prepared with the same ceramic volume fraction as composition 2 but with 20 vol % alumina replaced with zirconia.

These paints were diluted to 29 vol % ceramic with solvent and were applied by repeated brush out to give deposits of thickness up to 1 mm. For all thicknesses and substrates these formulations produced extensive cracking on drying which became evident after five coats (Fig. 2) and were abandoned.

Composition 4 was prepared using a resin with a slightly lower softening point and incorporating less powder. This produced no signs of drying cracks when multilayers were produced by brush out. For spraying, the dilution for compositions 4 and 5 gave 26 vol % ceramic. Sprayed multilayered coupons of paint composition 4, appropriately diluted, were produced, pyrolysed and sintered to yield monolithic plates. Fig. 3 shows a fracture surface after sintering in which individual paint layers cannot be distinguished. In this and subsequent experiments, ashless filter paper was used as the substrate because it facilitated drying and separated on pyrolysis. Its disadvantage was that it left a fibrous pattern on the base of the coupons.

Figure 2 Paint films of composition 2 deposited by brushing showing the cracks that appeared on drying.

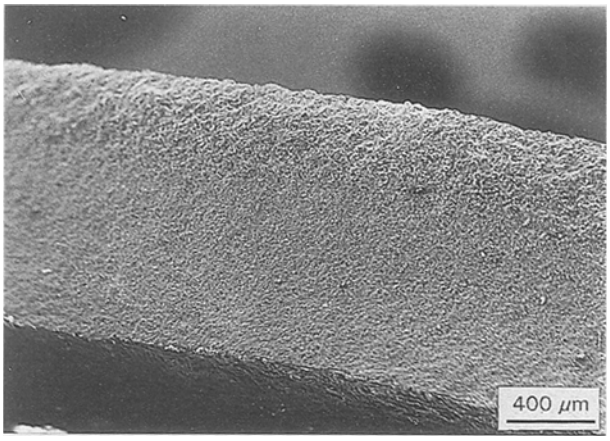

Figure 3 Fracture face of sintered film made from paint composition 4.

The top surfaces of the sprayed ceramic coupons were, in contrast, glossy and scanning electron microscopy showed them to be very smooth. The paint films were stacked between filter paper during drying to prevent deformation due to non-uniform loss of solvent which always occurred in unrestrained films. In addition to this drying defect, wrinkling of the top surface of the film occurred when insufficient drying time was allowed between passes. These defects are associated with the choice of solvent. A medium volatility solvent was selected for safety reasons.

The linear shrinkage which occurred on pyrolysis in air, as measured with a travelling microscope on the alumina coupons, was 1.0 ± 0.2% (95% confidence limits). This is comparable to the shrinkage observed for 60 vol % A16 alumina in a polypropylene vehicle when pyrolysed in air [15]. The initial measurement was made after drying was completed and therefore this shrinkage represents the loss of resin and dispersant. The shrinkage due to sintering was 14.8 ± 0.5% (95% confidence limits). The combined shrinkage, reflecting the change from 60 vol % to near full density, was 15.7%. This corresponds to 40.1 vol % which confirms the microstructural indication of nearly complete densification. It also indicates that insufficient residual solvent was present after drying to affect the shrinkage.

Laminated ceramic composites were then prepared by alternately spraying paints of diluted compositions 4 and 5. Twenty one layers were deposited and the laminates were pyrolysed and sintered. Fig. 5 shows the top and fracture surfaces of such a laminate. The top surface is smooth and shows little evidence of residual agglomerates. The layers are revealed partly by the enhanced back-scattered image from the ZrO_2 but mainly by the difference in grain size. The layers are in the region 20–30 μm in thickness. The alumina

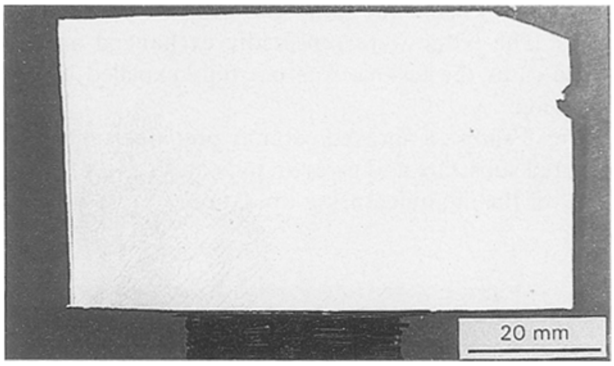

Figure 4 A sintered laminate made from paints 4 and 5.

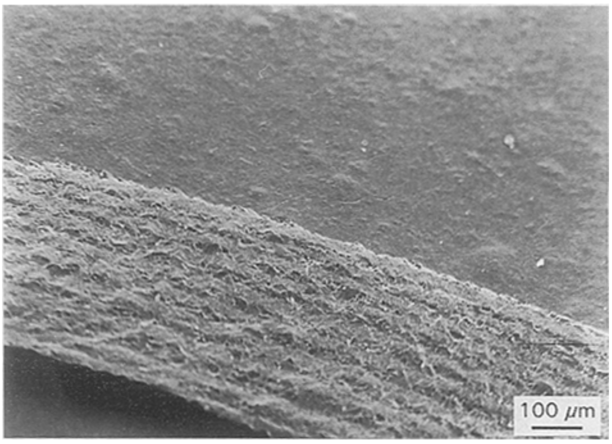

Figure 5 Fracture face of sintered laminate of Al_2O_3/Al_2O_3–20% ZrO_2 showing smooth upper surface and 21 layers.

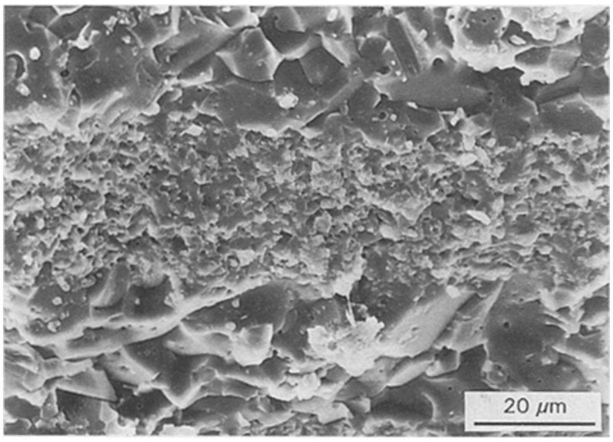

Figure 6 Fracture face of the sample in Fig. 5 showing grain growth in the alumina layers, and restricted grain growth in the ZrO_2 containing layers.

has undergone substantial grain growth (Fig. 6) while in the ZrO_2-containing layers, grain growth has apparently been inhibited by the zirconia. Grain growth inhibition by fine zirconia particles has been reported previously in Al_2O_3–ZrO_2 composites [16].

Fig. 7 shows a polished section of a laminate with 21 layers. In this micrograph the upper surface which was originally adjacent to the substrate, shows the roughness associated with the filter paper. In contrast, the sprayed surface is flat and smooth.

Fig. 7 shows regions where droplets of paint 4 have intruded into layers of paint 5. These laminates were prepared by using one spray gun with two paint reservoirs. The latter were repeatedly exchanged and in some cases the residue was not fully expelled before spraying.

Fig. 8 shows a sprayed ceramic prepared on a corrugated substrate and gives an indication of the versatility of this manufacturing operation.

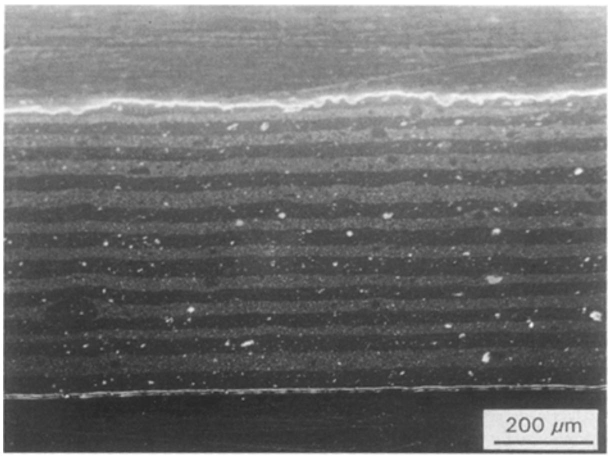

Figure 7 Polished section of a 21 layer laminate.

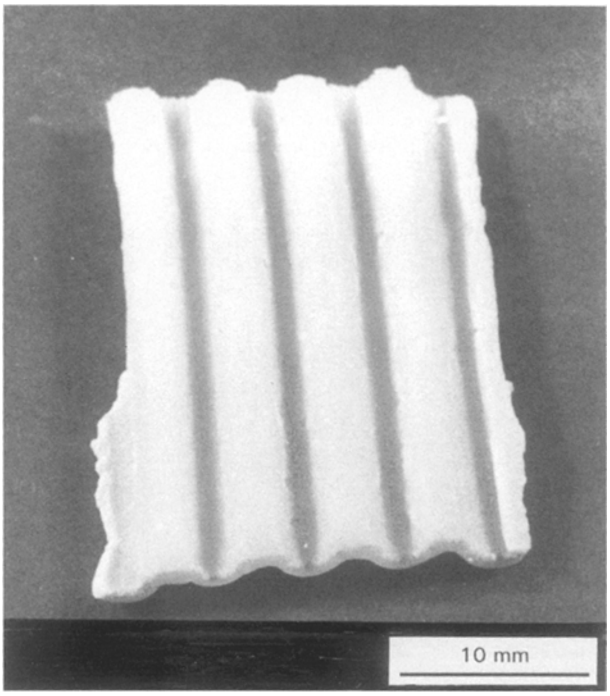

Figure 8 Sintered corrugated alumina substrate made by droplet deposition onto corrugated cardboard.

4. Discussion

The paint formulations were developed by fixing the ceramic volume fraction based on the ceramic–resin–dispersant system at 75 vol % initially. This is the system that remains after completion of the drying stage. The solvent addition was empirically selected to allow spraying.

The selection of compatible dispersants, resins and solvents is partly empirical and the materials selected for use in this work are used in commercial paint formulations. There are a number of similarities between the requirements of a paint formulation and a suspension designed for ceramic processing. The dispersion of powder and the stability of the suspension confer colour and gloss in paint applications and freedom from agglomerate-related strength-limiting defects in ceramic manufacture. The size of pigment particles is chosen for optical reasons and is comparable to that for ceramic particles which is dictated by sintering considerations. Furthermore, the availability of acrylic thermoplastic resins which do not develop a carbonaceous residue on pyrolysis mean that ceramic fabrication processes can benefit considerably from modern paint components.

The ceramic powders were selected to have particle sizes which are representative of the submicron powders used in high performance applications. The composite was chosen to give a laminated structure wherein the damage caused by differential sintering of the layers would be minimal but where the layers could be clearly distinguished as a result of the backscattered contribution to the electron microscope image. No attempt has been made in this work to optimize mechanical properties or achieve crack diversion. The aim was to relate the processing operation to the microstructure.

Ashless filter paper and aluminium foil were selected as sacrificial substrates but there is much scope for superior substrates such as those based on porous cellusosic membranes because the filter paper confers a rough surface finish on the ceramic.

A critical decision is the choice of ceramic volume fraction based on the dry paint, i.e. on the ternary ceramic–resin–dispersant system. The maximum packing fraction of A16 alumina based on relative viscosity data in a polypropylene vehicle is 73 vol %. [15]. Thus compositions 2 and 3 approximate to this volume fraction after drying and may produce a high elastic modulus [17] and low toughness; conditions for fracture under non-uniform shrinkage due to diffusion and evaporation of solvent. Compositions 4 and 5 used a volume fraction after drying compatible with melt processing. This offers the additional advantage that, in future developments, high shear mixing can assist in the dispersion of agglomerated ceramic powders and the melt-processed suspension can be diluted subsequently in solvent.

In the selection of solvent, enhanced drying time and hence speed of build up of layers must be balanced by the choice of a solvent with a reasonably high flash point. In practice, solvents are available with diverse drying times and a medium volatility solvent was selected in this work for safety reasons. Paint deposition is a well established technology in diverse industries and the safety procedures are well established.

The uniformity of thickness of the layers is largely dependent on operator skill although the process can be automated for mass production. By adjustment of the paint viscosity it may be possible to deposit layers down to 8–10 μm as achieved by automotive finishers which is likely to be the limit for this process.

Fig. 8 indicates the potential of the process for thin wall ceramic structures. More complex substrates could potentially be used. Since the paint has thermoplastic properties and has a ceramic volume fraction compatible with plastic forming, laminates may be joined before firing [18]. The method thus offers opportunities for the manufacture of ceramic heat exchangers and perhaps fuel cells in which corrugated laminated structures are employed [19]. This work also paves the way for the computer aided manufacture of ceramics by three-dimensional overprinting. Instead of the random deposition of droplets which prevails here, a jet printer can be used to allow the destination of each individual drop to be controlled [20].

5. Conclusions

The feasibility of producing monolithic and laminated composite ceramics by the random deposition of droplets of a stable dispersion of ceramic powder has been demonstrated. The sprayed surface finish is smooth and glossy and uniformity of layer thickness is possible. Layer thicknesses of 20–30 μm were produced. The lower limit may be 10 μm. The technique allows thin-walled ceramics to be made on profiled substrates so that complexity of shape is possible. The dried ceramic–polymer system has a thermoplastic vehicle and a ceramic volume fraction compatible with subsequent working- or joining-before-firing operations.

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