Experimental Studies of Particle Packing and Sintering Behaviour of Monosize and Bimodal Spherical Silica Powders

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Abstract

The packing arrangements and sintering characteristics of monosize and selected bimodal mixtures of spherical silica particles are reported. Gravitational sedimentation and simple drying from a droplet of suspension were used to form consolidated bodies of micron and sub-micron sized particles. Monosized sediments were composed of ordered domains of close packing, interspersed with regions of disordered packing. During the initial stages of sintering, preferential densification of the ordered domains was observed and this promoted pore growth at domain boundaries. Moving to bimodal mixtures containing at least 20 wt% of the minor component prevented the formation of ordered domains and allowed the production of sediments with a reduced spatial variation in packing density. The more even distribution of porosity in bimodal sediments led to more uniform sintered microstructures. Comparisons are made with the results of earlier work using computer simulation techniques to study packing geometry.

Die Packungsanordnung und die Sintercharakteristika von sphärischen Siliziumdioxid-Teilchen mit einerseits einheitlicher Größe und andererseits bestimmten bimodalen Größenverteilungen werden beschrieben. Gravitationssedimentation und einfaches Trocknen von Suspensionstropfen wurden angewandt, um konsolidierte Körper aus Teilchen der Größenordnung weniger Mikrometer oder weniger herzustellen. Die Sedimente der Teilchen einheitlicher Größe bestanden aus geordneten Bereichen dichter Packung, zwischen denen Bereiche ungeordneter Packung angeordnet waren. In den Anfangsstadien des Sinterns konnte hevorzugtes Verdichten der geordneten Bereiche beobachtet werden, was zu Porenwachstum an den Bereichsgrenzen führte. Beim Übergang zu bimodalen Mischungen, die mindestens 20 Gew.% der kleineren Komponente enthielten, wurde die Bildung geordneter Bereiche vermieden. Auf diese Weise konnten Sedimente mit einer geringeren räumlichen Variation der Packungsdichte hergestellt werden. Die gleichmäßigere Verteilung der Porosität in bimodalen Sedimenten führte zu gleichförmigeren Gefügen. Um die Packungsgeometrie zu untersuchen, wurden die Ergebnisse mit früheren Arbeiten verglichen, indem Berechnungen mittels Rechnersimulationen durchgeführt wurden.

Cet article présente le comportement au frittage d'empilements de particules sphériques de silice, soit de même dimension, soit en mélanges bimodaux, en fonction de leur arrangement topologique. Une technique consistant en une sédimentation et en un séchage d'une gouttellette de la suspension a été utilisée pour préparer des compacts de particules dont les tailles étaient de l'ordre du micron et sub-microniques. Les sédiments de particules monodisperses etaient composés de domaines ordonnés d'empilement désordonné. Durant les phases initiales du frittage, on a constaté une densification préférentielle des domaines ordonnés. Ce phénomène s'accompagne d'une croissance des pores aux joints entre les domaines. Lorsque l'on examine les mélanges bimodaux contenant au moins 20% en poids de l'espèce mineure, il apparaît que la formation de domaines ordonnés est inhibée, ce qui autorise la production de sédiments dont la densité compactée, donc la porosité initiale, est beaucoup plus homogène. En conséquence, le frittage conduit à une microstructure plus uniforme. Enfin, les résultats sont comparés à ceux d'un travail précédent basé sur des techniques de simulation de la géométrie de compacts par ordinateur.

1 Introduction

The attainment of a fully dense microstructure of uniform grain size remains an important goal of modern ceramic processing. In recent years the quality of the starting powders has been identified as an area in which considerable improvements are possible. By gaining better control over particle size, size distribution and particle shape, it may be possible to achieve improvements in sintering behaviour and a reduction in the number of defects in the ceramic product.

One of the most important features of any ceramic powder is the manner in which individual particles pack together in the powder compact. Studies of particle packing extend back over many years,[1-3] and recent developments in ceramic powder science have renewed interest in examining particle packing behaviour.[4-8]

Monosize spherical particles have been proposed as offering the 'ideal' means of achieving a homogeneous microstructure,[9,10] the hypothesis being that the particles can be formed into close packed arrays which represent the optimum packing arrangement for a powder compact, viz. maximum density and coordination number.

However, some doubts have been raised as to the validity of this approach for ceramic processing; the structures formed have been shown to contain a variety of packing types and may not represent the ideal compact.[11] An alternative approach to achieving a green compact with a uniform spatial distribution of packing density is to formulate randomly packed structures. In an earlier study the authors used computer simulation methods to investigate the effects of particle size distribution on packing arrangements.[12-14] The authors now report the results of experimental work aimed at investigating the types of structure formed from monosize and bimodal systems. Information is also presented on the respective sintering behaviour of ordered and disordered compacts.

2 Experimental

Spherical, 0·35 μm diameter, nearly monosized silica particles were produced by the method of Stober et al.[15] Powders of other sizes were supplied by Advance Company Ltd, Japan. To prepare bimodal mixtures, individual suspensions containing 0·5 wt% of monosized particles in ethanol were prepared by ultrasonic dispersion. The suspensions were adjusted to pH = 10·5 by adding dilute ammonium hydroxide solution. Portions of each suspension were mixed in suitable ratios to produce the required bimodal systems.

Most of the work on bimodal systems was carried out using 0·5:1 and 1:1·5 μm size ratios; eight different number ratios were studied for each system.

In the text the notation used to depict number ratios in bimodal mixtures, e.g. 5:95, indicates the wt% present of the small and large components respectively.

For gravitational settling experiments, the suspensions were allowed to stand in 7 mm diameter, flat-based, stoppered glass tubes undisturbed for eight weeks. After this period most of the upper clear liquid was carefully removed and the remaining liquid allowed to evaporate slowly at room temperature. Once all the liquid was removed the compact was further dried in an oven at 100°C. Films were prepared by drying droplets of suspension onto clean, polished silicon wafers.

A semi-quantitative numerical assessment of the spatial domain size distribution was obtained by assessing visually the extent of each domain in the SEM micrograph, and measuring its area using a 'digitizer' image analysis facility. The number of domains containing ≥10 particles in equivalent total areas of 5000 μm^2 was plotted graphically.

For sintering studies, specimens were fired in a high purity alumina tube for 7 h at the required temperature. For direct observations of microstructure after sintering at progressively higher temperatures, particle structures were coated with carbon and examined by SEM before further calcination. This procedure enabled exactly the same area of a microstructure to be viewed before and after sintering; structures were observed using an Hitachi S700 scanning electron microscope.

3 Results and Discussion

3.1 Packing arrangements
'Monosize' silica particles when settled under gravity yielded highly ordered packing arrangements. A typical area of the top surface of gravitationally settled sediments is shown in Fig. 1. The structure is composed of domains of close packing and other ordered packing interspersed with disordered packing. Fracture surfaces reveal that the close packing observed in top surfaces extends into the bulk of the compact (Fig. 2). Within the domains are found a number of defects including vacancies and dislocations (Fig. 1). Some of these are analogous to defects present in atomic crystals that arise from thermodynamic considerations. However, many of the defects within ordered domains, as well as the more extensive disordered 'defect' regions between domains, owe their origin to the experimental conditions used to form the compact, as discussed later.
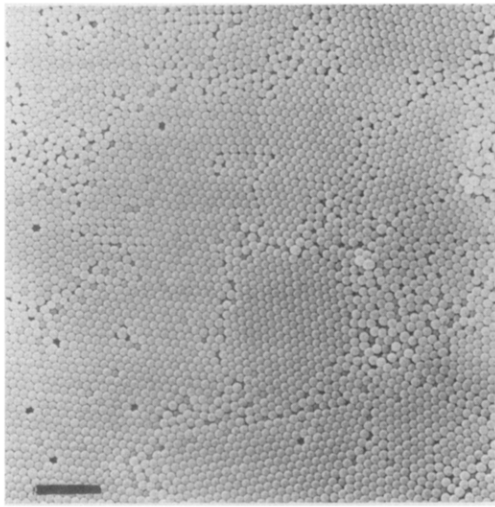
Fig. 1. Top surface of gravitationally settled 'monosized' powder compact. (Bar represents 2 μm.)

Fig. 3. Top surface of gravitationally settled compact highlighting the effect on packing of particles larger and smaller than the 'monosize' norm. (Bar represents 1 μm.)

To form the ideal colloidal crystal, truly monosize colloidal particles and ideal settling conditions are required. In order for monosize particles to adopt a close packed configuration, each settling particle must be free to move, independently under Brownian motion, to its lowest energy close-packed position. However, for practical experiments, the suspensions must be of sufficient concentration to allow a sediment to be obtained in a realistic time period. In the present work, solids contents of 0·5 wt% were used to yield 0·25 mm thick sediments after eight weeks. At these finite concentrations, in many cases there will have been insufficient time for particles to move to equilibrium sites before the arrival of other sedimenting particles, which inhibit local structural rearrangement and thereby disrupt the formation of perfectly ordered (or disordered) close packing.

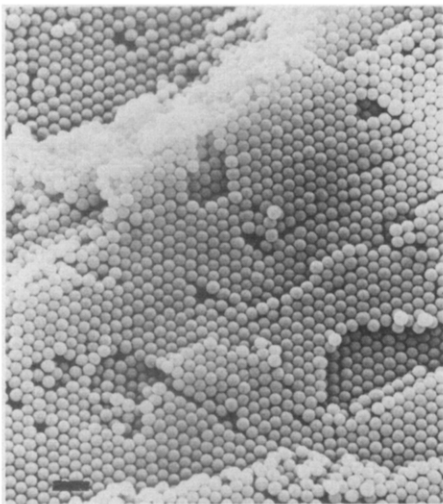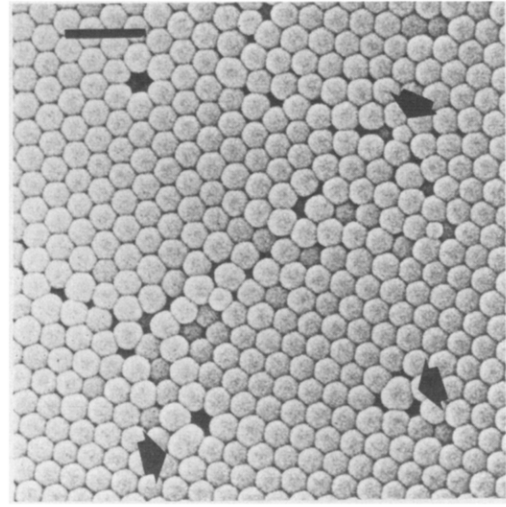An additional factor leading to defects in close packing is the variation in particle size which is

present in real 'monosize' powders, since the latter inevitably contain a finite distribution of particle sizes. Examples of particle size effects are quite clearly shown in Fig. 3. Other reasons for disruptions to close packing include the occurrence of convection currents and vibrations during sedimentation experiments, and the presence of particle aggregates.

Films of monosized powders were also examined. These were formed by drying drops of liquid suspension onto glass or polished silicon substrates. Here the experimental time-scale allowed for particle rearrangement was only a matter of minutes, which reduced the opportunity for rearrangement to close-packed sites compared with the sedimentation experiments. As a result, in the films, close-packed domains appear to be smaller (Fig. 4), and there is a greater portion of disordered packing than was observed in gravitationally settled sediments (Figs 1 and 3). Another difference in the formation of the two structures was that shrinkage stresses during film drying led to a series of cracks running predominantly along interdomain boundaries (Fig. 4).
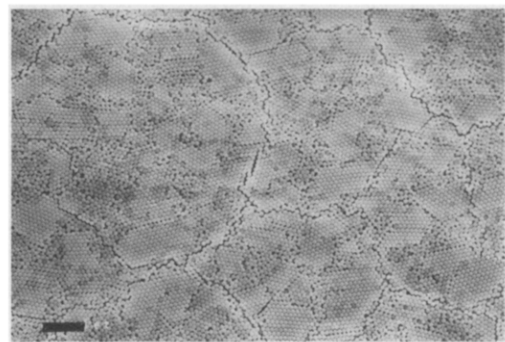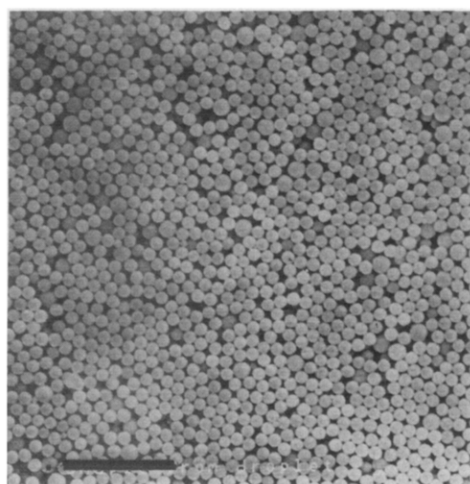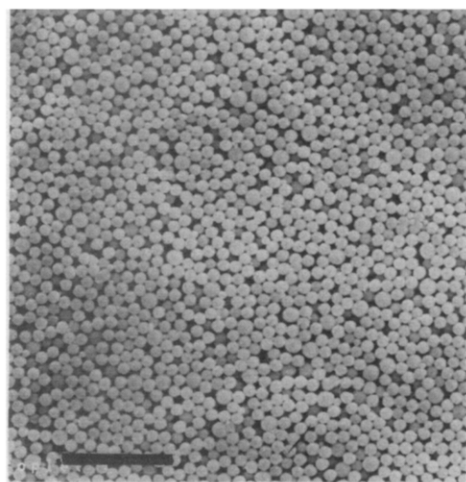

Fig. 2. Fracture surface of the 'monosized' compacts shown in Fig. 1. (Bar represents 1 μm.)

Fig. 4. Film of monosize particles: note the decreased size of ordered domains compared to sediments shown in Fig. 1. (Bar represents 10 μm.)
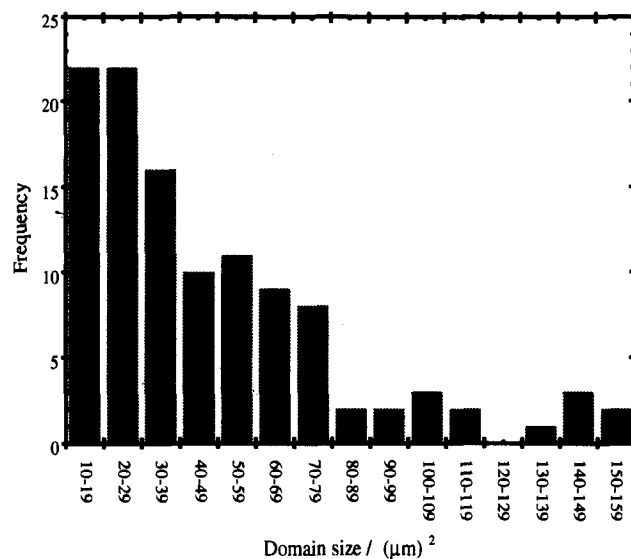
(a)

(b)

Fig. 5. Films of 1:1·5 μm bimodal particle mixtures: (a) 5 wt% of small component; (b) 20 wt% of small component. (Bar ≡ 10 μm.)

Domain size / (μm)^2

(a)

Domain size / (μm)^2

(b)

Fig. 6. Domain size distribution in an equivalent 5000 μm^2 area for (a) monosize system and (b) bimodal mixture containing 5 wt% of the smaller component.
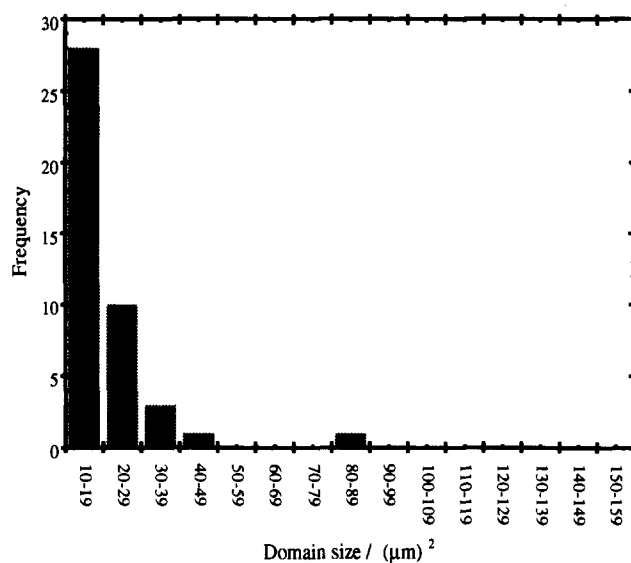
Visual assessments of monosized and bimodal film structures (Figs 4 and 5) suggest that approximately 20 wt% of a second component is required in bimodal systems to disrupt the highly ordered packing arrangements observed in monosize systems, and so to form disordered structures. Bimodal systems containing a smaller fraction than 20 wt% of a second component continue to exhibit domains of close packing (Fig. 5(a)). However, the size of the domains in the two cases are quite different. In the 5:95 mixture all the domains measured were less than 100 μm^2 in size, whereas the monosize sample was composed of domains extending up to twice this area (Fig. 6). Residual short-range order in the 20:80 samples was also apparent, but the few resulting domains were only ∼10 μm^2 in area. These residual, very small domains are in part due to segregation of the differently sized components.

3.2 Sintering

Silica powders sinter by a viscous flow mechanism, the end-point being a glass. On heating there is a

sudden change in viscosity and the material flows into an amorphous monolith. Consequently there is only a narrow range of temperature, at the onset of sintering, in which silica particles densify in an analogous manner to those of most other ceramic systems. This has inevitably imposed practical restrictions on the monitoring of microstructural evolution.

Firstly, sintering within ordered domains is considered. After heating at 1100°C for 7 h the three coordinate interstices in the upper surface of close packing disappear and the densifying particles take on a hexagonal honeycomb structure (Fig. 7). At this stage of the sintering process the size of six coordinate vacancies in the top layer has not changed significantly. The respective behaviours of these two types of pore are consistent with the concept of a critical pore coordination number.
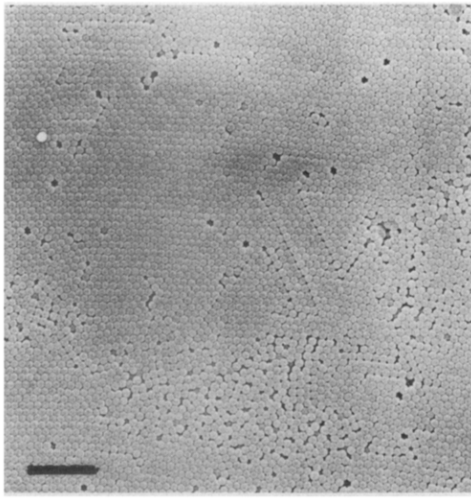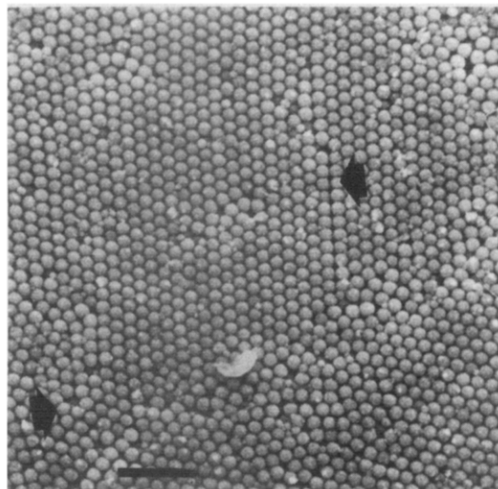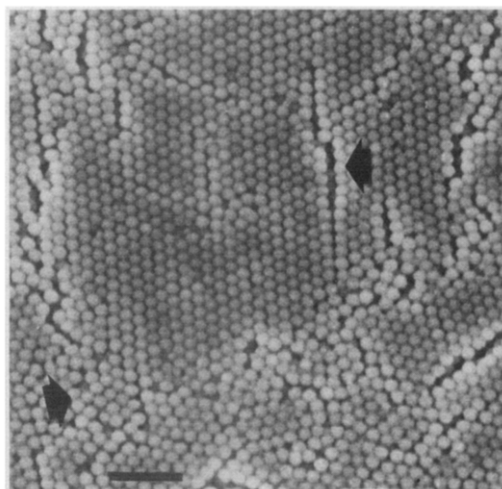
Fig. 7. Partially sintered surface of monosized sediment exhibiting a variation in density across the compact. (Bar represents 2 μm.)

(a)

(b)

Fig. 8. One area of a film of monosize particles: (a) before and (b) after heat treatment at 1150°C. Arrows are used to pinpoint identifying features such as line and point defects. (Bar represents 5 μm.)

Thermodynamic arguments have been used by several authors to correlate pore coordination number to pore shrinkage;[16,17] vacancies on the top surface of the sediments having a coordination number of 6 fall outwith the proposed pore shrinkage regime during this early period of sintering.' Dislocations also remain pronounced after heat treatment at 1100°C. The more porous interdomain regions of other packing arrangements within the sediment show little sign of densification at this stage.

Considering now the overall sintering pattern of the monosized sediments, it can be seen that the substantial differences in the packing density of ordered domains and disordered regions leads to large local differences in sintering rates. The more densely packed ordered domains, as expected, densify at an earlier stage of the sintering regime than do regions of disordered packing. Thus, as sintering proceeds, differences in packing density across the sediment become more pronounced. In general, such a situation is unfavourable for the development of uniform microstructures, since it is likely to lead to residual porosity in the final ceramic.

The effect that perturbations to close packing have on sintering is well illustrated in Fig. 8, which shows one area of a film of monosize particles before and after heat treatment at 1150°C. Defects and disordered regions give rise to pore growth as a result of the shrinkage of adjacent close-packed regions of high density.

The densification behaviour of a typical disordered bimodal system is shown in Fig. 9. Sintering is more regular than was the case for monosized sediments, but the structure contains voids which can be clearly correlated to localised low packing density in the unfired sediment. This effect is perhaps better illustrated in Fig. 10, in which one small region of a heat-treated bimodal sediment has not sintered, allowing an in-situ comparison to be made.

In the early stages of sintering shown in Figs 9 and 10, interconnecting particles are the first to densify, and shrink together, leaving behind porosity. Such a situation could only be avoided if each particle were to be surrounded by the maximum possible number of touching particles. Although this situation cannot be achieved in practice, the results demonstrate that the size of the voids can be minimised by using well-dispersed bimodal mixtures of appropriate number ratios.

The most striking difference between the sintering behaviour of monosize and bimodal systems lies in the spatial distribution of pores. In monosize sediments, pores are confined to specific regions of the compact, whereas their distribution is more uniform in bimodal structures, leading to more regular sintered microstructures in the latter.
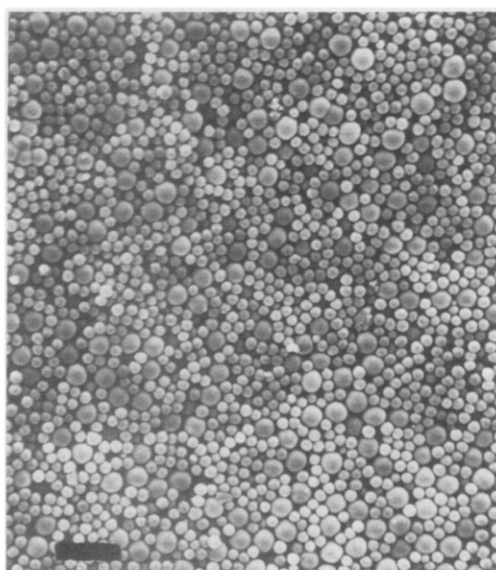
(a)
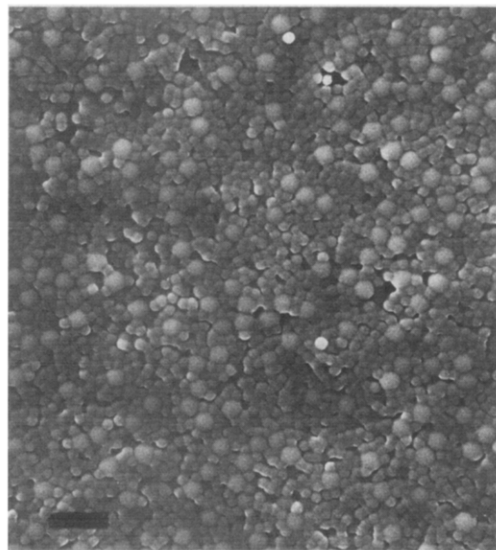
(b)

Fig. 9. Bimodal sediments (size ratio = 0·5:1 μm, weight ratio = 50:50); (a) before and (b) after heat treatment at 1150°C. (Bar represents 2 μm.)
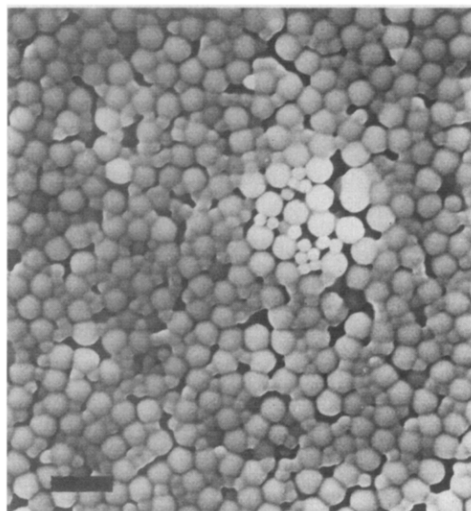

Fig. 10. In-situ comparison of sintered and non-sintered bimodal particles (0·5 and 1·5 μm; weight ratio 20:80). (Bar represents 2 μm.)

4 Discussion

It has been demonstrated that gravitationally settled sediments of monosize particles contain a wide variety of packing types which lead to a range of packing density throughout the sediment. This in turn promotes local differences in sintering rates; voids can develop as a result of the close-packed ordered regions, of maximum particle contact number, shrinking away from regions of lower initial density. Thus the monosize system is not ideal for ceramic fabrication where the goal is to achieve dense microstructures of uniform grain size. By moving to well-mixed bimodal size distributions with ≥20 wt% of the second component, close-packed domains can be avoided. For these the two components are present in sufficient volumes to prevent medium- to long-range particle order.

The experimental results reported here are broadly consistent with the computer simulation results reported previously[12-14] for the packings of polydisperse spheres and bimodal mixtures in two dimensions. Analysing the simulated structure in terms of the particle–particle pair distribution function, it was observed that monodisperse systems gave inhomogeneities in packing which extended over 10–20 particle diameters, whereas this range could be reduced to just 2–3 diameters by introducing a small degree of polydispersity into the system, or mixing together particles of two different sizes with a diameter ratio of less than 20%. Under visual observation, the graphical representations of the simulated structures look remarkably similar to the electron micrographs of the real monodisperse and bimodal systems investigated here. One has to be aware, however, of the limitations of the simulation approach, particularly its two-dimensional character, when real systems are never two-dimensional even when viewed from above or deposited in a thin film.

Although in the real bimodal systems studied the ordered domains disappeared, significant local variations in sintering behaviour were still observed. These arose due to local differences in particle packing. Groups of touching particles sintered preferentially, leaving behind a network of voids.

Given that spherical non-agglomerated powders of micron and sub-micron size are in principle advantageous for sintering purposes, the results indicate that bimodal rather than monosize systems should be adopted, since by so doing ordered domains of extreme packing density can be avoided. Earlier work using glass spheres also found that more uniform structures were possible from bimodal systems.[18] However, using real ceramic powders of micron dimensions, the authors have been able to demonstrate more extensive structures,

including those in three dimensions, and have illustrated problems associated with processing high-quality starting powders into compacts suitable for sintering into uniform microstructures. An overriding consideration for achieving uniform sintering is to maximise the number of interparticle contact points throughout the compact. In many of the bimodal sediments or films prepared, there continued to be significant variations in particle packing arrangements in different parts of the sediment—although this was less than for mono-sized systems. Until such time as more reproducible means of forming compacts can be achieved, the full potential benefits of high-quality powders for ceramic fabrication will not be realised.

Acknowledgement

References

1. Westman, A. E. R. & Hugill, H. R., Packing of particles. *J. Am. Ceram. Soc.*, **13** (1930) 767.

2. McGreavy, R. K., Mechanical packing of spherical particles. *J. Am. Ceram. Soc.*, **44** (1961) 513.

3. Owe Beng, T. G., McDonald, R. L. & Trainer, R. J. Jr. The packing of spheres. *Powder Technol.*, **3** (1969) 183.

4. Onoda, G. Y., Direct observation of two-dimensional synamic clustering and ordering with colloids. *Phys. Rev. Lett.*, **55** (1985) 226.

5. Weiser, M. W. & De Jonghe, L. C., *J. Am. Ceram. Soc.*, **69** (1986) 822–6.

6. Liniger, E. & Raj, R., Packing and sintering in two-dimensional structures made from bimodal particle size distributions. *J. Am. Ceram. Soc.*, **70** (1987) 843–9.

7. Sacks, M. D. & Tseng, T. Y., Preparation of SiO_2 glass from model powder compacts: I. Formation and characterization of powders, suspensions and green compacts. *J. Am. Ceram. Soc.*, **67** (1984) 526–32.

8. Sacks, M. D. & Tseng, T. Y., Preparation of SiO_2 glass from model powder compacts: II. Sintering. *J. Am. Ceram. Soc.*, **67** (1984) 532–7.

9. Barringer, E. A. & Bowen, H. K., Formation, packing and sintering of monodisperse TiO_2 powders. *J. Am. Ceram. Soc.*, **65** (1982) C199.

10. Barringer, E. A., The synthesis, interfacial electrochemistry, ordering and sintering of monodisperse TiO_2 powders. PhD thesis, Massachusetts Institute of Technology, 1983.

11. Milne, S. J., Preparation and ordering of spherical, submicron, monosized powders. *Brit. Ceram. Proc.*, **38** (1986) 81.

12. Dickinson, E., Milne, S. J. & Patel, M., Structure and porosity of simulated sediments of polydisperse particles. *Ind. Eng. Chem. Res.*, **27** (1988) 1941–6.

13. Dickinson, E., Milne, S. J. & Patel, M., Ordering in simulated packed beds formed from binary mixtures of particles in two dimensions: implications for ceramic processing. *Powder Technol.*, **59** (1989) 11–24.

14. Dickinson, E., Milne, S. J. & Patel, M., Structure of simulated beds containing solid particles of different sizes. In *Powders and Grains*, ed. J. Biarez & R. Gourves. A. A. Balkema, Rotterdam, 1989, pp. 47–53.

15. Stober, W., Fink, A. & Bohn, E., Controlled growth of monodisperse silica spheres. *J. Colloid Interface Sci.*, **26** (1968) 62.

16. Lange, F. F., Sinterability of agglomerated powders. *J. Am. Ceram. Soc.*, **67** (1984) 83–9.

17. Kellett, B. J. & Lange, F. F., Thermodynamics of densification: I. Sintering of simple particle arrays, equilibrium configurations, pore stability, and shrinkage. *J. Am. Ceram. Soc.*, **72** (1989) 725–34.

18. Liniger, E. G. & Raj, R., Spatial variations in the sintering rate of ordered and disordered particle structures. *J. Am. Ceram. Soc.*, **71** (1988) C408–C410.