DEVELOPMENT OF DIRECT OBSERVATION METHOD FOR INTERNAL STRUCTURE IN SILICON NITRIDE GRANULE AND GREEN BODY

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ABSTRACT

Silicon nitride granule and green body were made transparent by immersion liquid which have a refractive index close to that of silicon nitride. Their internal structures were examined directly by means of optical microscope. Sharp void spaces existed even in the green body which was isostatically pressed at 600MPa. Present method is very useful for studying the processing of ceramics, because it gives us more detailed information than other methods.

INTRODUCTION

Defects and heterogeneities in ceramic green body are often persisted after sintering [1] and govern various properties of ceramics. It is essential that their size and concentration are both minimized for producing high performance ceramics. Therefore numerous forming processes, such as die pressing, extrusion molding, slip casting , injection molding, etc., have been developed depending on required shape and characteristics.

Requirements to produce highly reliable ceramics with high strength through powder process follows: (1) to characterize the microstructure in granule and green body precisely, (2) to feed back the information obtained from this characterization to forming process. Up to now, however, detailed chracterization of the internal structure in granule and green body has been difficult.

Recently, authors have developed a unique characterization method for internal structure of ceramics [2-4]; alumina granule and green body which were made transparent by immersion liquid were observed directly with traditional optical microscope. This method is based on a reduced internal reflection in the presence of immersion liquid which has a refractive index close to that of alumina. This method is superior to conventional methods; we can obtain only two dimensional information about fracture surface with SEM and can characterize only very large defects with scanning acoustic microscope. With the present method, we can examine microscopic internal structures over entire volume of specimen. Some additional advantages over other methods include simple experimental procedure and no requirement of any special equipments.

In principle, this method can be applied not only to alumina but also to other ceramics. Silicon nitride granule and green body were used as a model in the present study. Refractive index of silicon nitride determined on thin film was reported to be 2.05 [5]. Immersion liquids applied in this study are yellow phosphorus - methylene iodide and yellow phosphorus - sulfur - methylene iodide. They have refractive indexes as high as silicon nitride [6].

MATERIALS AND METHODS

Materials

Prototype silicon nitride granule(NKK, Ltd., Tokyo, Japan) was used as specimen in the present study. According to the supplier, the granule was produced by spray-dry method with high purity powder synthesized by thermal decomposition of silicon diimide(E-10, UBE Indust., Ltd., Ube, Japan) and normal sintering additives. TABLE 1 lists the composition and refractive indexes at room temperature of immersion liquids. Refractive indexes of the liquids were determined by the measurement of minimum deviation angles through a home-made hollow 30° prism with He-Ne gas laser(λ=632.8nm; GLG5040, NEC, Ltd., Tokyo, Japan).

Direct observation of internal structure in granule

The granule was immersed in immersion liquid after dewaxing, and its internal structure was observed directly with an optical microscope (OPTIPHOT, Nikon, Ltd., Tokyo, Japan). Subsequently, the granule was molded in resin and polished with diamond wheels(#260,#3000). Polished surface of the granule was also observed by means of SEM(JSM-T100, JEOL, Ltd., Tokyo, Japan).

Direct observation of internal structure in green body

The granule was uniaxially pressed into pellet(14mmϕ*5mm) at 20MPa and isostatically pressed(QIC12, NKK-ASEA, Tokyo, Japan) at 20, 100 or 600MPa. After dewaxing, specimens thinned (<0.2mm) with sandpaper were immersed in an immersion liquid(#4 in TABLE 1) and evacuated for 10-20min for direct observation with an optical microscope.

TABLE 1

Composition and refractive indexes (λ=632.8nm) of immersion liquids.

LIquid No.	Composition	Refractive index
#1	CH_2I_2	1.75
#2	P and CH_2I_2 (2:8 by weight)	1.82
#3	P and CH_2I_2 (4.5:5.5)	1.90
#4	P , S and CH_2I_2 (8:1:1)	2.02

RESULTS

Figure 1 shows optical micrographs of silicon nitride granule immersed in various immersion liquids. When immersed in liquid #1(n=1.75), granule was opaque and internal structure could not be examined. For immersion liquid #2(n=1.82), internal structure of only small granule could be seen. Large one(>40μm) was opaque. For immersion liquid #3(n=1.90), the internal structure of all granule could be clearly observed.

Figure 2 shows scanning electron micrograph of polished surface of granule. Defects in granule can be found with SEM. However, only two dimensional information can be obtained on polished surface.

Figure 3 shows a rare example of internal structure observed with the present method. There were small particles (10-15μm) in the pore of some large granules(>60μm). In principle, We may be able to find such a structure with SEM when it is accidentally exposed to polished surface. In practice, it is very difficult to find it with SEM, because it is rarely exposed to polished surface. The present method is very useful for observation of such a structure.

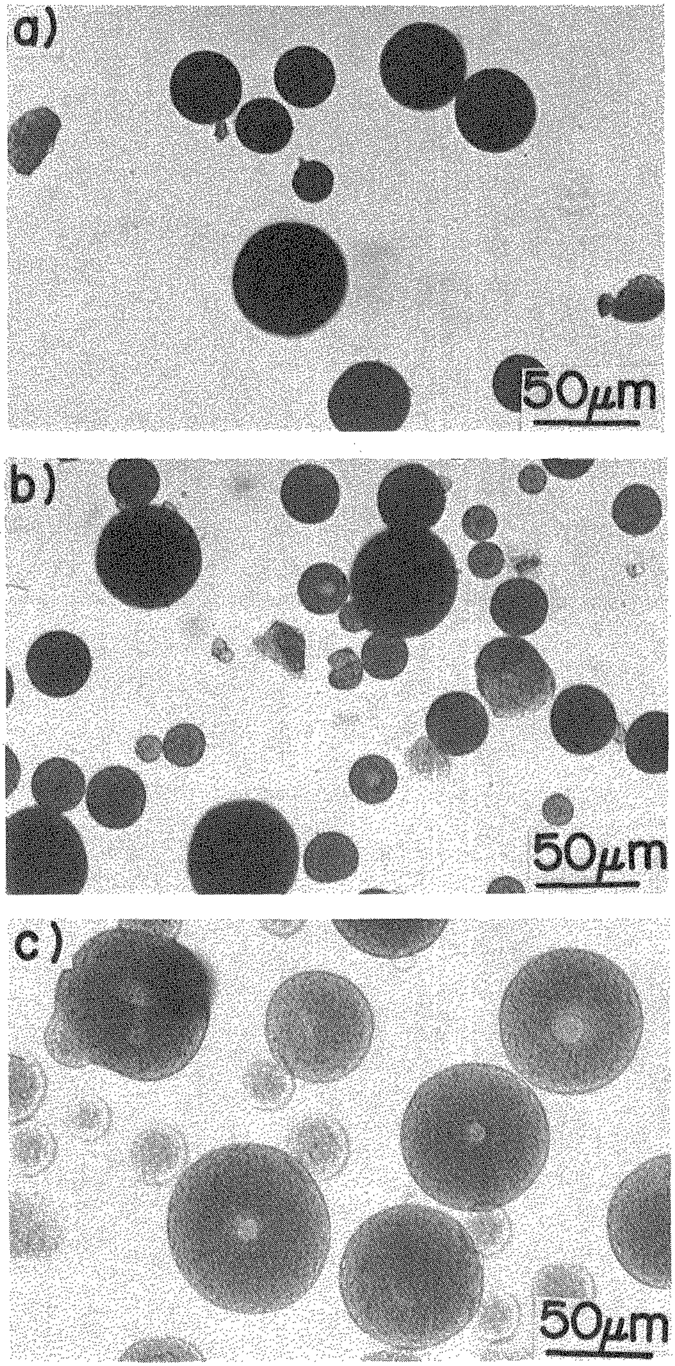

Figure 1. Optical micrographs of granule immersed in various immersion liquids. a)#1 in TABLE 1, b)#2, c)#3.

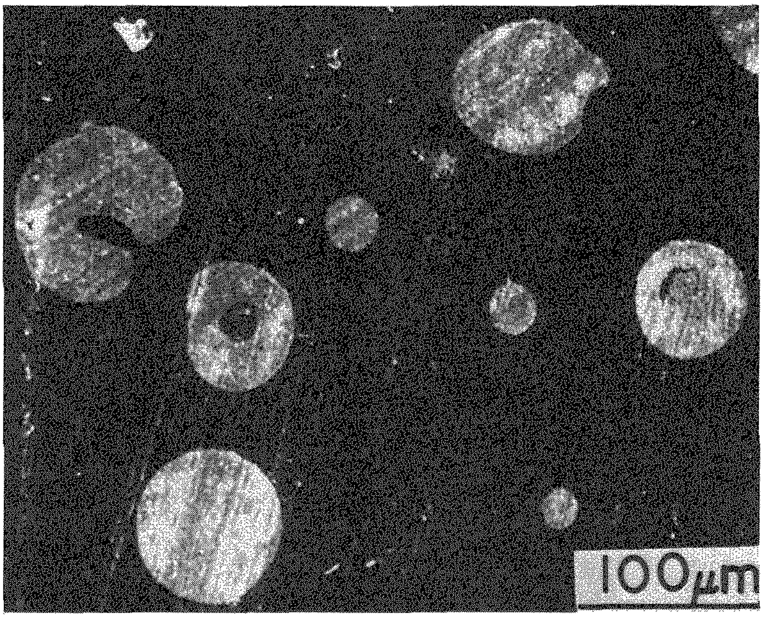

Figure 2. Scanning electron micrograph of polished surface of granule.

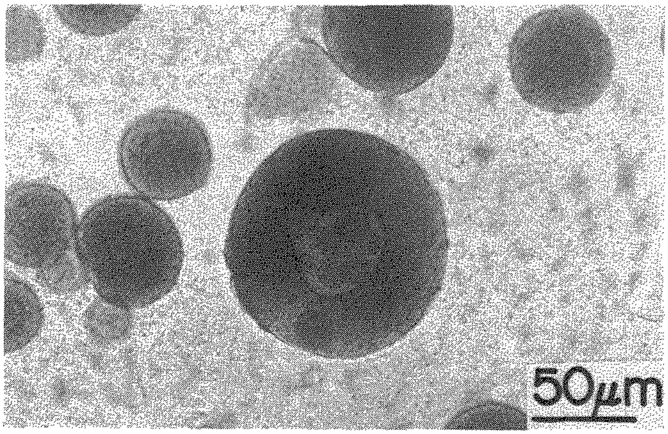

Figure 3. Optical micrograph of internal structure in large granule.

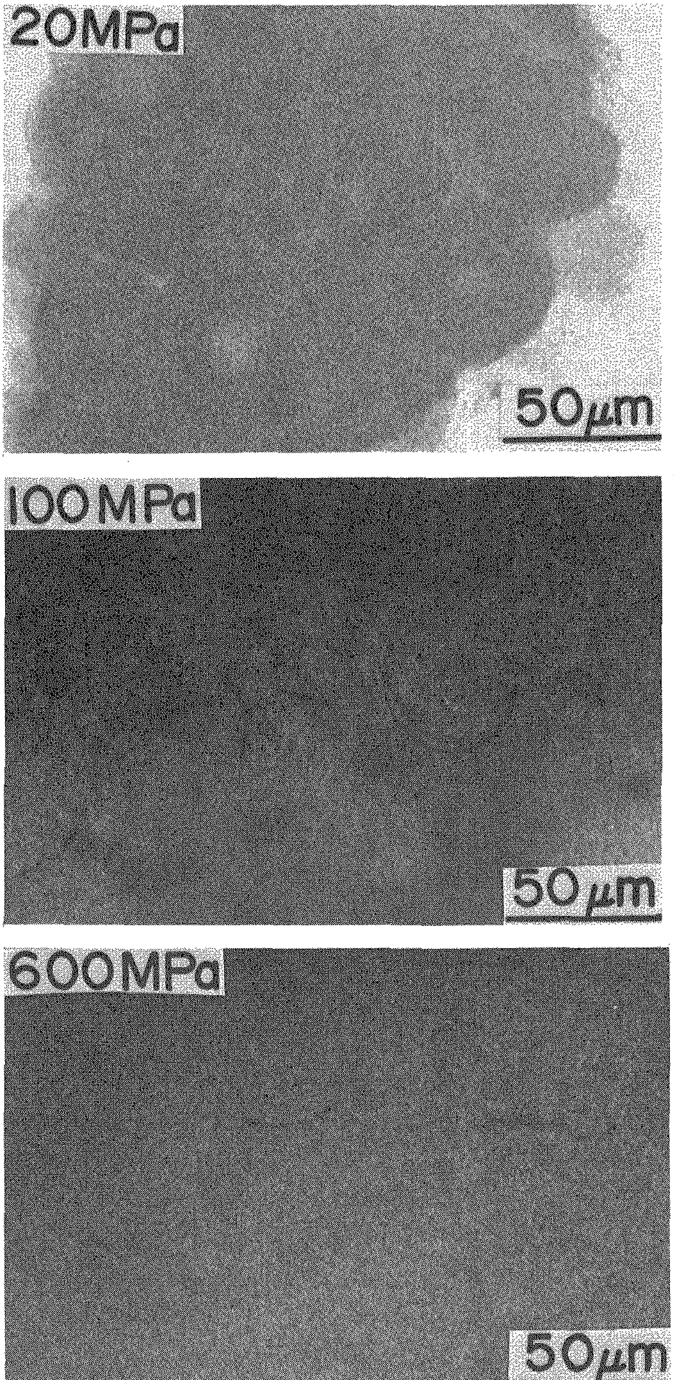

Figure 4. Optical micrographs of silicon nitride green bodies prepared at various pressures.

Figure 4 shows optical micrographs of typical internal structures in silicon nitride green bodies. Granule was not destroyed completely during powder compaction and sharp void spaces exist at interstices when isostatically pressed at 20MPa. Sharp crescent-like voids as large as 50-100 and 30-60μm were still found even at the applied pressure 100 and 600MPa, respectively.

DISCUSSION

The transparency of specimen in the immersion liquid is governed by scattering at the particle-liquid interface. Two governing factors for light scattering are; 1) Relative refractive index of the particle and the medium, 2) The ratio of the particle diameter to the wavelength of incident light [7]. The reflection of light R is related to the relative refractive index m by Eq.1 for normal incidence,

$$R=(m-1)^2/(m+1)^2 \quad (1)$$

The relative refractive indexes of silicon nitride and immersion liquid #1 and #2 are 1.17 and 1.13. For them, 0.61% and 0.37% of incidence light was reflected at each interface, respectively. Assuming that the granule is made transparent if 5% of incidence light were transmitted through specimen [3], number of interface allowed are 490 and 800, respectively. Recalling that the particle size of silicon nitride is 0.5μm and that light has to pass through two interfaces for each particle, the maximum diameter of granule allowed for transparency are estimated to be 120 and 200μm. This estimation does not agree to the experiment as shown in Fig.1. Granules could not be made transparent with immersion liquid #1 and only small one (<30μm) was made transparent with immersion liquid #2.

To explain the difference between estimation and experimental result, it is necesary to recall the second factor for light scattering. The maximum scattering occurs when the particle size is of the same magnitude as the radiation wavelength [7]. Particle size of silicon nitride (about 0.5μm) is close to the wavelength of white light used in optical microscope observation. The second factor is significant and reduces the maximum diameter of granule for which we can observe internal structure. We can similarly discuss the result on green body. The relative refractive index of silicon nitride and immersion liquid #4 is 1.01. Equation 1 suggests that reflection of light at each interface is 0.0025%. Assuming that direct transmission of 5% incident light corresponds to transparency, we can estimate the number of interfaces allowd to be $1.20*10^5$. The maximum thickness allowed for transparency is estimated to be about 30mm, which is much thicker than 0.2mm which was required for direct observation of internal structure.

CONCLUSIONS

The following conclusions are obtained:

(1) Silicon nitride granule was made transparent and its internal structure was successfully observed when the mixture of yellow phosphorus and methylene iodide, 4.5:5.5 by weight, were used as immersion liquid.

(2) Some interesting structures were observed in granule, e.g., small particles packed in a pore inside large granule.

(3) The internal structure in thinned(<0.2mm) silicon nitride green bodies could be observed with the ternary system of yellow phosphorus, sulfur and methylene iodide, 8:1:1 by weight, as immersion liquid.

(4) There were some narrow crescent-like void spaces in green bodies which were isostatically pressed at 100 and 600MPa. Their sizes were 50-100 and 30-60μm, respectively. They may cause heterogeneities in sintered bodies and deteriorate mechanical properties.

REFERENCES

1. Zheng, J., Reed, J.S., Effect of Particle Packing Characteristics on Solid-State Sintering. J. Am. Ceram. Soc., 1989, **72**, 810-17.
2. Uemastu, K., Kim, J.Y., Miyashita, M., Uchida, N., Saito, K., Direct observation of internal structure in ceramics:1. Spray-dried alumina granule. J. Am. Ceram. Soc., submitted for publication
3. Uematsu, K., Miyashita, M., Sekiguchi, M., Kim, J.Y., Uchida, N. and Saito, k., Direct observation of internal structure in ceramics:2. Alumina green bodies prepared by powder pressing, to be published
4. Uematsu, K., Kim, J.Y., Kato, Z., Uchida, N., Saito, K., Direct Observation Method for Internal Structure of Ceramic Green Body : Alumina Green Body as an Example, Seramikkusu Ronbunshi, submitted for publication
5. Tracy, C.E., Micromethod for Refractive Index Determination of Thin Films Using Liquid Standards, J. Electrochem. Soc., 1979, **126**, 103-6.
6. West, C.D., Immersion Liquid of High Refractive Index, Am. Mineral., 1936, **21**, 245-9.
7. Kingery, W.D., Bowen, H.K., Uhlmann, D.R., Chap.13 in Introduction to Ceramics, 2nd. Ed., Wiley, New York, 1976, pp646-706.