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Microspherical Agglomeration of Ceramic Powder in Organic Liquid With Extremely Small Quantities of Bridging Liquid

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Abstract

The possibility of using the method of spherical agglomeration in liquid with extremely small quantities of bridging liquid for the production of ceramic microspheres was investigated. The experiments were conducted using a suspension of zirconia powder in normal hexane agitated by a rotary shaker. No bridging liquid was added, instead, agglomeration was based only on the moisture content of the zirconia powder. The results indicate that by using this method it was possible to produce microagglomerates with diameters less than 500 μm and nearly theoretical density. In addition, the agglomerate size, size distribution, sphericity and density of sintered microagglomerates were greatly affected by the solids concentration, agitation intensity, agglomeration time and volume of suspending media. It is necessary to optimize these process parameters in order to produce agglomerates with desirable properties.

1. Introduction

The ever increasing utilization of media agitated mills for mixing, dispersing and ultrafine grinding of fine ceramics, super conducting materials, minerals, coals, etc. provides a natural impetus for the production of high strength ceramic microspheres with diameters less than 500 μm. However, conventional methods of agglomeration can hardly produce these microspheres. In a recent publication, the authors introduced three methods of agglomeration in liquid to produce microspherical ensemble from finely divided zirconia powder suspended in a liquid [1]. These three methods are: (1) agglomeration in organic liquid without the addition of bridging liquid in a relatively weak agitation environment, (2) agglomeration in aqueous media with bridging liquid addition in a strong agitation field and (3) agglomeration in organic liquid with bridging liquid addition in a strong agitation field.

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Published works on agglomeration in liquid have generally been concerned with processes involving high bridging liquid dosages, i. e. the second and third methods. The addition of bridging liquid results to strong interparticle forces in agglomerates. The strong agglomerates require considerable amount of external force, e. g. agitation energy, to produce close packing of particles or densification. In fact, in the third method the agitation power needed to produce highly dense agglomerates was reported to be 463 kW/m^3 [2]. The second method not only requires high energy input to produce dense agglomerates but also necessitates the use of surfactant to convert the naturally hydrophylic surface of the powder to a hydrophobic one. The surfactant complicates the agglomeration process and may present a problem of contamination. In contrast, the first method is carried out in a weak agitation environment without the addition of bridging liquid. The weak interparticle forces arise from pendular liquid bridges which are probably formed from the moisture adsorbed on the powder surface and suspending liquid. The agglomerates are relatively weak but the particles can easily rearrange to a closer packing and compaction can proceed with considerably less amount of agitation energy. Therefore, the economic significance of the first method can not be overlooked.

However, this novel method of spherical agglomeration in a weak agitation environment with small quantities of bridging liquid is not fully explored and only a few authors have addressed this subject. The first was Stock [3] who reported that when dried, finely divided barium sulphate suspended in dry benzene in cylindrical containers was shaken with reciprocating motion, discrete spheres were formed. Smith and Puddington [4] followed up on Stock's work and reported that the presence of a small quantity of water was necessary for agglomeration to occur. In a recent report, the authors also demonstrated that agglomeration would not occur if the powder and the suspending media were thoroughly dried [5]. In addition, by using different organic liquids the influences of the properties of the suspending media on agglomerate formation were elucidated.

This paper aims to demonstrate the possibility of producing highly dense microspherical agglomerates with diameters less than 500 μm from a ceramic powder by using the new method of spherical agglomeration in weak agitation field with extremely small quantities of bridging liquid. The agglomeration experiments were carried out in a rotary shaker using hexane as a suspending media and the moisture inherently adsorbed on the powder as bridging liquid. The effects of various process parameters such as agitation intensity, solids concentration, agglomeration time, etc. on the agglomerate size, size distribution, sphericity and density of agglomerates were investigated.

2. Experimental Procedure

Zirconia powder containing 2.6 mol% of Y_2O_3 was used in the agglomeration experiments. The powder was stored in a dessicator containing silica gel at 25 °C. The equilibrium moisture content of this material was 0.3%. The specific surface area measured by B. E. T. method was 6.76 m^2/g and the mean particle size by weight was 0.45 μm. Reagent grade normal hexane was used as suspending media. Normally, before agglomeration test, the moisture of the suspending liquid was reduced by using a molecular sieve. In the text this media was referred to as "dry suspending media". Whereas, in experiments where molecular sieve was not utilized, the term "wet suspending media" was used. Experiments were carried out using a 300 cm^3 erlenmeyer flask (maximum capacity: 370 cm^3) and a variable speed rotary shaker (EKDS No. 0266). A certain amount of zirconia powder and a desired volume of normal-hexane was placed in a previously dried flask, the flask was stoppered, set in a rotary shaker and agitated at a certain time and speed. Before and after agglomeration test, the water content of the suspending media was measured by using the Metrohm 684 Karl Fischer Coulometer.

After agglomeration, the agglomerates were dried at 60 °C for 24 hrs and sintered at 1450 °C for 2 hrs. The density of sintered agglomerates was determined by the Archimedes method using a pycnometer. The diameter and sphericity of sintered agglomerates were determined by using an image analyzer, Luzex II, equipped with a microscope. Sphericity is defined as ML/BD where ML is the maximum length and BD the breadth diameter.

3. Results and Discussion

The effect of the volume of suspending media was investigated by keeping the solid concentration or solid/liquid ratio at 0.03 g/cm^3 and agitation speed at 350 rpm for a period of 20 min. Fig. 1(a) shows the density, sphericity and the mean diameter of the sintered agglomerates. Illustrated in Fig. 1 (b) are the size distribution curves of the sintered agglomerates. The density of sintered agglomerates markedly decreased when the volume of suspending media exceeded 300 cm^3. This suggests that too much suspending media reduced the intensity of agitation, hence, lower degree of compaction was imparted on the agglomerates. When the volume of suspending media was in the range of 250 and 300 cm^3, the size distribution curves were relatively narrow indicating that homogeneous agglomerates were formed. Based on these results, 250 cm^3 was chosen as the appropriate volume to produce closely sized agglomerates with good sphericity and density. Thus, in the preceding experiments the volume of the suspending media was maintained at 250 cm^3.

The next parameter investigated was the period of agglomeration. Likewise, the shaker speed was kept at 350 rpm. The changes in density, sphericity and mean diameter of sintered agglomerates with agglomeration time when the solid/liquid ratio was 0.03 g/cm^3 are shown in Fig. 2(a). The value of sphericity approached 1.00 with an increase in agglomeration time. This indicates that the agglomerates approach the shape of a perfect sphere with increasing agglomeration time. Density of the sintered agglomerates was noted to be highest when the agglomeration time was 60 min. With this agglomeration time, high degree of compaction was imparted on agglomerates. The size distribution curves of the sintered agglomerates when the solid/liquid ratio was 0.03 g/cm^3, shown in Fig. 2(b), were significantly affected by the agglomeration time. These results suggest that in the process of agglomeration in liquid the rate of breakage and coalescence of agglomerates changes progressively [6]. When

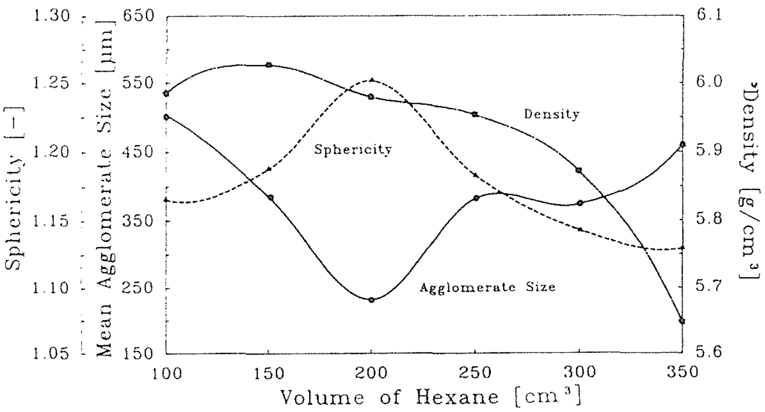

Fig. 1(a) The effects of volume of suspending media on mean agglomerate size, sphericity and density of sintered agglomerates.

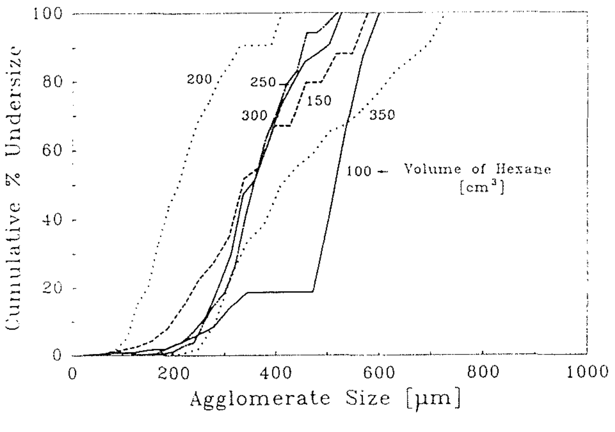

Fig. 1(b) The effect of volume of suspending media on size distribution of sintered agglomerates.

agglomeration time ranged from 10 to 30 min, breakage of large size agglomerates predominately occurred. Beyond this range coalescence of agglomerates took place and large agglomerates with high densities were formed. The phenomenon of agglomerate breakage was also observed in the size distribution curves of sintered agglomerates obtained in experiments with low solids concentration, i.e. 0.01 g/cm³, shown in Fig. 2(c).

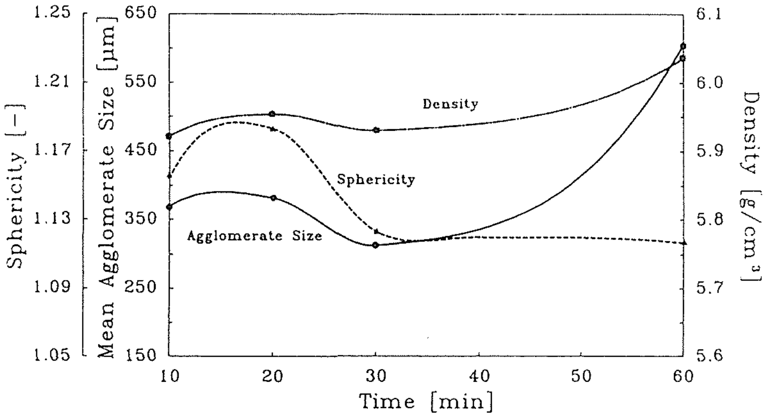

Fig. 2(a) The effects of agglomeration time on mean agglomerate size, sphericity and density of sintered agglomerates.
Solids conc. = 0.03 g/cm³

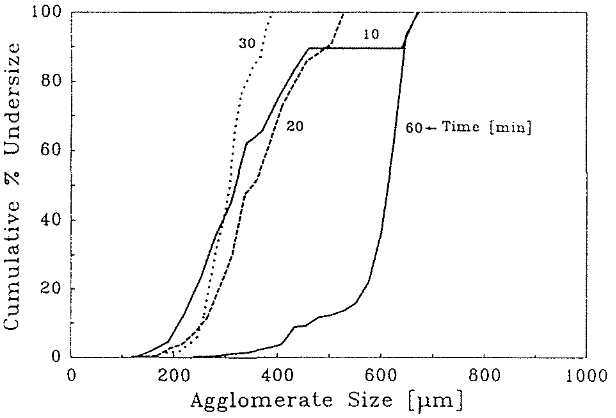

Fig. 2(b) The effect of agglomeration time on size distribution of sintered agglomerates. Solids conc. = 0.03 g/cm³

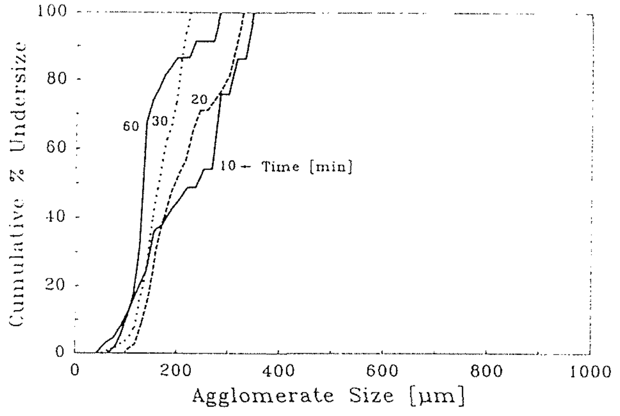

Fig. 2(c) The effect of agglomeration time on size distribution of sintered agglomerates. Solids conc. = 0.01 g/cm³

The effects of solid concentration on agglomerate properties and size distribution are shown in Figs. 3(a) and 3(b). In these tests the agglomeration time and shaker rotation speed were maintained at 20 min and 350 rpm, respectively. The size and sphericity of agglomerates both showed tendencies to increase with increasing solid concentration. With high solid concentration, the number of suspended particles and the number of nuclei formed are initially high. The probability of collision and coalescence of these nuclei during the process of agglomeration is high thereby the rate of agglomerate growth increases [6]. These are considered as the reasons for the increase in agglomerate size when the solid concentration was increased.

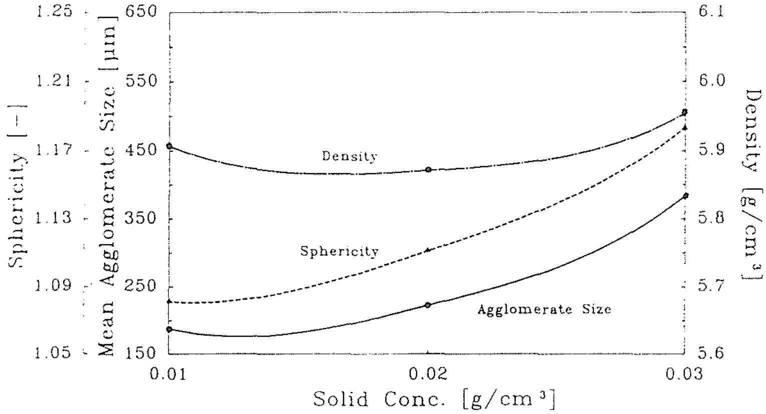

Fig. 3(a) The effects of solids concentration on mean agglomerate size, sphericity and density of sintered agglomerates.

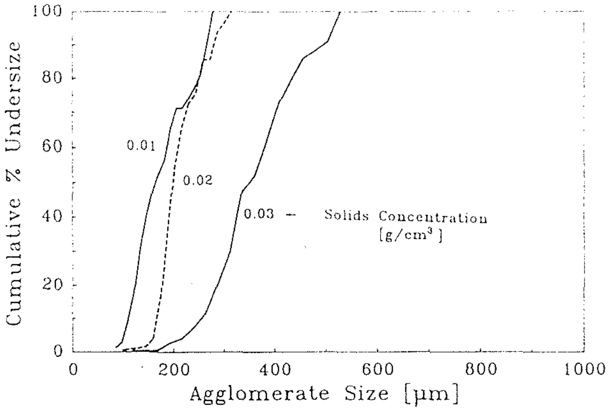

Fig. 3(b) The effect of solids concentration on size distribution of sintered agglomerates.

The effect of agitation intensity was investigated by varying the rotation speed of the shaker and maintaining the agglomeration time and solid concentration at 20 min and 0.03 g/cm^3, respectively. The results are shown in Figs. 4(a) and 4(b). Significant increase in the density of the sintered agglomerates was noted with an increase in rotation speed. It is

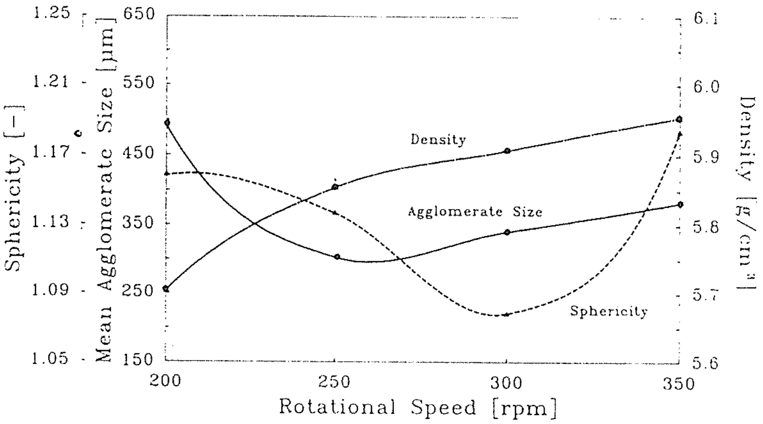

Fig. 4(a) The effects of agitation intensity on mean agglomerate size, sphericity and density of sintered agglomerates.

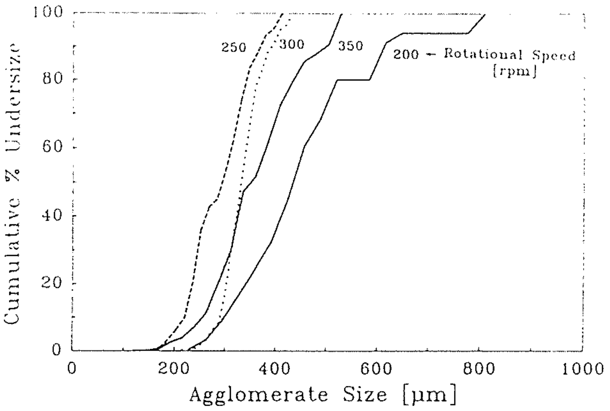

Fig. 4(b) The effect of agitation intensity on size distribution of sintered agglomerates.

considered that increasing the agitation intensity will increase the energy of agglomerate-agglomerate or agglomerate-wall collisions thereby facilitating the progress of compaction and results to less porous, denser agglomerates.

Typical changes of water content of the suspending media before and after agglomeration tests are shown in Table 1. In these experiments, dry suspending media and undried zirconia powder were used. Generally, the moisture content of the suspending media increased after agglomeration test. With constant amount of zirconia powder in suspension, no significant change in the water content of the suspending media after agglomeration test was observed even when the agglomeration time was increased from 10 to 60 min. However, when the amount of zirconia powder was increased from 2.5 to 7.5 g, the water content of the suspending media after agglomeration tests also increased. This indicates that some of the moisture in the powder is adsorbed by the suspending media. In a totally dry system, i.e. where dry suspend-

Table 1 Variations of the water content of the suspending media

Wt. of Powder (g)	Agg. Time (min)	W_i (ppm)	W_f (ppm)
2.5	10.0	5.0	36.2
2.5	30.0	5.0	38.1
2.5	60.0	6.1	37.7
7.5	10.0	5.0	46.9
7.5	30.0	5.0	50.6
7.5	60.0	6.1	48.7

Vol. of suspending media = 250 cm^3 : Rotational speed = 350 rpm
W_i = water content of the suspending media before agglomeration
W_f = water content of the suspending media after agglomeration

ing media and dry zirconia powder (vacuum dried at 200 °C for 2 hrs) were used, agglomerates were not formed and the water contents of the suspending media before and after the experiment were almost the same. In another experiment where dry zirconia powder and wet suspending media were used, small agglomerates were formed and the water content of the suspending media after the experiment was less than that before the experiment. Based on these results, it can be inferred that the moisture content of the suspending media and zirconia powder both play significant roles in the formation of agglomerates.

4. Conclusion

The technical feasibility of producing zirconia microspheres with nearly theoretical density and diameters less than 500 μm, by using the method of spherical agglomeration in organic liquid without the artificial addition of bridging liquid, was amply demonstrated. The properties of agglomerates in terms of agglomerate size, size distribution, sphericity and density were affected by process parameters such as solid concentration, agglomeration time, volume of suspending media and intensity of agitation. Low solids concentration produced agglomerates with diameters less than 500 μm. Agglomerate size and density changed with agglomeration time. Initially, breakage of large agglomerates predominated. This was followed by coalescence and densification of agglomerates. Increasing the rotation speed improved the density of sintered agglomerates whereas the opposite trend was observed when the volume of suspending media was increased. Proper selection and combination of these process parameters are essential to produce microspherical agglomerates with desirable properties.

In a totally dry system, i.e. dry suspending media and dry zirconia powder, agglomerates were not formed. The small amount of bridging liquid that comes from the moisture of the powder and suspending media was essential in the formation of agglomerates. Moisture from the powder can be adsorbed by the suspending liquid and vice versa.

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