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Role of powder size, packing, solid loading and dispersion in colloidal processing of ceramics

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Abstract

The packing characteristics of various kinds of particle size distributions are described in terms of their variance and skewness. For a suspension comprising two or more powders of different size distributions, a search procedure is proposed for obtaining the composition that matches the mixture size distribution, to the maximum extent possible, with an ideal dense packing distribution, such as the Andreasen distribution. The method, which obviates the need for time consuming experimental search, is efficient and accurate when tested against published data for the density of green compacts. It is stressed that a dense packing size distribution by itself may not be sufficient to obtain high density green compacts. An example is included which demonstrates that it is necessary to concurrently control the rheology of the suspension by optimizing its solid loading and dispersion dosage. It is further pointed out that high green density does not necessarily guarantee an optimal sintering path, especially if it is achieved by incorporation of excessively coarse powder. This point is illustrated with the fabrication of zirconia–alumina composite ceramics by the colloidal processing route. This important system is interesting by virtue of the fact that the constituent powders differ not only in size but also in their surface properties in the suspension.

Keywords: Colloidal processing; Ceramics; Powder properties

1. Introduction

Convention wisdom dictates that green compacts formed in suction or pressure dewatering step of colloidal processing of ceramics should be as densely packed as possible with uniform fine pores. This is because firing cycle, shrinkage, residual porosity and uniformity of the microstructure depends not only on the size distribution and reactivity of powder(s) employed but also the physical attributes of the green compact. It is well known that packing is, in the first instance, a function of the size distribution of powder. Accordingly, researchers have sought densely packed green compacts by manipulating the size distribution of starting powders [1–6]. However, it turns out that the dense packing of particles in green compacts is only one aspect of the problem and it cannot be examined in isolation for improving the ceramic fabrication process as a whole. There are important other issues, such as overall powder fineness, presence of coarse particles, solid loading and dispersion of the suspension, that must also be taken into account simultaneously. The objective of this paper is to draw attention to some of the factors that impact on green density and quality of the sintered product.

1.1. Particle distributions for dense packing

The factors that influence dense random packing are well known, at least in so-called mechanical or geometric packing of dry powders, where friction, adhesion and other surface forces are ignored [7,8]. Continuously size distributed powders, which are invariably encountered in colloidal processing, generally pack denser than mono size particles. The extent of improvement depends strongly on the spread in size range [2] and also on the shape of the distribution, as represented, for example, by variance and skewness, respectively. It is convenient to describe the former by a normalized interquartile range (NIQR):

$$\mathrm{NIQR} = \frac{X_{75} - X_{25}}{X_{50}} \geqslant 0 \quad (1)$$

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and the latter by a normalized interquartile coefficient of skewness (NIQCS):

$$\mathrm{NIQCS} = \frac{X_{75} + X_{25} - 2X_{50}}{X_{75} - X_{25}} \; ; \qquad -1 \leqslant \mathrm{NIQCS} \leqslant 1 \tag{2}$$

where X_p is p-ile or p-fractile of the distribution.

Fig. 1 is based on Suzuki's extensive data [9] for dense random packing of glass beads distributed as Gaudin–Schuhmann, Rosin–Rammler or Weibull, LogUniform and LogNormal distributions. It shows that the packing of standard statistical distributions increases with an increase in the spread in size. A noteworthy exception to this trend is the Gaudin–Schuhmann distribution:

$$F_{GS}(X) = \left(\frac{X}{K}\right)^n; \qquad 0 < X \leqslant K \tag{3}$$

which is actually a specialized version of the classical dense packing distribution, namely, the Andreasen distribution:

$$F_{And}(X) = \left(\frac{X^n - X_o^n}{K^n - X_o^n}\right); \qquad X_o < X \leqslant K \tag{4}$$

where $F(x)$ is the volume fraction of particles less than or equal to size X; n is a shape parameter, the so-called distribution modulus; and K and X_o are, respectively, the largest and the smallest size particles in the distribution. It turns out that both the Gaudin–Schumann and the Andreasen distributions have an optimum spread in size for maximum packing. In the former, densest packing is obtained at NIQR$\sim$2 when n lies in the range of 0.5 to 0.4, and in the latter best n is stated to be about 0.37.

Fig. 2 shows packing as a function of distribution shape, as quantified in the normalized interquartile coefficient of skewness, defined in Eq. (2). Although packing improves as the distribution shifts from left to right skewed, the trend, unlike in Fig. 1, is strongly dependent on the functional form of the distribution.

In theory, it is always possible to construct an idealized dense packing distribution by mixing a number of components of different size distributions and minimizing a vector of error functions whose j-th element is:

$$E(j) = [f_{id}(j) - \sum_{k=1}^{N} v_k f_k(j)]^2; \qquad j = 1, 2 \ldots S \tag{5}$$

with following two constraints due to volume balance:

$$\sum_{k=1}^{N} v_k = 1 \tag{6}$$

and normalizability of the mixture distribution:

$$\sum_{j=1}^{S} f_k(j) = 1; \qquad k = 1, 2 \ldots N \tag{7}$$

Here f_{id} (j) is the ideal or target frequency in volume fraction in j-th discrete size interval, $j = 1,2\ldots S$; v_k is volume fraction of k-th component in a mixture of N powders, $k = 1,2,\ldots N$; and $f_k(j)$ is volume-size discrete frequency of the k-th component. Note, the total number of discrete size intervals S need not be same in all

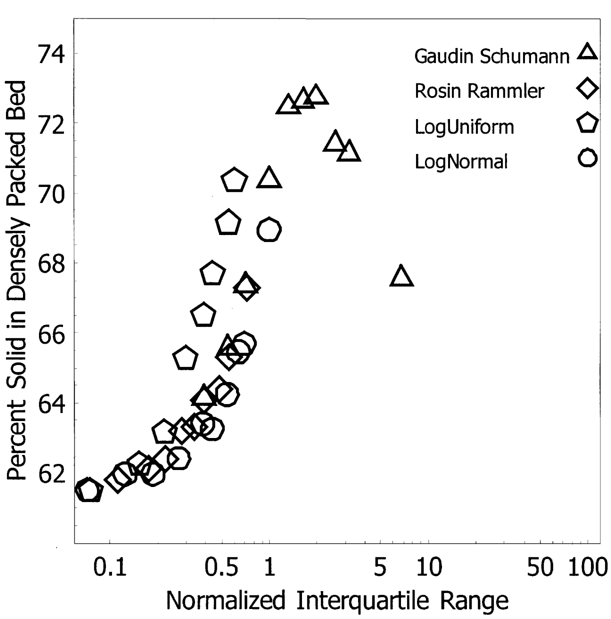

Fig. 1. The extent of random packing as quantified by percent solids in the densely packed bed as a function of normalized interquartile range (NIQR), defined in Eq. (1), for different statistical size distributions.

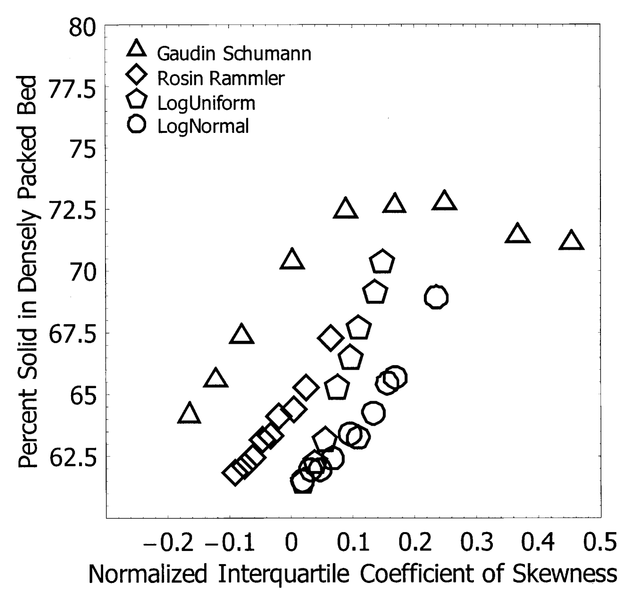

Fig. 2. The extent of random packing as quantified by percent solids in the densely packed bed as a function of distribution shape (quantified in the normalized interquartile coefficient of skewness), defined in Eq. (2) for different statistical size distributions.

the distributions, and the search for minimizing the error vector is on volume fractions of the components v_k Depending upon the nature of the size distributions of components, it may not be possible in practice to drive the error functions $E(j)$ down to zero simultaneously for all j's. It is then sufficient, and also computationally convenient, to minimize a scalar error function given by:

$$E = \sum_{j=1}^{S} W_j E(j) \quad (8)$$

where W's are a set of weights which can be chosen to force a closer agreement with the ideal distribution in some size range(s) of interest.

Smith and Haber [6] prepared slips containing 50 vol.% solids by blending coarse alumina of 6 μm mean size and fine alumina of 0.6 μm mean size in different proportions. They reported that a mixture containing 85 vol.% coarse component gave the best packing of 60% relative density in the green compacts, and that this distribution was close to the ideal Andreasen distribution. Actually, by minimizing the error function in Eq. (8), we ascertain that the optimal distribution, closest to the ideal Andreasen distribution, contains 81% coarse in the mixture. Fig. 3 shows that the optimized distribution is quite similar to the actual distribution. Not only the former is arrived at without going through a series of time consuming experimental trials, it is also closer to the ideal Andreasen distribution, which is also included in the figure. Earlier, Velamakanni and Lange [3] prepared suspensions of bimodal distributions of alumina from a mixture of coarse and fine components. Again based on empirical trials, they found that compositions having around 60% coarse component gave the highest density in green compacts formed by the pressure filtration technique. Our procedure using Eq. (8), on the other hand, indicates that a composition containing 63% coarse is closest to the Andreasen distribution.

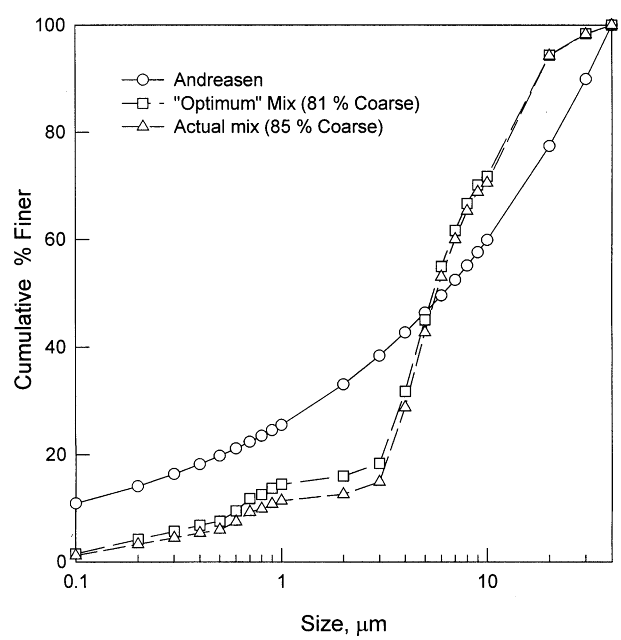

Fig. 3. Effect of relative proportion of "coarse" and fine alumina on the slip cast green densities- the one with 85 vol.% coarse yielded maximum packing. The distribution is closer to the ideal Andreasen distribution having 81% coarse fraction. Data taken from Smith and Haber [6].

The next example is taken from our detailed investigation of the colloidal/semi-colloidal processing of alumina–zirconia composite ceramics [10–18]. The density of green compacts in multi-component ceramic systems has not been adequately treated in the literature. The system is complicated by the fact that the constituent powders differ not only in size but also in their surface properties in the suspension. The powder components were coarse grade alumina SR (Indian Aluminium Co.) of mean particle size 5 μm and fine grade zirconia Unitech (Uinitech Ceramics, Stafford, UK) of 0.735 mean size. The suspensions with 50% total solids by volume were dispersed with 1% dwd Darvan C at pH 10 and sonificated with a horn operating at 20 kHz and 250 W power. The viscosity of suspensions was measured with a Brookfield viscometer using a disk spindle rotating at 50 rpm. The green compacts were prepared by slip casting in plaster-of-paris moulds. Fig. 4 shows viscosity and green density as a function of the alumina volume fraction in the mixture. The viscosity is minimum for a composition having about 75% coarse alumina by volume, which is quite close to composition of 78% alumina for maximum density (experimentally derived). It is well known that, keeping other conditions fixed, suspensions of dense packing size distributions yield the lowest viscosity. On the other hand, optimization shows

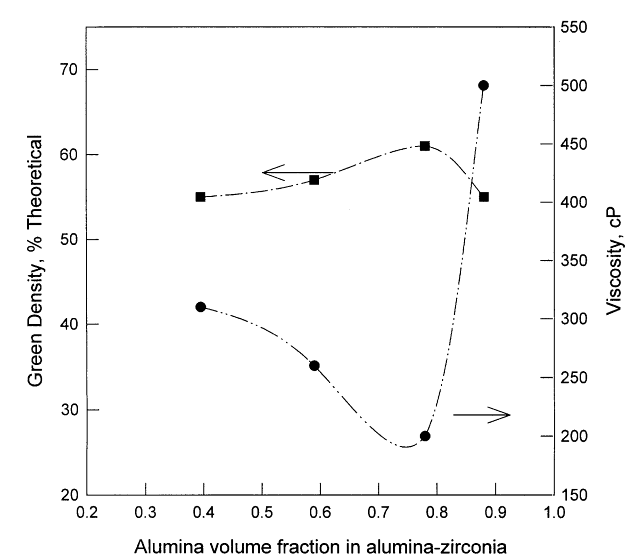

Fig. 4. Green density of alumina (SR)–Zirconia (Unitec) compacts made by slip casting of mixed suspensions as well as the viscosity of slips at 50% by volume, solid loading as a function of relative proportions of the two components.

that the minimized distribution should have 81% alumina. The discrepancy is primarily in coarse size range, which has only a limited impact on packing as compared to the distribution of fine particles. Both the actual and the optimized distributions match the Andreasen distribution in the fine size range and deviate significantly in the coarse size region.

From the detailed analysis of packing data cited above, we conclude that (1) the commercially available powders are unlikely to conform to a dense packing ideal distribution such as the Andreasen distribution; (2) blends of two or more powders of different fineness are unlikely to match the ideal distribution exactly; (3) a minimization procedure can be employed to zero in on optimal or near optimal compositions efficiently and reasonably accurately; and (4) densities of green compact are, more often than not, less than those predicted by geometric packing data for dry powders.

2. Solid loading and dispersion of suspension

Although geometric packing is important, it may not be the decisive factor in the formation of green compacts by dewatering/consolidation of suspensions. Apart from the size distribution of the powder(s) employed, the outcome is impacted by other factors such as dispersion and stability of suspensions, solid loading, and hetero-coagulation in multi-component systems [11–14,19,20]. For illustration, we consider an alumina–zirconia system in which the components were Alumina A16 (Alcoa Industrial Chemicals) of 0.426 μm mean particle size and, as before, zirconia Unitech of 0.735 μm mean size. Because of roughly comparable fineness of the powders, it is reasonable to assume that in this system the geometric packing is to a large extent decoupled from the effects of solid loading and dispersion of the suspensions.

Fig. 5 shows the effects of dispersant (Darvan C) dosage and solid loading on the density of green compacts having 88% alumina by volume. Although dispersant dosage is seemingly insensitive to solid loading, there exist optimum levels for both the variables. This behavior has an explicit connection with the suspension rheology. Initially, viscosity drops with increasing dosage, finally reaching a minimum at about 1% dwd Darvan C, where maximum packing occurs. Subsequently, viscosity rises again concurrently with a drop in density of the green compacts. Systematic measurements of the size distributions of solids in suspensions [14] also show a similar behavior, namely, the mean aggregate size increases beyond a critical dosage. Consequently, viscosity increases and packing decreases because of the more open structure of the larger aggregates. The upper limit on solid loading is again dictated by the viscosity. In this system, suspensions having more than 40% solids are too viscous for slip casting, even in the presence of an

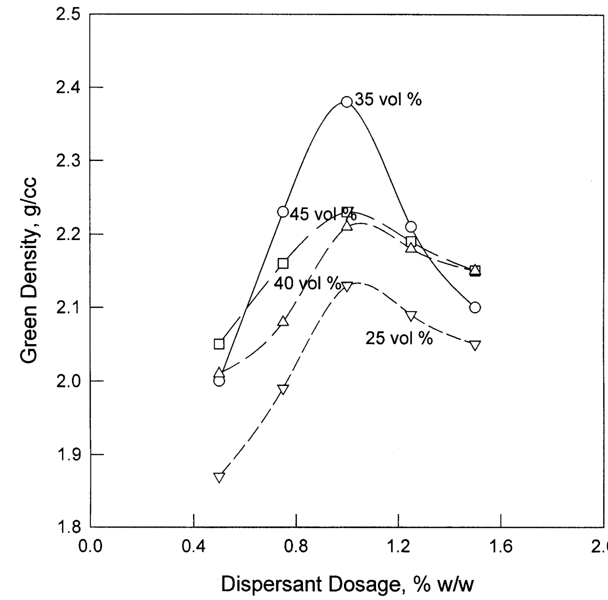

Fig. 5. Optimization of dispersant (Darvan C) dosage for alumina (A16)–zirconia (Unitec) slip containing 88% alumina by volume; a sharp peak in the green density is observed.

optimal dosage of the dispersant. We may conclude that not only size distribution but solid loading and dispersant dosage also must be optimized simultaneously in order to obtain high green densities. The choice of the dispersant—including the molecular weight—its dosage and solid loading are, however, specific to the powder(s) employed and its fineness.

3. Effect of particle fineness and green density on sintering

A high green density, obtained from a dense packing distribution with broad spread in size, is not necessarily the best option for sintering. Because of practical and technical limitations on the smallest size particles in a powder, a broad size distribution requires the presence of coarse particles. These, in turn, are likely to introduce heterogeneities in the microstructure of the sintered product. Moreover, sintering is initiated at the point of contact between particles. It turns out that the number and nature of contacts can vary widely and depend strongly on the size distribution, and to a much lesser extent on packing [9]. As an illustration, dispersed suspensions of zirconia Unitech admixed with three different aluminas were prepared under optimized conditions stated above. The aluminas were A16 of median size 0.43 μm, SG of median size 0.61 μm, and SR of median size 5.3 μm. The green densities (g/cc) of the slip cast compacts were 2.38, 2.41. and 2.57, respectively. The samples were sintered in air at 1500 °C for different time intervals under identical conditions. Fig. 6 shows the sintered density as a function of sintering time for the

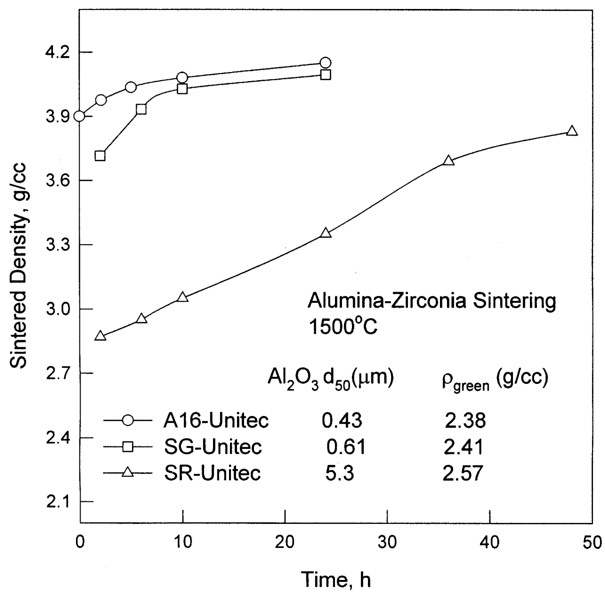

Fig. 6. Densification profiles for sintering alumina-zirconia green compacts at 1500 °C for varying durations; the corresponding green densities as well as mean particle size of coarser alumina fraction are also shown for comparison.

three samples. In spite of starting with the lowest green density, the zirconia Unitech-alumina A16 composition exhibited the best sintering profile. Evidently, in this system the role of powder fineness and its reactivity in sintering overwhelm that of the green density whose importance seemingly is only marginal.

4. Summary and conclusions

A narrow focus on obtaining high density of green compact through packing consideration is unlikely to yield the most desirable ceramic fabrication practice based on colloidal processing. A high density of green ceramic compact requires not only a dense packing distribution but also optimized solid loading of the suspension coupled with the correct selection of the dispersant and its dosage. However, a high density could be detrimental to sintering if it is realized with excessive amount of coarse particles.

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References

[1] T.S. Yeh, M.D. Sacks, Low temperature sintering of aluminium oxide, J. Am. Ceram. Soc. 71 (10) (1988) 841–847.
[2] T.S. Yeh, M.D. Sacks, Effect of particle size distribution on the sintering of alumina, J. Am. Ceram. Soc. 71 (12) (1988) C–484-C-486.
[3] B.V. Velamakanni, F.F. Lange, Effect of interparticle potentials and sedimentation on particle packing density of bimodal particle distributions during pressure filtration, J. Am. Ceram Soc. 74 (1) (1991) 166–172.
[4] P.A. Smith, R.A. Haber, Characterisitics of large extension in the size distribution for alumina slips, Ceram. Eng. Sci. Proc. 12 (1-2) (1991) 93–96.
[5] P.A. Smith, R.A. Haber, Use of particle packing in optimization of slurry solids loading, Ceram. Eng. Sci. Proc. 10 (1–2) (1989) 1–11.
[6] P.A. Smith, R.A. Haber, Effect of particle packing on the filtration and rheology behaviour of extended size distributed alumina suspensions, J. Am. Ceram. Soc. 78 (7) (1995) 1737–1744.
[7] D.J. Cumberland, R.J. Crawford, The Packing of Particles, Elsevier, Amsterdam, 1987.
[8] R.M. German, Particle Packing Characteristics, Metal Powder Industries Federation Publication, Princeton, USA, 1989.
[9] M. Suzuki, T. Oshima, Coordination number of a multi-component randomly packed bed of spheres with size distribution, Powder Technol. 44 (1985) 213–217.
[10] V. Ramakrishnan, Pradip, S.G. Malghan, Yield stress of alumina-zirconia suspensions, J. Am. Ceram. Soc. 79 (1996) 2567–2576.
[11] Pradip, R.S. Premachandran, S.G. Malghan, Electrokinetic behaviour and dispersion characteristics of ceramic powders with cationic and anionic polyelectrolytes, Bull. Mater. Sci. 17 (1994) 911–920.
[12] V. Ramakrishnan, Pradip, S.G. Malghan, The stability of alumina–zirconia suspensions, Colloids and Surfaces 133 (1998) 135–142.
[13] S. Manjunath, Pradip, S.G. Malghan, Shear yield stress of flocculated alumina–zirconia mixed suspensions: effect of solid loading, composition and particle size distribution, Chem. Eng. Sci. 53 (17) (1998) 3073–3079.
[14] S. Manjunath, S. Kokil, P.C. Kapur, Pradip, S.G. Malghan, An aggregation index for monitoring the state of the suspensions, Langmuir 14 (1998) 7364–7370.
[15] S. Manjunath, P.C. Kapur, Pradip, S.G. Malghan, Population balance model for solid state sintering I. Pore shrinkage and densification, Ceram. Int. 27 (2001) 57–62.
[16] S. Sivakumar, M. Subbanna, S.S. Sahay, V. Ramakrishnan, P.C. Kapur, Pradip, S.G. Malghan, Population balance model for solid state sintering II, grain growth, Ceram. Int. 27 (2001) 63–71.
[17] M. Subbanna, P.C. Kapur, Pradip, Computer-aided control of the evolution of microstructure during sintering, Mater. Chem. Phys. 67 (2001) 17–24.
[18] S. Sivakumar, Pradip, P.C. Kapur, S.G. Malghan, A size interval-by-size interval marching algorithm for modelling grain growth in the intermediate stage of sintering, Colloids and Surfaces 133 (1998) 173–182.
[19] P.C. Kapur, P.J. Scales, D.V. Boger, T.W. Healy, Yield stress of suspensions loaded with size distributed particles, AIChE J. 43 (1997) 1171–1179.
[20] P.J. Scales, S.B. Johnson, T.W. Healy, P.C. Kapur, Shear yield stress of partially flocculated colloidal suspensions, AIChE J. 44 (1998) 538–544.