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Investigation on the pressure infiltration of sol–gel processed textile ceramic matrix composites

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A pressure infiltration apparatus was used to fabricate textile ceramic matrix composites using sol–gel processing with added solid particles. A parabolic rate kinetics model for the infiltration process has been developed and experimentally verified. Darcy's law and a global permeability of the whole material system were adopted in the model. Experiments were conducted using both a 3-d angle interlock and a 2-d woven carbon fibre preform, and a silica sol containing silica particles of submicrometre sizes. The thickness of the particle compaction layer inside the 3-d preform is proportional to the square root of the processing time. The total infiltration time was inversely proportional to the constant processing pressure and increased significantly with reducing the solid particle size by a factor of two. The addition of a non-ionic surfactant reduced the surface energy which resulted in higher composite green density values of up to 90%. Sol–gel processing with added solid particles proved to be a viable method to fabricate textile ceramic matrix composites with a higher density and improved properties.

1. Introduction

Sol–gel processing has attracted wide interest for the fabrication of ceramics and ceramic composites due to its low processing temperature and versatility in terms of the materials and microstructures obtained. However, a major problem in sol–gel processing is excessive shrinkage during drying, leading to extensive matrix cracking in composites where a stiff fibre preform constrains matrix deformation. Liu and Parvizi-Majidi [1] studied the control of shrinkage by the addition of solid particles to the sol. The mixture of sol and particle suspension was infiltrated into a 3-d angle-interlock woven preform by pressure infiltration. Drying cracks were reduced and the density of the composite was increased. A combined slurry/gel approach such as this could conceivably offer the advantages of both the sol–gel and slurry infiltration techniques [2]. The relationships amongst processing parameters such as infiltration pressure, green density, and permeability can be better understood if the kinetics of pressure infiltration are known. Lange and Miller [3] proposed a parabolic form for the rate kinetics of pressure filtration of an alumina slurry. From their results, the permeability of a consolidated layer can be obtained by a model derived from Darcy's law. Danforth and Gauthier [4] also proposed parabolic rate kinetics of filtration for bimodal mixtures of colloidal silica and monosized colloidal silica. The thickness of the cake is proportional to the square root of time. They also found that the permeability of the packing cake decreased with an increased fraction of fines in bimodal packing. In another work [5], several filtration models have been discussed. Amongst these were the analysis of Kim which showed that the casting rate and casting uniformity for colloidal powders can be substantially enhanced by the use of increased filtration pressure. Another discussed model is that of Bridger *et al.* who were able to evaluate average specific cake resistance (reverse of permeability) for several different filter cakes from their model. Marple and Green [6] used multiple infiltrations to increase the green density of a composite, but since pressure was not introduced this infiltration procedure is not efficient. In the work of Advani [7], the weighted average of in-plane permeabilities of all preform layers in the thickness direction is used to approximate the effective in-plane permeability in the plane of the flow field. He also commented that for thin shell geometries, the through thickness flow is much less important than the in-plane flow. Based on Darcy's law, Scherer [8, 9] measured the permeability of a gel by applying a pressure differential across the porous material and measuring the rate of flow. He also found that for a porous gel with an homogeneous microstructure, the order of magnitude of permeability was found to be in agreement with the Carmen–Kozeny equation. However, for a porous gel with some large pores, the experimental results are larger than those predicted.

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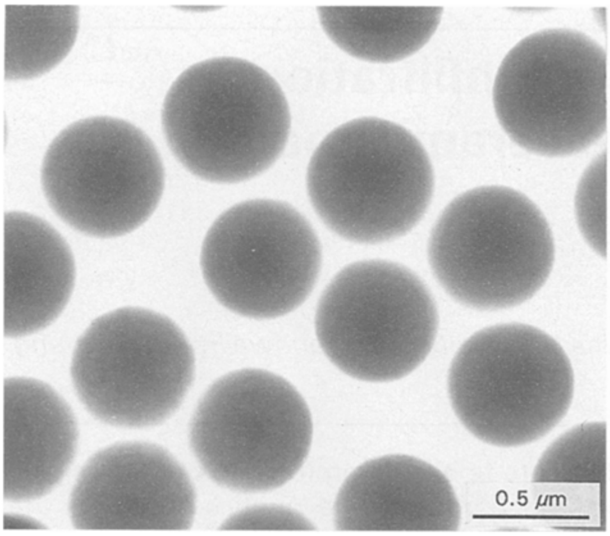

Figure 1 TEM micrograph of silica particles with average particle size of 0.5 μm.

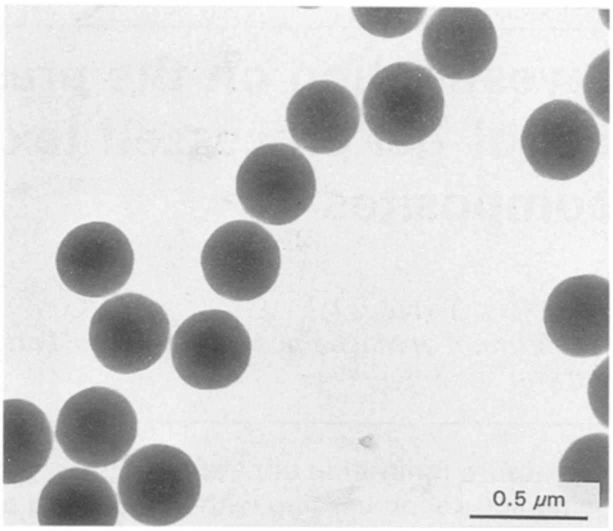

Figure 2 TEM micrograph of silica particles with average particle size of 0.25 μm.

On the other hand, Lukasiewicz and Reed [10] found that the permeability of porous alumina compacts were not well described by the Carmen–Kozeny model but were better described by a capillary model based on a mean entry pore radius. The specific permeability varies directly with the square of this mean entry pore radius.

In this paper, a parabolic rate kinetics model has been developed and verified by experiments for the pressure infiltration of textile ceramic matrix composites using sol–gel processing with added solid particles. The permeability of the whole system consisting of fibre preform, particle compaction, and filter was derived from the individual permeabilities of the fibre preform and particle compaction inside the preform. Experiments were conducted using 3-d angle interlock and 2-d woven carbon fibre preforms and a silica sol containing silica particles of submicrometre sizes. The addition of a surfactant influences the composite green density which may affect the permeability of the material system. The relationship among the permeabilities of material system, the processing time, the processing pressure and the particle size has been studied.

2. Experimental procedures

2.1. Materials

The infiltrate combined both a sol and a suspension. The silica sol was prepared by the following procedure. Tetraethyl orthosilicate (TEOS) (Aldrich Chemicals) was used as the precursor, water as the carrier, and ethyl alcohol (Aldrich Chemicals) as the mutual solvent for TEOS and water. The hydrolysis was carried out under acidic conditions. The procedure consisted of dissolving 27.8 vol % TEOS in 27.8 vol % ethyl alcohol and adding 44.4 vol % water along with 0.01 moles of nitric acid per mole of TEOS to the mixture while constantly stirring the mixture. All reagents were at room temperature. Colloidal suspensions of silica particles with particle sizes of 0.25 μm and 0.5 μm were obtained through the procedure reported by Liu and Parvizi–Majidi [11]. Particle sizes were examined by transmission electron microscopy (TEM) and are shown in Figs 1 and 2. The infiltrates were prepared by mixing appropriate volumes of the sol and the particle suspensions. Table 1 gives the characteristics of the infiltrates used.

TABLE 1 Volume fractions and viscosities of the two infiltrates used in the experiments

Infiltrate	v_1	v_2	v_c	v_0	Viscosity (cP)
Sol + 0.25 μm particles	0.036	0.0498	0.6	0.0429	2.2
Sol + 0.5 μm particles	0.036	0.0577	0.59	0.0477	2.34

v_1: volume fraction of solids in sol
v_2: volume fraction of particles in suspension
v_c: volume fraction of solids in particle compaction
v_0: volume fraction of solids in infiltrate

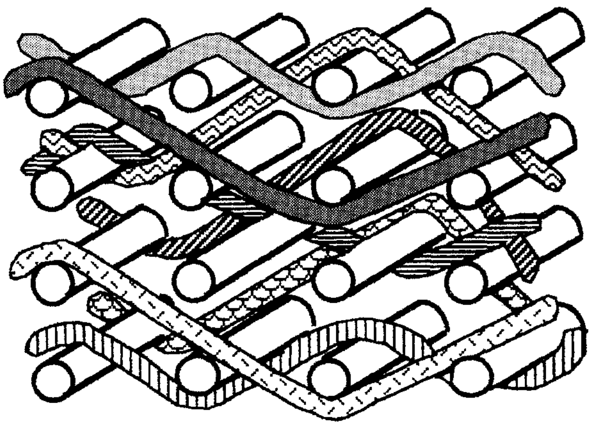

Figure 3 Schematic of layer to layer 3-d angle interlock preform.

The fibre preform for the kinetics study was a 3-d angle-interlock woven fabric of PAN (polyacrylonitrile)-based type I carbon fibre with a fibre volume fraction of 48 % and a thickness of 6.2 mm. A schematic diagram of the preform is shown in Fig. 3. In the

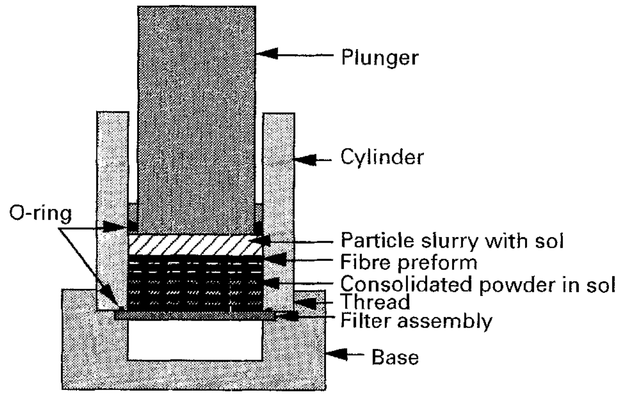

Figure 4 Schematic of pressure infiltration apparatus.

layer-to-layer architecture the warp yarns only interlock the adjacent layers of the weft yarns. A 2-d satin weave preform was used to study the influence of surfactants on the green density of the composite.

2.2. Processing of the composite

Infiltration was conducted in the pressure infiltration apparatus shown in Fig. 4. The infiltrate was pushed through the thickness direction of preform, i.e., perpendicular to warp and weft yarns, using an Instron testing machine. The pressure infiltration apparatus was specifically designed to obtain data on the matrix deposition [1]. The preform was placed above the filter assembly and 300 ml of the infiltrate was poured into the cylinder and then pushed through the preform by pressing down the plunger. A hydraulic Instron (type 1321), set at constant load mode, was used to provide pressure. To prevent rupture of the filter paper, infiltration was initially carried out at a low level of pressure. Once a significant layer of powder compaction had formed inside the preform, the pressure was raised to the desired level. Displacement of the moving plunger was recorded during infiltration. The infiltration experiments were terminated after different processing times. Pressure exerted on the infiltrate was calculated by dividing the applied load by the cross-sectional area of the inner circle of the cylinder which is 7.5 cm in diameter. After infiltration, the specimen was ejected and dried in an oven at 50 °C for 18 h. The weight of the specimen was measured before and after drying and the composite green density was calculated from its dimensions and weight after drying. In order to facilitate cutting and specimen preparation for microscopy, the composite green body was infiltrated with epoxy by soaking it in epoxy and then curing at 150 °C for 2 h. It was then cut and polished down to 1 μm finish for examination of the microstructure and for the determination of the thickness of the particle compaction layer in the preform, by optical microscopy.

2.3. The addition of surfactant

For the study of surfactant effect on the green density, particles with different sizes, 4 and 0.8 μm was selected to mix with the sol. Cyclohexanone and sodium dodecyl sulfate which are a non-ionic and ionic surfactant, respectively, were added to the mixture in order to control the surface tension between particles and fibres. The preform is a stacking of a 6-layer 2-d woven carbon fabrics. The carbon fabric is plain weave with 6K fibre yarn. The volume fraction of preform is 62 %. The carbon fabric was cut in a circular shape with a 7.5 cm diameter in order to fit the pressure infiltration mould. The infiltration procedure is the same as that discussed in section 2.2.

3. Analytical modelling

The flow through a porous medium can be described by Darcy's law [7]

$$J = \frac{\kappa_x P_x}{\mu \delta} \tag{1}$$

where J is the flow rate per unit area; κ_x is the effective permeability of the porous medium; P_x is the pressure difference across the medium; μ is the viscosity of the fluid; and δ is the thickness of the medium. For the present problem, balancing the moving distance of the plunger "d" and the fluid flowing through the porous medium by integrating Equation 1 over the processing time t gives

$$d = \left(\frac{2\kappa_e P x t}{\mu(L_f + L_1)}\phi\left(\frac{v_c}{v_0} - 1\right)\left(\frac{v_1 + v_2}{v_2}\right)\right)^{1/2} \tag{2}$$

where $\phi = 1 - v_f$ is the preform porosity; v_1, v_2, v_c, and v_0 are the volume fractions of the solids in the sol, the particle suspension, the particle compaction, and the sol/suspension mixture, respectively; P is the constant processing pressure; L_f and L_1 are the thicknesses of the fibre preform and filter paper, respectively; and x is the thickness of the powder compaction layer inside the preform. x is given by

$$x = \frac{d\left(\frac{v_2}{v_1 + v_2}\right)}{\phi\left(\frac{v_c}{v_0} - 1\right)} \tag{3}$$

and the global permeability of the whole system, κ_e, by

$$\kappa_e = \frac{\kappa_1 \kappa_2 \kappa_3 (L_f + L_1)}{L_1 \kappa_2 \kappa_3 + x \kappa_1 \kappa_3 + (L_f - x)\kappa_1 \kappa_2} \tag{4}$$

where the Carmen–Kozeny equation has been used for the individual permeabilities [12]. The usual form of the Carmen–Kozeny equation for permeability is $\kappa_{CK} = \phi^3/k_0(L_e/L)^2(1-\phi)^2 S_0^2$ where $(L_e/L)^2$ is called the "tortuosity", and $k_0(L_e/L)^2$ is called the Kozeny constant which equals 5 to fit most experimental data. S_0 is the specific surface area based on the volume of solid which can be related to the mean particle diameter D_p or mean fibre diameter D_f. Thus

$$\kappa_2 = \phi \kappa_4 \tag{5}$$

$$\kappa_3 = \frac{D_f^2}{K}\frac{\phi^3}{(1 - \phi)^2} \tag{6}$$

$$\kappa_4 = \frac{D_p^2 (1 - v_c)^3}{180\, v_c^2} \tag{7}$$

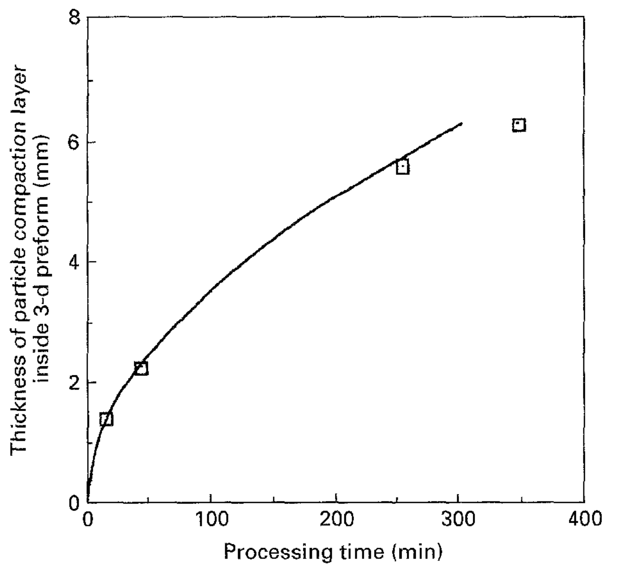

Figure 5 (☐) Experimental and modelling results (solid line) for pressure infiltration of a 3-d angle interlock fibre preform with sol and 0.25 μm particles suspension under constant pressure at 123.2 psi (8.5×10^5 Pa)

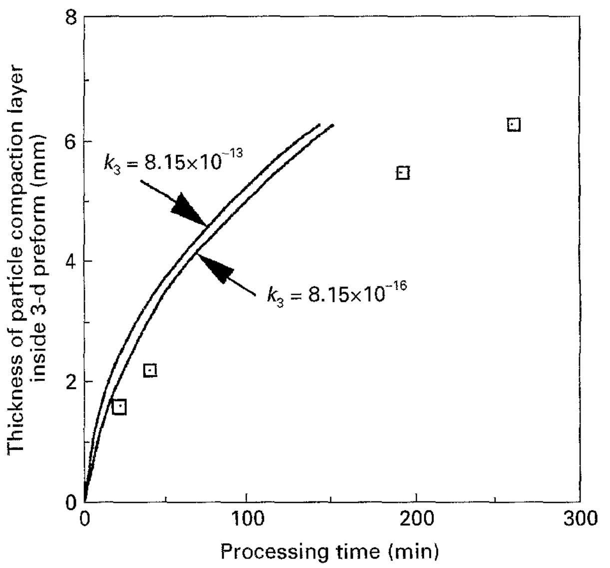

Figure 6 (☐) Experimental and modelling results (solid line) for pressure infiltration of a 3-d angle interlock fibre preform with sol and 0.5 μm particles suspension under constant pressure at 82.14 psi (5.66×10^5 Pa)

κ_1, κ_2, κ_3 [13] and κ_4 [3] are the permeabilities of the filter assembly, the combination of particle compaction and preform, the preform, and the particle compaction only, respectively; the constant K is assumed to be 38.8, from the work of Loos *et al.* [13], who used 16 layers of 8 harness satin plain weave; D_f is the fibre diameter; and D_p is the mean particle diameter in suspension. κ_1 is 3.43×10^{-14} for the 0.45 μm pore size and 6.86×10^{-15} for the 0.1 μm pore size nitrate cellulose membrane filter papers* used in the experiments. Combining Equations 2–4 gives:

$$Ex = \frac{AD}{B + Cx} \tag{8}$$

where

$$A = \kappa_1 \kappa_2 \kappa_3$$

$$B = L_1 \kappa_2 \kappa_3 + L_f \kappa_1 \kappa_2$$

$$C = \kappa_1 \kappa_3 - \kappa_1 \kappa_2$$

$$D = \frac{2Pt}{\mu} \frac{v_2}{v_1 + v_2}$$

$$E = \phi\left(\frac{v_c}{v_0} - 1\right)$$

It is to be noted that the model here assumes that the sol has no time to undergo gelation during processing. Solving Equation 8 yields

$$x = \frac{-BE + ((BE)^2 + 4ACDE)^{1/2}}{2CE} \tag{9}$$

4. Results and discussion

Fig. 5 shows the experimental and modelling results for pressure infiltration of sol and suspension with 0.25 μm particles through the 3-d angle interlock preform under a constant pressure of 123.2 psi (8.5×10^5 Pa). As can be seen the correlation between experimental and analytical results is very good. Experimental results verify that the processing follows parabolic rate kinetics, i.e., the thickness of the particle compaction layer inside the 3-d preform is proportional to the square root of time. Thus we can use this experiment to measure the permeability of the combination of particle compaction and preform.

Fig. 6 shows the results for the infiltrate containing 0.5 μm particles under a constant pressure of 82.14 psi (5.66×10^5 Pa). As is shown in Fig. 6, the experimental data are lower than those predicted from the model. This may be due to the following reasons. First, sedimentation of the 0.5 μm particles was observed and this phenomenon may explain the longer processing times experienced with this particle size. Second, the application of the pressure may cause the 3-d preform to deform slightly due to a combination of warp and weft yarn deformations. This changes inter-yarn and intra-yarn pores and decreases the rate of infiltration. We may suspect that this result is affected by the architecture of the fibre preform. Since the real value of permeability κ_3 for a 3-d preform, which has a more complicated fibre architecture than a laminate, may be lower compared to the prediction of Loos *et al.* [13]. However, as is shown in Fig. 6, using a smaller κ_3 in the analysis only slightly affects the processing time which could indicate that the permeability of particle compaction is the dominant factor. Thus we may conclude that the sedimentation of particles results in a lower permeability which causes the difference between experimental and predicted data.

Based on Darcy's law and a series arrangement of the porous media, a global permeability, κ_e, was provided for the whole system. The permeability of each

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* data from Whatman Co.

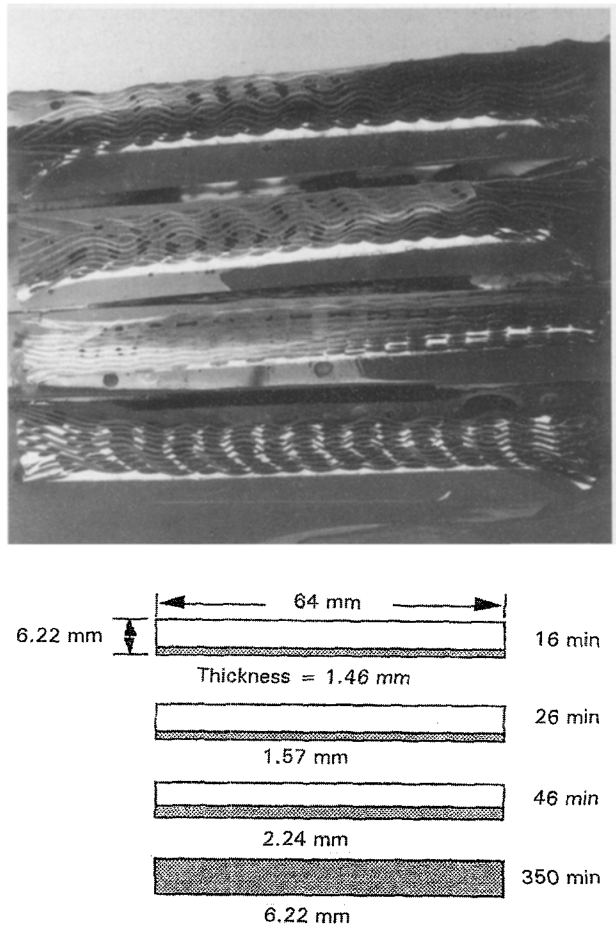

Figure 7 Photograph and schematic drawing comparing the thicknesses of the particle compaction layer inside the preform obtained at different processing times for the experimental condition of Fig 5.

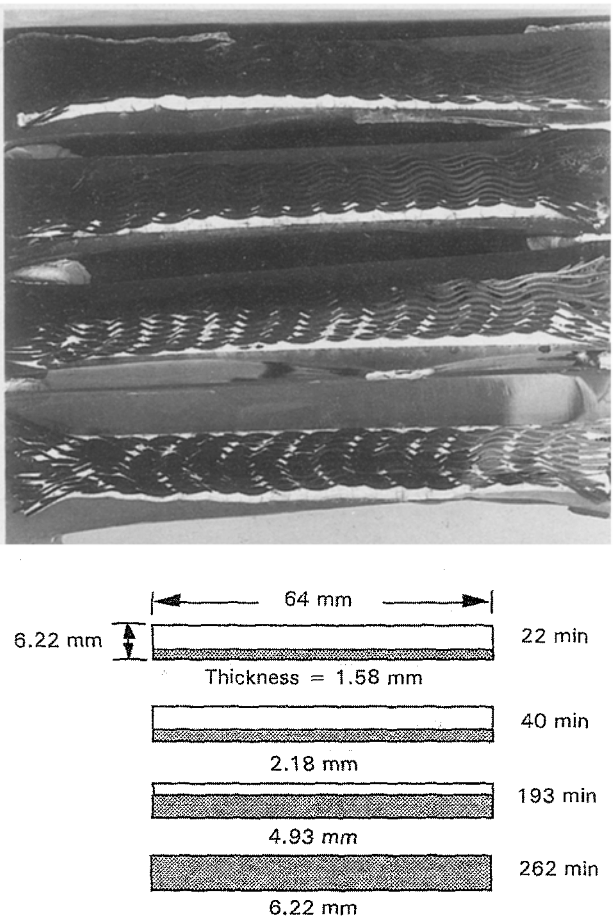

Figure 8 Photograph and schematic drawing comparing the thicknesses of the particle compaction layer inside the preform obtained at different processing times for the experimental condition of Fig. 6.

porous medium was derived from the Carmen–Kozeny equation since for a porous gel with homogeneous microstructure, the order of magnitude of permeability should follow the Carmen–Kozeny equation. Low pressures were adopted during infiltration in order to prevent flattening of the preform. However, this resulted in long processing times because pressure and time are inversely proportional according to the model. Figs 7 and 8 each show a schematic and a picture of the thickness of the particle compaction layer inside the preform as a function of the processing time, for a sol containing 0.25 μm and 0.5 μm particles, respectively. The optical micrographs of Figs 9 and 10 corresponding to Figs 7 and 8, respectively, show that the front of the consolidated layer is clear and uniform and that the infiltration is quite good. Processing at constant pressure produces better packing and provides a longer time to obtain stable packing compared to processing at a constant flow rate [1].

The effect of the addition of surfactants on the green density of 2-d ceramic composites are summarized in Fig. 11. For “A”, the addition of a non-ionic surfactant, cyclohexanone, in the infiltrate results in the highest observed density because the surfactant reduces the surface energy and also increases the repulsive force between the fibre and particles. This may reduce the permeability of the system since the pores are expected to be small and uniform. The mechanism

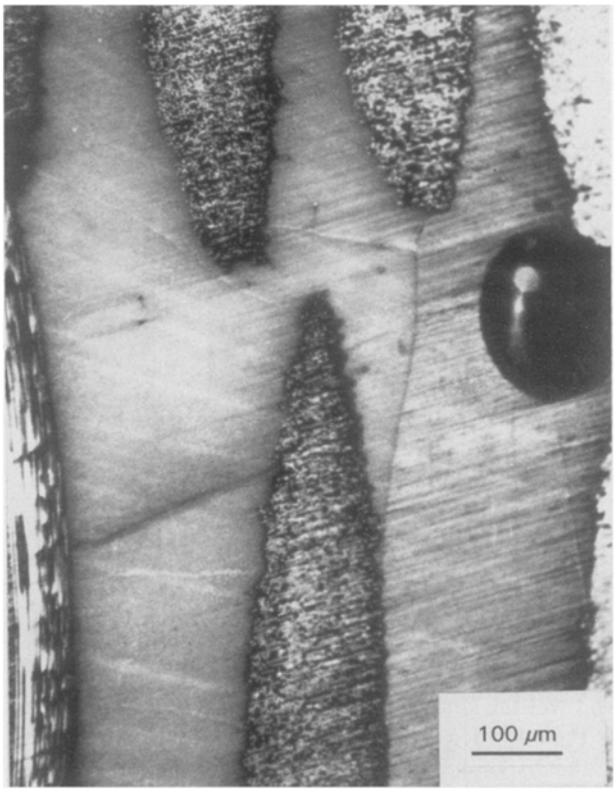

Figure 9 Photograph of third specimen from the top in Fig. 7 after 46 min of infiltration. Good infiltration and a clear and uniform compaction front are observed.

Figure 10 Photograph of third specimen from the top of Fig. 8 after 193 min of infiltration. Good infiltration and a clear and uniform compaction front are observed.

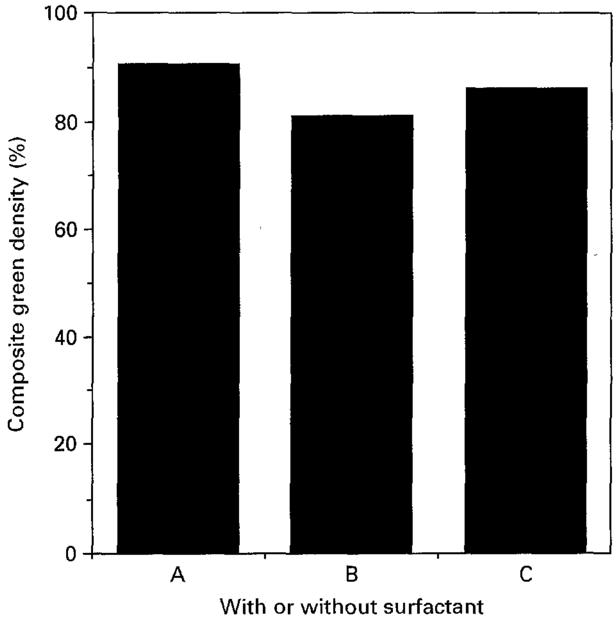

Figure 11 2-d composite green density as a function of the addition of surfactants; A: adding Cyclohexanone, B: adding Sodium dodecyl sulfate, C: without surfactant.

for the dispersion of particles by surfactants is summarized as follows. Initially the surfactants adsorb and wet the surface of the silica particles which reduces their surface energy and thermodynamic instability of the dispersion system. Second, suitable ionic surfactants increase the electrical repulsive forces amongst particles. Third, the surfactants adsorb on to particles and produce a solvation layer among the particles, which enhances their hydrophilic properties as well as their dispersion stability. All the above processes result in particle dispersion and its stability, and therefore better particle packing and a higher green density. However, the addition of a negative ionic surfactant, sodium dodecyl sulfate, in "B" results in a low density because it neutralizes the positive electric charge of the silica particles. Therefore the particles flocculate due to Van der Waals force. "C" is the case where no surfactant was added and it shows a medium density. The conditions for good infiltration are (1) particles must be small enough to flow within both inter-yarn and intra-yarn pores in the preform, (2) particles repulse each other, and (3) particles and fibres repulse each other [3]. Since in the above three conditions, the particles can pack as individuals and thus produce a higher density. The effect of a surfactant meets the second and third requirements and thus increases the composite green density from 86 % to 90 % as shown by a comparison of "B" with "A".

5. Conclusions

The parabolic rate kinetics of pressure infiltration for the sol–gel processing of 3-d ceramic composites was verified by experimental and modelling results. The thickness of a particle compaction layer inside the 3-d preform is proportional to the square root of time. The total infiltration time was inversely proportional to the constant processing pressure and increased significantly with reducing the solid particle size by a factor of two. This is because the permeability of the particle compaction layer is the dominant term and it is proportional to the square of particle size. There was an excellent correlation between the experimental and theoretical results for the infiltration of a composite using a sol plus 0.25 μm particles. The total processing time for this case was 350 min at a processing pressure of 123.2 psi (8.5×10^5 Pa). For the 0.5 μm particles, the experimentally measured thicknesses of the particle compaction layer were somewhat below the theoretical predictions and a total processing time of 262 min was determined at a pressure of 82.14 psi (5.66×10^5 Pa). Optical microscopy also showed better infiltration of the preform with the smaller particle size. The addition of a non-ionic surfactant in the infiltrate containing silica particles and silica sol results in higher green density.

Acknowledgements

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