Journal of the European Ceramic Society 17 (1997) 161-169
PII: S0955-2219(96)00126-4
Printed in Great Britain. All rights reserved
0955-2219/97/$17.00

Particle Contact Before Firing

J. R. G. Evans

Department of Materials Technology, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK

(Received 15 September 1995; revised version received 14 June 1996; accepted 15 July 1996)

Abstract

If our picture of the unfired ceramic body is of the classical three-sphere sintering model repeated in space we have deployed the fallacy of composition. Most fabrication routes can produce non-uniform density and regions of reduced coordination which will mature into defects under conditions of differential or restrained shrinkage. Injection moulding and the related plastic forming processes are particularly vulnerable because of the almost complete absence of particle contact during shaping which is essential for the flow of suspensions. Between the end of shaping and the beginning of sintering a series of mechanisms can lead to heterogeneity and anisotropy in the arrangement of particle contacts. These include the relaxation of stress and of orientation in the organic vehicle, flocculation and the non-uniform loss of organic vehicle from junctions. © 1996 Elsevier Science Limited.

1 Introduction

In order to understand the mass transport processes in ceramic sintering, it is sufficient to consider the geometry of particle junctions and so the classical three sphere-model is employed.[1] Approximations can then be made for overall shrinkage on the assumption that the body is composed of similar spheres arranged in a similar way throughout the whole. If the particles remain monodisperse, the final grain shape will be the truncated octahedron with a maximum possible coordination number of 14. In practice, the initial coordination number of such spheres is dependent on the packing arrangement and hence efficiency. Dense random packing gives a coordination number of 8–11 and an efficiency of 63·6%.[2] In more general terms, and based on ordered arrangements, German[3] suggests the relationship between coordination number N and packing efficiency V;

$$N \sim 2 \exp (2{\cdot}4\ V) \qquad (1)$$

Strictly, the coordination number for random packing cannot be deduced from ordered arrangements and eqn (1) does not predict the theoretical maximum of $N = 14$ for dense packing but it is plotted here (Fig. 1) to give an indication of the relationship between packing and coordination.

In this paper, the two tacit assumptions in composing the whole from the sum of its parts are examined to help understand the cause of defects in macroscopic particle assemblies. They are: (i) that the coordination number, and hence packing efficiency, is everywhere uniform and (ii) that the particles are everywhere in contact with their nearest neighbours when sintering begins.

2 Compaction Processes

By far the most work has been done in understanding particle arrangements in compacted bodies. It will be of interest to see how the knowledge so gained can be applied to the more complex plastic forming processes. Just over a decade ago, Lange and co-workers[4-6] examined the consequences of differential sintering by incorporating artificial agglomerates in matrices of different prefired density by means of multiple compaction. Severe cracking was observed even when the prefired density ratios (between agglomerate and matrix) were 0·98–1·02. Interestingly, the agglomerates separated from their matrices precisely at their boundaries irrespective of whether they had higher or lower prefired densities to the matrix.[5] What is not known, principally because of the formidable experimental difficulties, is whether particles at the boundary had separated from their neighbours during assembly, before sintering began, perhaps by differential springback during multiple compaction. This would mean that a significant fraction of coordination contact was lost from particles at the boundary. But why should not the boundary heal up again in the case where the matrix sinters faster? In other words, if particles are out of contact at the beginning of sintering,

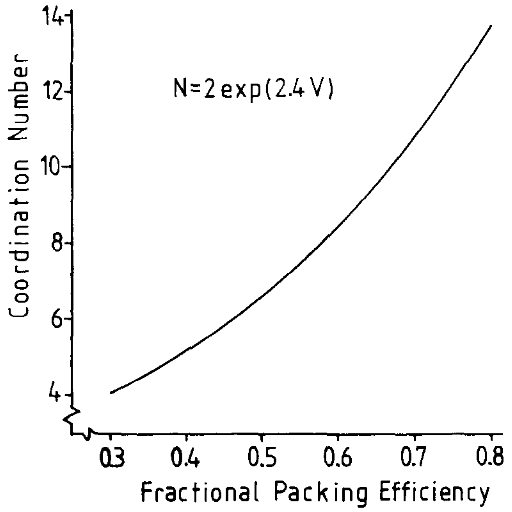

Fig. 1. The relationship between coordination number and packing efficiency deduced by German (Ref. 3) for monodisperse spheres.

should they not soon be brought back into contact when shrinkage starts?

Mackenzie and Shuttleworth's[7] poetic description of sintering would imply that this would happen: 'to an observer situated on a pore and moving with it, all distant pores will appear to approach with a velocity proportional to their distance'. Their reference is to *The Expanding Universe* by A. S. Eddington.

However, the local situation is that on both sides of the boundary two rigid skeletons, namely agglomerate and matrix, quickly develop as a result of high coordination sintering. A particle at the boundary has little chance of recovering its coordination. Because of the differential sintering, the agglomerate effectively moved in its socket.[5] However, loss of boundary contact does not always result from differential sintering, even when the agglomerate has the lower prefired density, the condition for separation. Kendall[8] shows a microstructure in which the boundary holds and the agglomerate sintering is apparently restrained by the matrix. Stearns *et al.*[9] show an example of a superconducting ceramic powder in which no damage results when the agglomerate density is higher than the matrix. It seems that particle assemblies which should demonstrate differential sintering damage show a recalcitrant disinclination to obey the theories.

These problems are resolved if it is hypothesized that defects are already present in the particle assembly before firing and may be matured but not necessarily created during sintering. Thus, in a very important study of constrained sintering in which alumina rings were slip cast around sintered alumina discs, Lange[10] makes the following observation: 'If the constrained ring specimen survived the drying and heating to 800°C without cracking, no subsequent heat treatment schedule was found that could produce a major crack within the ring upon heating to a relative density of > 0·97 at 1550°C'. Clearly it is in the unfired particle assembly that the precursors to defects reside. A similar point is made in relation to cracks in filter-pressed bodies which are thought to occur during springback as pressure is released.[11] Of course it is not necessary for a complete crack to form in the unfired assembly. Under constrained sintering conditions, particle bridges resulting from reduction, but not total loss, of coordination can break during sintering for thermodynamic reasons.[12]

The broad implications of these insights are that if a region of organized loss of contact or reduction in coordination develops in a particle assembly before firing, that region can mature into a critical defect if it is prevented from healing. Among the conditions for its maturation are (i) the existence of a restraint to sintering, (ii) differential sintering on either side brought about by different relative density, or (iii) differential sintering brought about by temperature gradients in the ceramic body.

The development of defects in powder assemblies made by compaction and casting allows us an insight into the more complex processes of plastic forming where particle contact is almost completely absent after shaping and before removal of organic vehicle. It is this single characteristic of the plastic forming processes that makes them so vulnerable to a wide range of defects.

3 Plastic Forming Processes

Practically all the manufacturing processes used for shaping thermoplastic polymers have been tested for ceramics manufacture and several are now used commercially. They include injection moulding,[13] extrusion,[14] vacuum forming,[15] blow moulding,[16,17] melt spinning,[18] joining before firing,[19-21] solvent casting,[22] thermolamination,[23] film blowing,[24] the manufacture of foams from thermosets[25] and thermoplastics[26] and recently the use of thermoplastic resins in paint formulations.[27] In the first two, shaping is effected mainly by the shear flow of suspensions while in most of the others it is elongational flow which is responsible for shaping. In both cases, this occurs because particles are sufficiently well-spaced in the binary ceramic–polymer system to allow relative displacement and rotation. If particles were not able to execute these manoeuvres there would be no flow and no shape. Thus, in a perfectly dispersed suspension the coordination contact is zero and that is both the great advantage in allowing complex

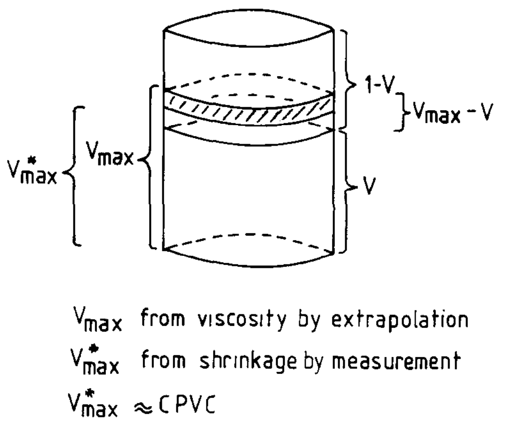

Fig. 2. Occupation of space in ceramic suspensions. (CPVC is the critical powder volume concentration.)

shape to be developed and, later in the process, the great weakness because it facilitates defect development.

Figure 2 illustrates the occupation of space for a suspension having ceramic volume fraction V for a powder with a maximum packing fraction in the particular suspension of $V_{\max}$. This maximum fraction can only be inferred from the extrapolation of apparent viscosity data[28] and the methods used produce slightly different values of $V_{\max}$ but the objective existence of a maximum fraction is not in dispute. The fraction $1 - V_{\max}$ therefore refers to the minimum interstitial binder in the efficiently packed immobile array and the fraction $V_{\max} - V$ can be regarded as the 'free volume fraction' of organic vehicle.[29] The free volume fraction confers fluidity and appears in the denominator of expressions for relative viscosity as well as controlling the change from fluid to quasi-solid as binder is removed.[29] Of more practical significance is the maximum packing efficiency at which shrinkage ceases on binder removal $V^*_{\max}$. Since particles are unable to rotate at this stage and must approach close to their final orientation $V^*_{\max}$ is always less than $V_{\max}$.

In crowded suspensions, the separation distance x_0 between particles can be very low, typically < 10 nm.[29] Its dependence on packing efficiency can be estimated using an expression deduced from the ordered packing of monodisperse spheres of diameter d_0:[30]

$$\frac{x_0}{d_0} \approx 0{\cdot}4\left(1-\frac{V}{V_0}\right) \qquad 0<\frac{x_0}{d_0}<0{\cdot}15 \qquad (2)$$

In dealing with the shrinkage associated with binder removal V_0 must be taken as $V^*_{\max}$. Thus for A16 (A16SG, ex Alcoa USA, 0·3–0·5 μm) alumina powder with $V^*_{\max}$ at 0·64, processing the powder at $V = 0{\cdot}6$ gives x_0/d_0 as 2·5%. The corresponding measured linear shrinkage is 2·3%[29] and in absolute terms this gives $x_0 \approx$ 10 nm.

4 Rearrangement Begins — the Solid State

Adsorbed layer thicknesses of polymers on high-energy surfaces can be 5–100 nm depending on molecular weight.[31] It follows from a comparison of these dimensions with interparticle distances that some molecules may be attached to more than one particle, so-called bridge molecules. These act as a spring with an optimum distance between particles.[32] The suspension may thus have a 'structure'.

Any non-uniform change in polymer conformation must, *ipso facto*, move ceramic particles. Such changes could result from the relaxation of residual stress. These stresses are set up in all injection mouldings to some extent during solidification in the cavity. They can be estimated[33] and measured by the deformation of beams subject to layer removal.[34] In extreme form their presence is revealed by the cracking of mouldings in the cavity or shortly after removal from the cavity.[35] Relaxation of residual stress necessarily implies differential strains in the body and hence the displacement of particles conveyed in, and attached to, the matrix.

The suggestion that the defects seen in sintered ceramic components have, as their origins, small local regions of loss of contact in the unfired body which are practically unobservable, represents a very weak philosophical position. If, for practical purposes, the existence of such precursors cannot be studied on the grounds that the separation distance is below the level of detection or that the experimental protocol interferes with particle arrangement, the hypothesis is irrefutable and hence has no scientific status.[36] In the absence of direct observation, therefore, resort must be had to the somewhat looser inference of the existence of antecedents of observable defects which can be observed in fired ceramics.

In an early study of the evolution of ceramic injection moulding defects Thomas[37] drew attention to the way in which defects appearing after sintering had their origin in the moulding processes. No defects could be seen in radiographs of as-moulded bars (Fig. 3(a)). After reheating to the softening point (Fig. 3(b)) one tiny crack could be seen (arrowed). After binder removal (Fig. 3(c)) this crack was seen to be the largest of a vast array of cracks which surrounded the gate. Clearly our ability to discern cracks in the radiograph is dependent on their orientation and width as well as the limited resolution of the method. We are not in a position to say whether cracks are present in Fig. 3(a), but the similarity in form with Figs 3(b) and 3(c) strongly implies that all the cracks visible in the latter were present in

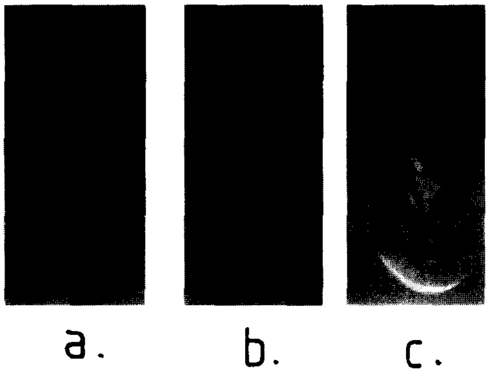

Fig. 3. Prints of X-ray radiographs of injection moulded step wedge bars which are at the following stages (a) as moulded; (b) reheated to the softening point of the vehicle; (c) after binder removal (Ref. 37).

'potential' form in the former. What this 'potential' is we cannot say; it may be no more than molecular arrangements in the organic vehicle which, if allowed to relax, will cause particles to separate from their neighbours.

The effect of relaxation of molecular orientation on particle displacement is potentially more severe than stress relaxation because the deformations can be larger. The problem first came to light when attempts were made to measure thermal expansion coefficients on samples cut from mouldings.[38] Unless the samples were annealed first the results were dependent on position and orientation of the sample in the moulding. In injection moulding, the pattern of flow into the cavity is influenced by cavity and gating design and by the rheological properties of the fluid. The pattern of flow influences the orientation of any anisotropic particles conveyed and also the orientation of polymer molecules which can undergo chain extension as they are trapped by the advancing solid interface. Similarly, the final stage of mould packing involves low-temperature flow under high pressure into shrinking channels to compensate for shrinkage.

The effects of such orientation are displayed when mouldings are cut to remove the restraint on the structure, and reheated to confer molecular mobility.[39] Dramatic changes in apparent thermal expansion are seen; negative expansion coefficients are displayed (Fig. 4).[39] The deformation can be seen in the cut and polished sections of moulding after reheating to the softening point (Fig. 5). Since the displacements are heterogeneous and anisotropic throughout the moulding, substantial movements of particles must accompany them. It is significant that these deformations do not involve detectable volume change. The average expansion coefficient in three orthogonal axes corresponded to the value for the annealed material.

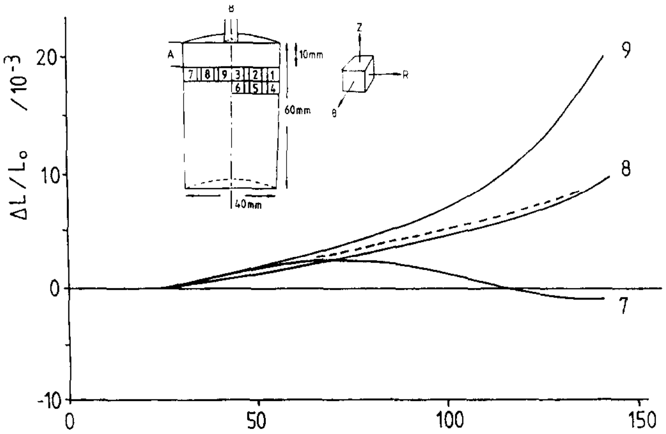

Fig. 4. Apparent thermal expansion curves for samples cut from overpacked modulated pressure mouldings of alumina–polypropylene and measured in the 'θ' direction (Ref. 39).

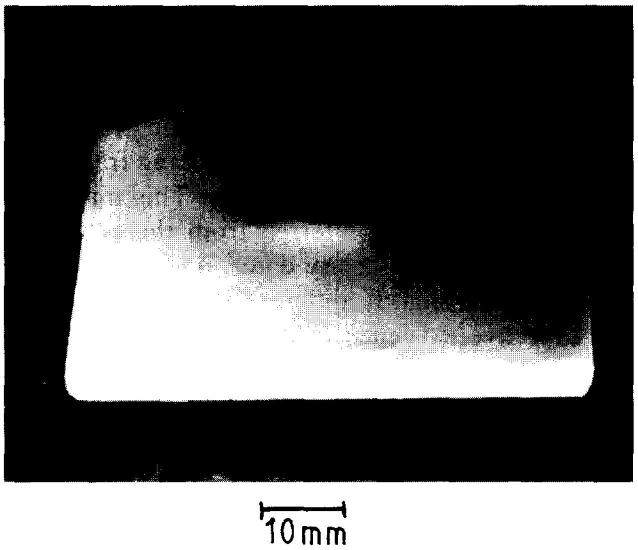

Fig. 5. The deformation of a cut and polished section of the moulding referred to in Fig. 4 after heating to the softening point.

A process known to produce substantial polymer orientation is butt fusion welding. In this process for joining thermoplastics, the two surfaces are heated and quickly pressed together. Radial extrusion takes place at all temperatures down to the softening point. When this technique was applied to ceramics[20] the characteristic 'cracking' consisted of a line of reduced coordination with many particle bridges (Fig. 6). This kind of defect is also consistent with particle displacement caused by molecular relaxation.

5 Rearrangement in the Liquid State

As a ceramic suspension is heated, particle separation increases because most organic vehicles have a higher expansion coefficient than the ceramic ($\beta_p > \beta_c$) and a semicrystalline polymer or wax undergoes a dilation on melting ΔV_p. Neglecting

β_c in comparison with β_p, the volume fraction of ceramic V_c', in the melt at a temperature ΔT above the melting point is related to the volume fraction in the solid V_c, by;

$$\frac{1}{V_c} = 1 + \frac{(1 - V_c)}{V_c}(1 + \Delta V_p + \beta_p \Delta T) \qquad (3)$$

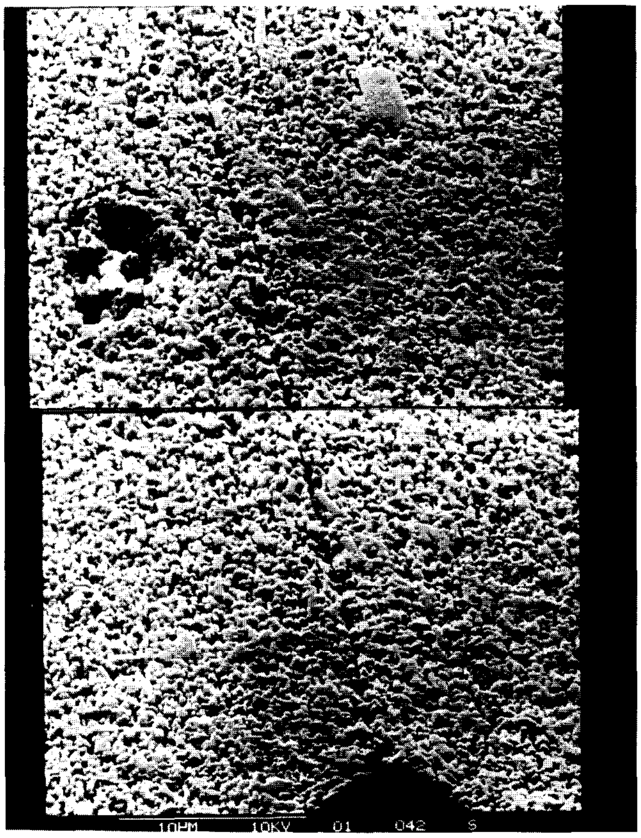

Fig. 6. A crack at the edge of the junction of a sintered butt fusion welded ceramic rod (Ref. 20).

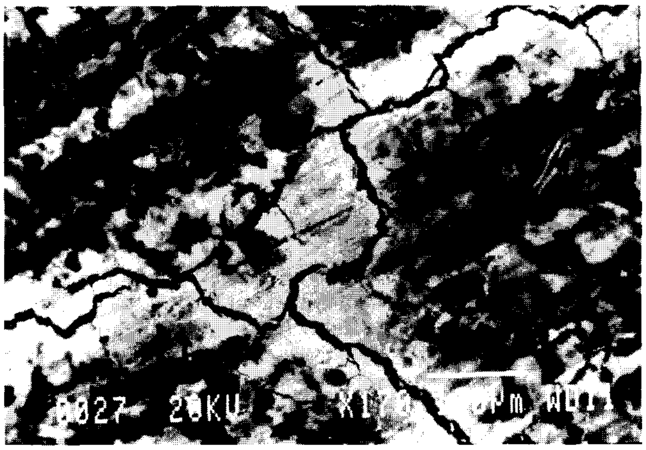

Fig. 7. Cracks resulting from flocculation of a zirconia–wax moulding after reheating to 90°C. No binder has been lost. (Ref. 30). The dimension marker represents 100 μm.

This can have a significant effect on interparticle distance and rheological properties. Thus, Hammond[40] found that the high heating rates that were possible in overpressure debinding as a result of the suppression of boiling of degradation products, resulted in slumping not seen at lower heating rates. The postponement of weight loss to higher temperature which occurs in thermally activated decomposition, combined with the expansion of the vehicle, meant that the yield stress was reduced.

Once the vehicle is molten, the well-separated particles may become free to move under the influence of London dispersion forces. Stability against flocculation in polymeric vehicles is conferred by the 'elastic' or 'excluded volume' effects but in low-viscosity vehicles, such as waxes, the addition of dispersants is necessary. Thus, Song[30] found that in poorly stabilized suspensions, flocculation occurred after injection moulding shortly after reheating mouldings to above the melting point of the wax (60°C) and before any wax had been lost by evaporation. The particles reorganized themselves into blocks leaving fissures between them which were wax-filled (Fig. 7). What this amounts to is cracking in the liquid state! Calculation of the time to impact for particles under the acceleration caused by London dispersion forces compared with intercollision time calculated from the Brownian motion showed that in crowded suspensions, van der Waals attraction is of overriding influence (Table 1). The solution to the problem is to add sufficient dispersant based on the powder surface area to provide the potential energy well associated with steric stabilization.[41]

6 Rearrangement as Organic Vehicle Departs

An early report on ceramic injection moulding speaks of the annoying phenomenon of cracking which is caused during binder removal but which is unaffected by the rate of thermolysis.[42] These authors say: 'This type of flaw cannot be eliminated by slower binder removal. The cause of this cracking is evidently a rearrangement of the interior

Table 1. Effect of initial particle separation on the time to impact for particles of diameter d_0 100 nm under London dispersion forces and the intercollision time for Brownian motion

x_0/d_0	*0·1*	*0·5*	*1·0*	*5*	*10*
Volume fraction	0·39	0·16	0·065	0·024	0·0004
Time (s) London Forces	$3·3 \times 10^{-3}$	$1·2 \times 10^{-2}$	$3·8 \times 10^{-2}$	3·0	33
Time (s) Brownian motion	$1·16 \times 10^{-5}$	$1·45 \times 10^{-3}$	$1·2 \times 10^{-2}$	1·5	12

Fig. 8. Fracture of ceramic wire after binder removal showing circumferential cracks due to non-uniform binder removal (Ref. 14).

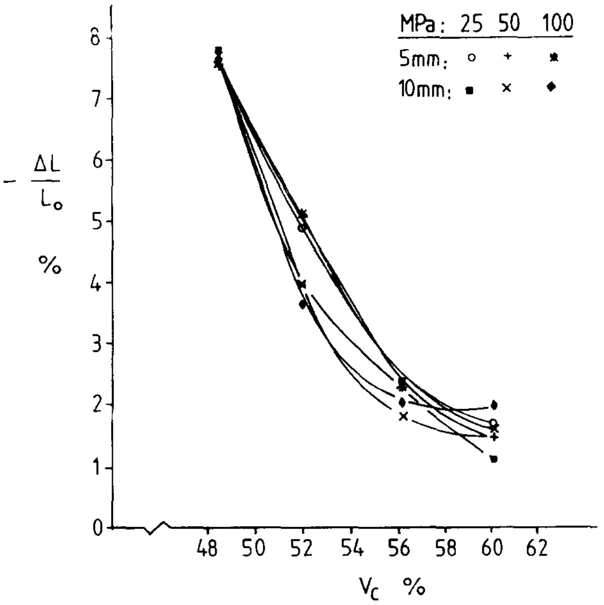

Fig. 9. Shrinkage caused by pyrolysis of alumina (RA6 ex Alcan Chemicals UK) mouldings as a fraction of initial volume fraction for various moulding pressures from 25 to 100 MPa and for two thicknesses, 5 mm and 10 mm (Ref. 43).

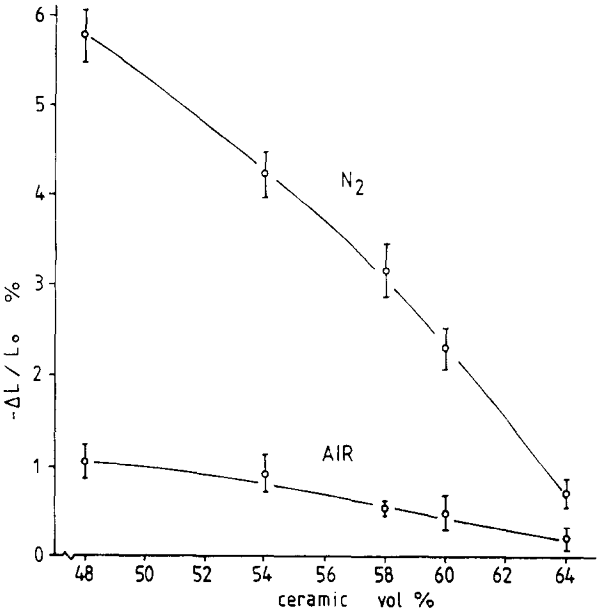

Fig. 10. Shrinkage caused by pyrolysis of alumina (A16SG ex Alcan UK) as a function of initial ceramic volume fraction (Ref. 29).

ceramic particles during binder removal, resulting in a denser packing.' Here, at an early stage in the comprehension of ceramic processing, is the clear recognition of the main problem in the plastic forming of ceramics. The particles are separate after shaping but must arrive in contact before firing.

This problem is illustrated in the removal of binder from extruded ceramic springs. The binder is a mixture of polystyrene and a phthalate ester. The core of the extrusion pulls away from the outer skin. The defects are seen after binder removal in Fig. 8 and after sintering.[14] This effect is accentuated by the extreme strength of a cylindrical shell. Binder is lost initially from the outer shell. The shell cannot subsequently collapse but binder has yet to be lost from the core. When it emerges from the core, the shrinkage cannot be accommodated by the shell. Clearly, the development of highly coordinated three-dimensional structures once sintering begins rules out a healing mechanism at that late stage.

Often the shrinkage associated with binder removal is dismissed because it is very small. Viewed from the point of view of its effect on the reproducibility of component dimensions it may be unimportant. However, viewed mechanistically from the point of view of bringing particles together, it is surely the most critical stage in the plastic forming processes.

Figures 9 and 10 taken from different studies with different powders[29,43] show the extent of shrinkage during binder removal and its dependence on initial ceramic volume fraction. The experiments span a wide ceramic volume fraction range. Suspensions close to V^*_{max} can be processed by injection moulding but for the elongational flow process such as film blowing[24] lower loadings are needed (typically 50–55 vol%) for these powders. In oxidative atmospheres the formation of a rigid network at the surface, as a result of enhanced local reaction, creates a restriction on shrinkage. The results in Fig. 10 are for discs 1 mm in thickness. The application of eqn (2) to these data gives the approximate shrinkage in terms of particle separation x_0 as a fraction of diameter d_0. If this shrinkage takes place non-uniformly throughout a moulding then the precursors to defects may be established.

In a study of solvent welding[19] the problem of space occupation is accentuated. Solvent is added to the interfacial region before joining and it reduces the ceramic volume fraction. At the

Fig. 11. The interface in a sintered joint made by solvent welding of alumina–polystyrene suspensions using ethyl acetate (Ref. 19).

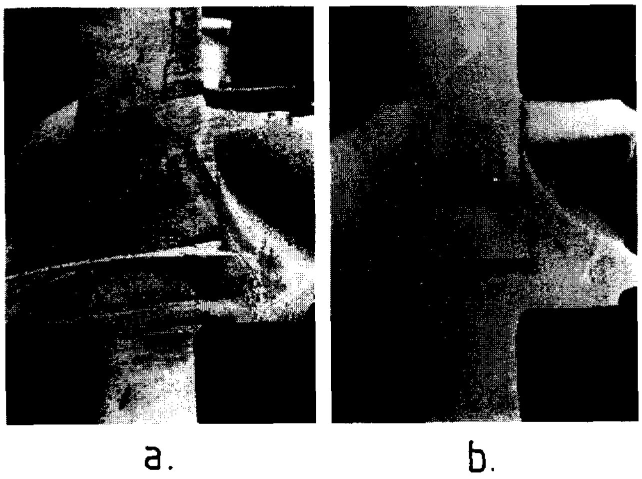

Fig. 12. Cracking in injection moulded rotors after binder removal with (a) coarse setter powder (b) fine setter powder (Ref. 44).

binder removal stage, residual solvent and binder are driven out. The result is enhanced shrinkage in the interfacial region and reduced particle coordination. This appears in the final sintered body (Fig. 11) because it cannot be healed once the high coordination sintering on both sides has created rigid skeletons.

The study by Bandyopadhyay and French[44] shows the effect for a large injection moulded ceramic rotor. The cracks (Fig. 12) are the result of non-uniform shrinkage on binder removal which cannot be eliminated by slowing down the thermal cycle or changing the atmosphere during pyrolysis. However, these authors do manage to improve the situation by changing the powder bed in which the compact is heat treated. A fine powder with high suction causes the pattern of cracks to change. Thus, the rate at which the liquid vehicle is extracted influences the extent of differential shrinkage and hence the development of particle separation.

7 Removal of the Organic Vehicle

It is a popular view that the binder removal stage is the most problematic in plastic forming operations for ceramics. How far does the culpability of this stage extend? If a defect presents itself after the binder removal stage, was it caused by the mechanisms inherent in mass displacement? This is not just an academic question. If the diagnosis of defects deploys the fallacy of false cause, the remedy will be ineffective and resources will be wasted.

It is well established that binder removal by thermolysis follows three steps: an initial fast heating to the softening point, a very slow heat treatment at the stage where evolving porosity is discontinuous and a fast temperature ramp once the percolation threshold is reached and continuous porosity has developed. The critical second stage is where the organic vehicle may experience defects due to boiling of degradation products or low molecular weight additions in solution in the molten organic phase. These produce a distinct bloating of the body and the cause is not in question. Models for this stage have been developed[45,46] and are being refined.[47]

Similarly an excessive rate of heating after the percolation threshold has been reached may cause the ceramic skeleton, which has formed by this stage, (that is, coordination contact has developed) to burst as a result of gas pressure.[48]

These two defect mechanisms can therefore be controlled, in principle, by rate of heating but they do not represent an exhaustive aetiology of cracks seen in finished components. The thesis offered by this keynote paper is that our search for the causes of the remaining defects could profit by being guided towards the manoeuvres executed by particles as they advance into coordination contact.

8 Summary

In powder assemblies manufactured by conventional processes there is growing evidence that defects which appear after sintering have their origin in the arrangement of particles established by the shaping process. This insight gives a clearer picture of the defects produced in the plastic forming processes. A feature of the plastic forming processes is that particles must be sufficiently separated in the organic vehicle to allow flow. This means that a range of mechanisms such as molecular relaxation, flocculation and non-uniform accommodation of space, can establish precursors to defects. These defects may become detectable after binder removal or only after sintering.

Acknowledgements

The author is grateful to the Science and Engineering Research Council (now the Engineering and Physical Science Research Council) for supporting some of the work which is summarized here. Mrs K. Goddard is thanked for typing the manuscript.

References

1. Burke, J. E. & Coble, R. L., Sintering in Ceramics. In *Progress in Ceramic Science*, ed. J. E. Burke, Vol. 3, Pergamon, Oxford, 1963, pp. 197–251.
2. Swinkels, F. B. & Ashby, M. F., Second report on sintering diagrams. *Acta Met.*, **29** (1991) 259–281.
3. German, R. M., *Powder Injection Moulding*. Metal Powder Industries Federation, NJ, 1990, p. 31.
4. Lange, F. F., Processing-related fracture origins 1. Observations in sintered and isostatically hot pressed Al_2O_3/ZrO_2 composites. *J. Amer. Ceram. Soc.*, **66** (1983) 396–398.
5. Lange, F. F. & Metcalf, M., Processing-related fracture origins II. Agglomerate motion and cracklike internal surfaces caused by differential sintering. *J. Amer. Ceram. Soc.*, **66** (1983) 398–406.
6. Kellet, B. & Lange, F. F., Stresses induced by differential sintering in powder composites. *J. Amer. Ceram. Soc.*, **67** (1984) 369–371.
7. Mackenzie, J. K. & Shuttleworth, R., A phenomenological theory of sintering. *Proc. Phys. Soc.*, **62** (1949) 833–853.
8. Kendall, K., Microstructure of submicron powders and green compacts. *Proc. Brit. Ceram. Soc.*, **42** (1989) 81–90.
9. Stearns, L. C., Harmer, M. P. & Chan, H. M., Effects of inclusions on the sintering behaviour of $YBa_2Ca_3O_{6+x}$. *J. Amer. Ceram. Soc.*, **73** (1990) 2740–2742.
10. Lange, F. F., Densification of powder rings constrained by dense cylindrical cores. *Acta Metall.*, **37** (1989) 697–704.
11. Lange, F. F. & Sudre, O., Effect of inclusions on densification I. Microstructural development in an Al_2O_3 matrix containing a high volume fraction of ZrO_2 inclusions. *J. Amer. Ceram. Soc.*, **75** (1992) 519–524.
12. Sudre, O. & Lange, F. F., The effect of inclusions on densification III. The desintering phenomenon. *J. Amer. Ceram. Soc.*, **75** (1992) 3241–3251.
13. Edirisinghe, M. J. & Evans, J. R. G., Review: Fabrication of engineering ceramics by injection moulding. *Int. J. High Tech. Ceramics*, **2** (1986) 1–31; 249–278.
14. Wright, J. K., Thomson, R. M. & Evans, J. R. G., On the fabrication of ceramic windings. *J. Mater. Sci.*, **25** (1990) 149–156.
15. Haunton, K. M., Wright, J. K. & Evans, J. R. G., The vacuum forming of ceramics. *Br. Ceram. Trans. J.*, **89** (1990) 53–56.
16. Renlund, G. M. & Johnson, C. H., Thermoplastic moulding of ceramic powder. *US Pat.* 4571414, 18 Feb. 1986.
17. Hammond, P. & Evans, J. R. G., On the blow moulding of ceramics. *J. Mater. Sci. Lett.*, **10** (1991) 294–296.
18. Cass, R. B., Fabrication of continuous ceramic fibre by the viscous suspension spinning process. *Bull. Amer. Ceram. Soc.*, **70** (1991) 424–429.
19. Rashid, H., Lindsey, K. & Evans, J. R. G., Joining ceramics before firing by solvent welding. *J. Euro. Ceram. Soc.*, **7** (1991) 165–175.
20. Rashid, H. & Evans, J. R. G., Joining technical ceramics before firing by butt fusion welding. *Ceramics International*, **17** (1991) 259–265.
21. Rashid, H., Hunt, K. N. & Evans, J. R. G., Joining ceramics before firing by ultrasonic welding. *J. Euro. Ceram. Soc.*, **8** (1991) 329–338.
22. Richerson, D. W., *Modern Ceramic Engineering*, 2nd edn. Marcel Dekker, NY, 1992, pp. 471–478.
23. Clegg, W. J., Kendall, K., Alford, N. McN., Burton, T. W. & Birchall, J. D., A simple way to make tough ceramics. *Nature (London)*, **347** (1991) 455–457.
24. Greener, J. & Evans, J. R. G., Film blowing of ceramics. *J. Mater. Sci.*, **28** (1993) 6190–6194.
25. Powell, S. & Evans, J. R. G., The structure of ceramic foams prepared from polyurethane–ceramic suspensions. *Mat. and Manuf. Proc.*, in press.
26. Williams, E. J. A. E. & Evans, J. R. G., Expanded ceramic foam. *J. Mater. Sci.*, **31** (1996) 559–563.
27. Willoughby, C. E. P. & Evans, J. R. G., The preparation of laminated ceramic composites using paint technology. *J. Mater. Sci.*, **31** (1996) 2333–2337.
28. Zhang, T. & Evans, J. R. G., Predicting the viscosity of ceramic injection moulding suspensions. *J. Euro. Ceram. Soc.*, **5** (1989) 165–172.
29. Wright, J. K., Edirisinghe, M. J., Zhang, J. G. & Evans, J. R. G., Particle packing in ceramic injection moulding. *J. Amer. Ceram. Soc.*, **73** (1990) 2653–2658.
30. Song, J. H. & Evans, J. R. G., Flocculation after injection moulding in ceramic suspensions. *J. Mater. Res.*, **9** (1994) 2386–2397.
31. Priel, Z. & Silberberg, A., The thickness of adsorbed polymer layers at a liquid–solid interface as a function of bulk concentration. *J. Polym. Sci. Polym. Phys.*, **16** (1978) 1917–1925.
32. Hesselink, F. Th., On the theory of the stabilization of dispersions by adsorbed macromolecules 1. Statistics of the change of some configurational properties of adsorbed macromolecules on the approach of an impenetrable interface. *J. Phys. Chem.*, **75** (1971) 65–71; 2094–2103.
33. Hunt, K. H., Evans, J. R. G., Mills, N. J. & Woodthorpe, J., Computer modelling of the origin of defects in ceramic injection moulding IV. Residual stress. *J. Mater. Sci.*, **26** (1991) 5229–5238.
34. Kostic, B., Zhang, T. & Evans, J. R. G., The measurement of residual stresses in injection moulded ceramics. *J. Amer. Ceram. Soc.*, **75** (1992) 2773–2778.
35. Zhang, J. G., Edirisinghe, M. J. & Evans, J. R. G., The use of modulated pressure in ceramic injection moulding. *J. Euro. Ceram. Soc.*, **5** (1989) 63–72.
36. Popper, K. R., *The Logic of Scientific Discovery*. Hutchinson, London, 1972, pp. 40–42.
37. Thomas, M. S. & Evans, J. R. G., Non-uniform shrinkage in ceramic injection moulding. *Br. Ceram. Trans. J.*, **87** (1988) 22–26.
38. Zhang, T. & Evans, J. R. G., Anomalies in the thermal expansion of ceramic injection moulded bodies *J. Mater. Sci. Lett.*, **9** (1990) 673–674.
39. Zhang, T. & Evans, J. R. G., Relaxation effects in large injection moulded ceramic bodies. *J. Euro. Ceram. Soc.*, **12** (1993) 51–59.
40. Hammond, P. D. & Evans, J. R. G., The use of overpressure in thermolytic debinding of moulded ceramic bodies. *J. Euro. Ceram. Soc.*, **15** (1995) 117–125.
41. Israelachvili, J. N., *Intermolecular and Surface Forces*, 2nd edn. Academic Press, NY, 1991, pp. 288–311.
42. Quackenbush, C. L., French, K. & Neil, J. T., Fabrication of sinterable silicon nitride by injection moulding. *Ceram. Eng. Sci. Proc.*, **3** (1982) 20–34.
43. Gil-Medina, E. M. & Evans, J. R. G., Ceramic injection moulding: some effects of powder volume fraction. *Proc. Adv. Mater.*, **4** (1994) 57–65.
44. Bandyopadhyay, G. & French, K. W., Injection moulded ceramics: critical aspects of the binder removal processes and component fabrication. *J. Euro. Ceram. Soc.*, **11** (1993) 23–34.
45. Calvert, P. D. & Cima, M. J., Theoretical models for binder burnout. *J. Amer. Ceram. Soc.*, **73** (1990) 575–579.

46. Evans, J. R. G., Edirisinghe, M. J., Wright, J. K. & Crank, J., On the removal of organic vehicle from moulded ceramic bodies. *Proc. Roy. Soc. Lon. A*, **432** (1991) 321–340.
47. Matar, S. A., Edirisinghe, M. J., Evans, J. R. G. & Twizell, E. H., The effect of porosity development on the removal of organic vehicle from ceramic and metal mouldings. *J. Mater. Res.*, **8** (1993) 617–625.
48. Tsai D-S, Pressure build-up and internal stress during binder burnout: Numerical analysis. *A. I. Cl. E. Journal*, **37** (1991) 547–553.