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Direct observation of internal structure in spray-dried yttria-doped zirconia granule

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Spray-dried yttria-doped zirconia granules were made transparent by immersion in a liquid and the internal structure was characterized using an optical microscope. This unique technique was found to be applicable for this system by using an immersion liquid with appropriate refractive index, and it enabled observation of the internal structure to be made over the entire volume of granules, in clear contrast to conventional SEM observation. Distinct features, which were considered to be agglomerates, were found in the granules. This was supported by SEM observation.

1. Introduction

Properties of ceramics are dictated by their microstructure. It is important to characterize fully the internal structure of powder granules in producing high-performance ceramics by the powder compaction process, because the microstructure of the final products depends largely on that of the starting powders [1–3]. In the absence of a convenient and sensitive method, however, detailed characterization of powder granule has been difficult.

In general, the internal structure of powder granules can be observed with an SEM, by carefully impregnating them with epoxy, followed by polishing. However, with this technique, only internal structure accidentally exposed to a polished section of powder granule can be examined. Recently, Uematsu *et al.* [4] investigated characterization of internal structure in spray-dried alumina granule using a unique method; a granule which is rendered transparent by an immersion liquid is observed using a traditional optical microscope under transmitted light. The achievement of "transparent granules" is based on a reduced internal reflection in the presence of the immersion liquid which has a refractive index close to that of alumina powder [5]. With this technique, all the internal structure over the entire volume of the alumina granule can be examined. Furthermore, having proved applicable for various kinds of powder granules, this technique is promising as a universal method in characterizing spray-dried granules for the fabrication of high-performance ceramics using the powder compaction process.

The purpose of this study was two-fold; to examine the applicability of this unique technique for observation of internal structure of yttria-doped zirconia powder granule, which has a relatively large refractive index (2.15 to 2.22) and contains two phases, monoclinic and tetragonal, and to characterize more completely the internal structure of yttria-doped zirconia granules by amalgamation of information obtained by the technique with that from other conventional techniques.

2. Experimental procedure

A commercial spray-dried yttria-doped zirconia granule (TZ-3YA, Tosoh Co. Ltd, Tokyo) was used for the specimen. According to the supplier, it is a high-purity zirconia doped with 3 mol % yttria, two phases (80% tetragonal + 20% monoclinic), average particle size 0.3 μm (average crystallite size 0.024 μm) and average granule size 60 μm. Methylene iodide having different amounts of yellow phosphorus and sulphur, was prepared as the immersion liquid, the refractive index of which was determined by the minimum-deviation method. Granules were heated at 800 °C for 2 h to burn out the binder, and then immersed in the liquid. The transparent granules were examined under an optical microscope with transmitted light (Optiphot, Nikon Ltd, Tokyo). To examine the internal structure along the vertical direction, a series of micrographs were taken by changing the specimen to lens distance at 10 μm intervals. To obtain references, granules were impregnated with resin and moulded. SEM (JSM-T100, Jeol Ltd, Tokyo) was used to examine polished sections of granules moulded in resin.

3. Results

Fig. 1 shows scanning electron micrographs of specimen. The granules had a nearly spherical shape. Hollow granules with an abnormally large internal pore were often observed. A more detailed micrograph taken at higher magnification showed the presence of various types of agglomerate in the granules.

Table I shows characteristics of the immersion liquids. It was found that the refractive indices of the liquids varied with their compositions.

Fig. 2 shows observation of internal structure of the

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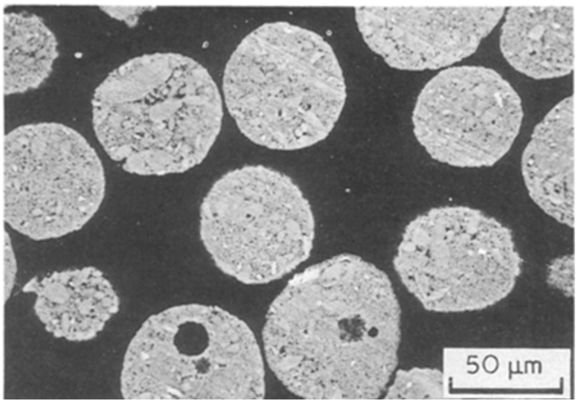

Figure 1 Scanning electron micrograph of polished sections of granules moulded in resin.

TABLE I Composition and refractive index of the immersion liquid

Liquid no.	Composition	Refractive index
1	CH_2I_2	1.75
2	P and CH_2I_2 (4.5:5.5 by weight)	1.90
3	P, S and CH_2I_2 (8:1:1)	2.02

powder granule by using immersion liquids with various refractive indices. The refractive indices of the monoclinic and tetragonal phases of zirconia are known to be 2.15 and > 2.15, respectively [6]. However, it is generally reported that the refractive index of zirconia is 2.15 to 2.22, irrespective of the phase [7]. With pure methylene iodide as immersion liquid, no internal structure of the granules could be observed. With liquid 2, the internal structure of larger granules was not observable, but that of smaller granules could be discerned. With liquid 3, the internal structure of all granules was clearly observed. It was found that the granule was made more transparent and clearer observation of the internal structure was possible, by using an immersion liquid with a refractive index closer to that of the powder.

Fig. 3 shows a series of observations along the vertical direction, in which the specimen to lens distance was varied at a fixed interval. Most of the granules have a nearly spherical shape with various sizes. Hollow granules with an abnormally large internal pore were often observed. The internal structure located at various depths of granules was brought into focus by changing the granule to objective lens distance. In some granules, large internal defects were observed at the top of the granule. When the position in focus was varied from the top to the bottom of the granule, observation became increasingly difficult.

Fig. 4 shows a more detailed micrograph taken at higher magnification. This micrograph shows the presence of three-dimensional features in all large granules. Distinct features, which were considered to be agglomerates, were found in the granules. Less distinct dark–light contrast was also found in all granules, showing the presence of some kind of non-uniformity.

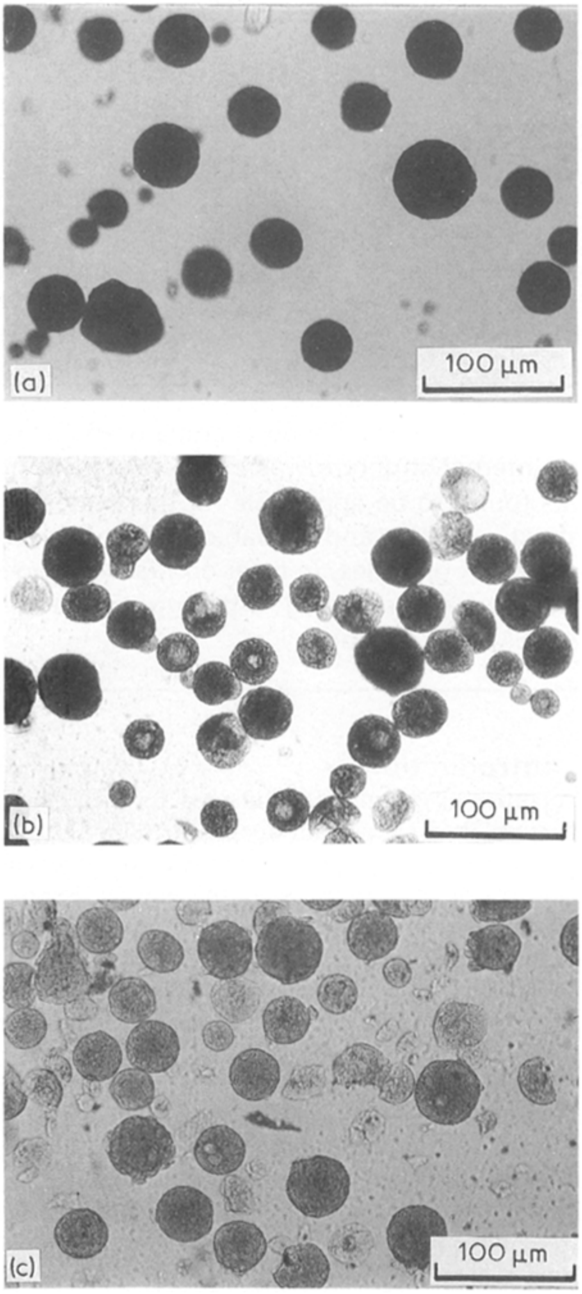

Figure 2 Optical micrographs of granules immersed in various immersion liquids. (a) Pure methylene iodide, (b) liquid 2, (c) liquid 3.

4. Discussion

The present method is very powerful for characterizing the internal structure of spray-dried granules. With this method, in principle, all the internal structures over the entire volume of all the granules can be examined. This is in clear contrast to SEM observation, with which only pores and/or internal structure accidentally exposed to the fracture surface or polished section of granule can be observed.

Scattering at the particle–liquid interface governs the transparency of the specimen in the immersion liquid. The reflection of light, R, is related to the relative refractive index, n, by Equation 1 for normal incidence,

$$R = (n-1)^2/(n+1)^2 \qquad (1)$$

Assuming that yttria-doped zirconia used in this study has a refractive index of 2.2, the refractive indices of

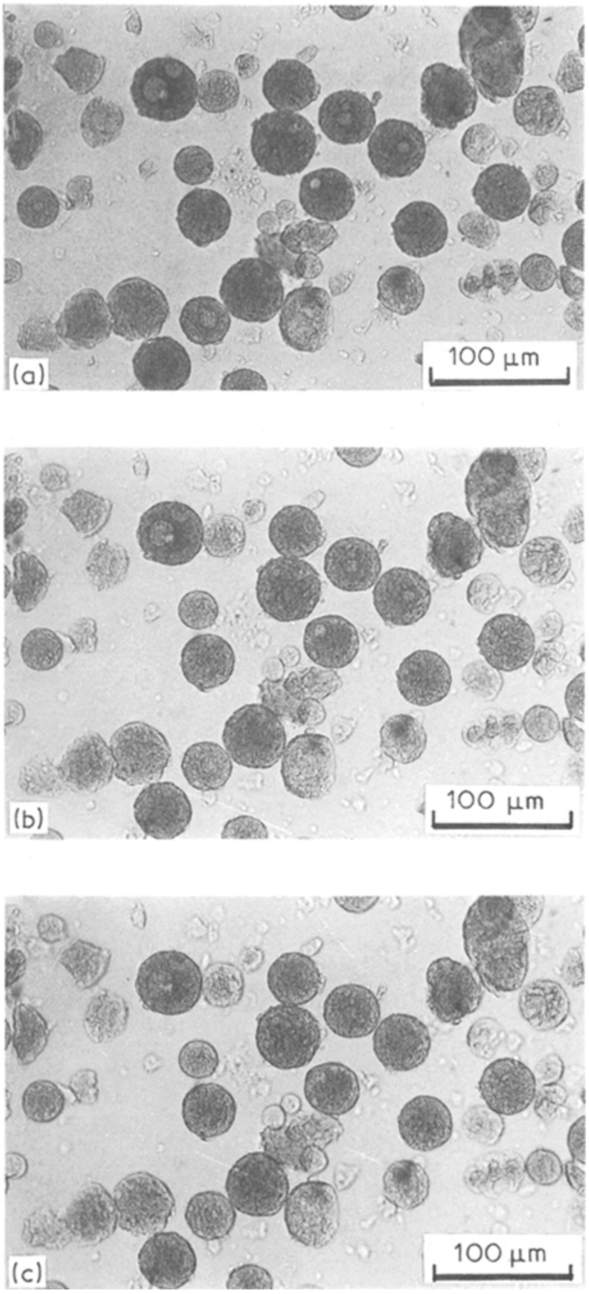

Figure 3 Optical micrographs of transparent granules, in which the position in focus was varied at 10 µm intervals. Liquid 3 was used as immersion liquid.

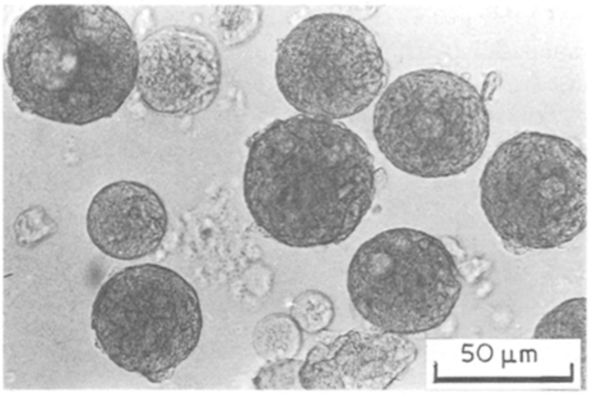

Figure 4 Optical micrographs of transparent granules using higher magnification. Liquid 3 was used as immersion liquid.

yttria-doped zirconia relative to pure methylene iodide, liquid 2 and liquid 3 are 1.26, 1.16 and 1.09, respectively, causing 1.32%, 0.55% and 0.19% reflection or loss of incident light at each interface. Along the centre axis of the granule, approximately 200 particles are present. Recalling that two interfaces are present in each particle, Equation 1 shows that 0.5%, 11% and 47% incident light is transmitted directly through the granule when pure methylene iodide, liquid 2, or liquid 3, respectively, is used as the immersion liquid. The proportion of directly transmitted light must be even smaller than the calculated value. Scattering of the lightwave depends strongly on the size of the particles, and becomes significant for particles, the size of which are comparable to the wavelength. This is considered to be the case for the specimen used for this study. However, the concept explained above suggests that the granule is made transparent by using an appropriate immersion liquid, and the present results are very consistent with the concept.

There are at least two possible mechanisms which produce contrast and make the internal structure visible in the optical micrographs. One is the difference in the light absorption between the immersion liquid and yttria-doped zirconia, and the other the light loss by scattering at the yttria-doped zirconia–liquid interface. To obtain a high contrast in the former mechanism, the relative difference of the absorption coefficient should be high for two relevant phases. High contrast by the latter mechanism requires a large relative difference of refractive index between the two phases. This is, however, not compatible with high transparency of the specimen required for microscopic examination. In the present system, experimental conditions are not optimized. However, the contrast obtained by this study was sufficient for detailed characterization of the granules, as shown above.

For the spray-drying process, the formation mechanisms of hollow granules have been discussed by Lukasiewicz [8]. However, because the supplier gave no information on the conditions of spray drying, the formation mechanism of the hollow granules observed is not discussed here.

SEM observation supported the view that the distinct features in the granules observed by the present technique can be attributed more to the larger agglomerates than the particles. It is not certain whether the agglomerates were formed during spray-drying or persisted before, because no information on untreated powders was available. Apart from the formation period and mechanism, the presence of the agglomerates largely influences subsequent processes and the properties of the final products. Previous studies [9–12] showed that the complete breakdown of the agglomerates is extremely difficult during the forming process; the agglomerates can persist through subsequent processes, and may act as critical flaws detrimental to properties of the final products.

Because the present technique is a simple procedure and powerful in detecting flaw dimension and population, information obtained in this way allows accelerated feedback to spray-drying process for improved granulation. Furthermore, the technique shows promise as a useful method for understanding and controlling the spray-drying process as well as quality control.

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