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Breakthrough in Evaluation Method for Packing Structure of Powders

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This paper shows innovative methods for examining the packing structure of powder particles in ceramic green bodies with the optical microscopy developed in our research group. They include, liquid immersion methods with normal and polarized light microscopy of visible and near visible infrared regions. All these techniques provide the information on the bulk and also on rare features, which are transformed into fracture origin of ceramics in sintering. The information is often much more detailed and useful than that given by conventional characterization tools. This paper will show both outline of the tools and typical structure in green compacts.
Key words; characterization, Packing, Powder, Optical microscopy, Ceramics

1. INTRODUCTION

Characterization of structure in all processing steps is very important for the production of ceramics. Especially, the packing structure of powder particles in green compact needs to be fully understood, since this is the most important factors, which govern the microstructure and thus the properties of sintered ceramics [1]. However, accurate characterization of packing structure has not been easy in green compacts. Conventional tools such as SEM and mercury porosimetry provide information only on characters which prevail in the green compact. They seldom show us unusual structures, which are directly responsible for the formation of detrimental defects such as large pores and cracks etc, one of which behaves as fracture origin in sintered ceramics. Inaccurate knowledge causes confusion in production and application of ceramics, and retards the progress of ceramics. New characterization tools are strongly needed to make a breakthrough in the production of ceramics.

This paper presents various new techniques of high potential, which are developed in our research group based on optical microscopy [2-10]. The specimens for examination are made transparent in these tools with an adequate immersion liquid, and the internal structure is observed in the transmission mode of microscope. Various types of microscope can be applied to examine the structures of interest. Table I summarizes the selection of proper microscope for their examination. They are all bulk examination and are best suited to examine special structures, which are extremely rare in green compacts. This paper presents The details of the tools and examples of structures clarified with these tools.

2. CHARACTERIZATION TOOLS

In these tools, the specimens are made transparent with an adequate immersion liquid and the internal structure is observed with an optical microscope in the transmission mode [2]. The selection of liquid is the key point of the tool, since it governs the degree of suppression of light at the interface. The reflection of light at the interface is governed by the ratio of refractive indices (RI) of relevant phases, i.e., the refractive indices of solid and liquid. No reflection of light happens when the refractive indices are the same for the solid and the liquid.

Table II shows refractive indices of various materials. Liquids with the RI under 1.79 can be made with safe chemicals only. For those with high RI, the liquid may be highly toxic. The highest RI attainable is around 2.05 in the liquid at the room temperature. In the visible light range, the refractive index of solid should be under this value. In the infrared region, the transparency is easily achieved. Infrared microscopy can extend the range of materials to be examined by the current tool [8,9]. With this tool, there is no practical limitation in the structural examination for systems made of fine powders. A slight disadvantage of IR microscopy is a slightly reduced resolution of optical image. Nevertheless, IR microscopy has very high potential since the size of important defects is very large. In the laser scanning microscope, fluorescent dye is dissolved in the immersion liquid, and its distribution is visualized. The image represents negative image of particles in the green compact at very high resolution; i.e., dark image corresponds to regions of high packing density of powder particle, and bright image the region of low density.

Table I Microscope used to examine various features in green compacts

Type of microscope	Features to be examined
Optical microscope	pores, cracks, additives (binder, etc.), foreign materials
Polarized light	large particles, particle orientation, aggregates
Infrared	pores, cracks, additives (binder, etc.), foreign materials
Laser scanning	pores, cracks, additives (binder, etc.), foreign materials, large particles

Table II Refractive indices of various materials

Materials	R.I.
Alumina	1.77
Zirconia	2.05
Solicon nitride	2.05
Silicon carbide	2.3
Bromo-naphthalene	1.69
Methyleneiodide	1.74
+Sulfur (saturated)	1.79
+Phosphor (saturated)	2.05

The requirement on immersion liquid varies with the observation method, i.e., the mechanism of image generation. With the polarized light microscopy, the best matching is desirable for refractive indices of the liquid and the solid. The quality of optical image increases with increasing transparency, since the optical contrast is developed by the anisotropy in optical property of solid. Liquid having slight mismatching of refractive index is needed to observe pores and cracks with the normal transmission mode. The optical contrast is generated by the residual scattering of light at the interface of liquid and solids. No structure can be seen when the matching of refractive index is complete. The requirement of refractive index matching is much reduced in IR microscope. The light with long wave length reduces the reflection of light at the interface. The best matching is needed in the examination of confocal laser scanning fluorescent microscopy.

3. STRUCTURES

3.1 Defects formed by presence of binder

Fig. 1 shows the normal optical micrographs of alumina compact made with the alumina powder granules with PVA binder, before and after the binder removal. The granule shape persists in the powder compact, forming network structure. Clearly, granules are not destroyed in the compaction. They are rather very well preserved; they are just deformed slightly to fill the space between granules. The deformation is different in parallel and normal to the pressing direction. The granules are nearly circular when viewed from the pressing direction. They are elliptical when viewed from the direction normal to the pressing. These difference of shape should be easily understood without explanation. The dark region disappears after the binder is removed by heating. Faint structure is left at the boundaries of granules. Clearly, binder forms regions of low density at the boundary and is detrimental for the production of uniform green compact. The mechanism of binder segregation on the surface of granules has been discussed elsewhere [12]. The

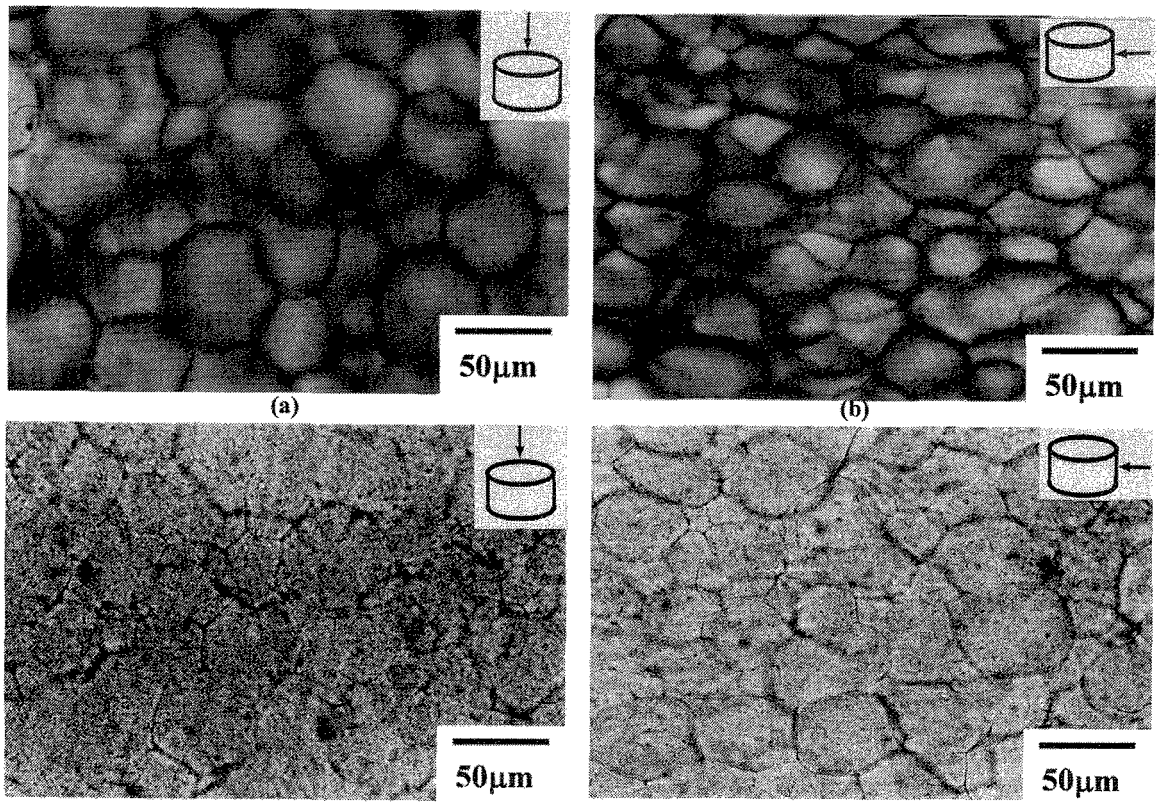


Figure 1 Liquid immersion micrographs of alumina compact before and after binder removal viewed from two Directions; (a) and (b) structure viewed from pressing direction before binder removal, (c) and (d) viewed from direction normal to pressing direction after binder removal

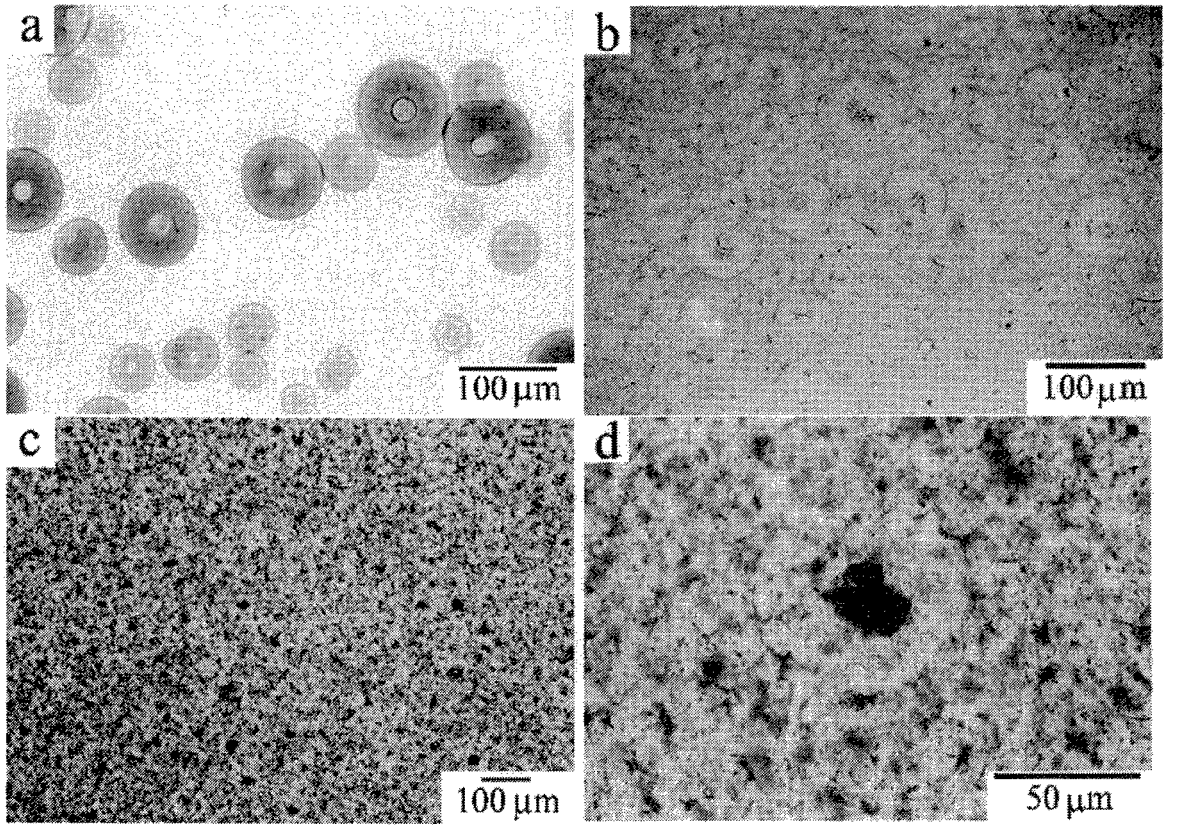


Figure 2 Liquid immersion micrographs showing the change of structure from granules to sintered alumina ceramics; (a) granules, (b) compact, (c) and (d) sintered body (low and high magnification)

binder appears dark due to a large mismatching of refractive index for binder/liquid interface. The added immersion liquid has a refractive index very close to that of alumina, and far apart from that of the binder. Organics, such as the binder has a refractive index much lower than that of alumina.

3.2 Defects formed by the defect in the granules

Fig. 2 shows another example of structures which was formed with the granules containing dimples [12]. These granules are typically formed through spray drying of well dispersed slurry. The structure is different from that of the solid granules used to produce the green compact in Fig. 1. The flocculated slurry tends to produce the solid granules. It is of interest to note, that the shapes of these granules are almost identical. Even the small granules contain dimples. This result must be very important to discuss the formation mechanism of these dimples in a future study. The traces of dimple are left in the green compact which was formed by uniaxial pressing at low pressure and subsequently CIPed at high pressure. Cracks are noted in some of the pressed granules in the compact. Many darks spots are noted in the sintered ceramics. Clearly, cracks located at the center of deformed granules grow in the densification period and develop defects in sintered bodies [13].

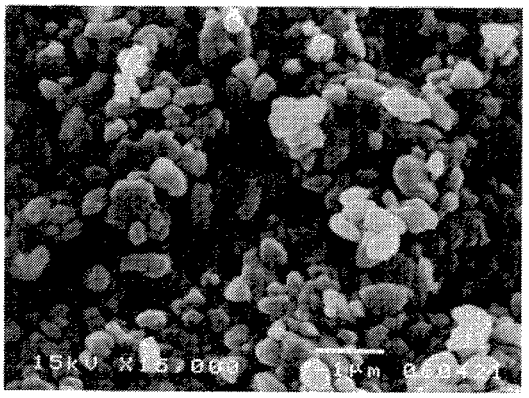


Figure 3 alumina particles

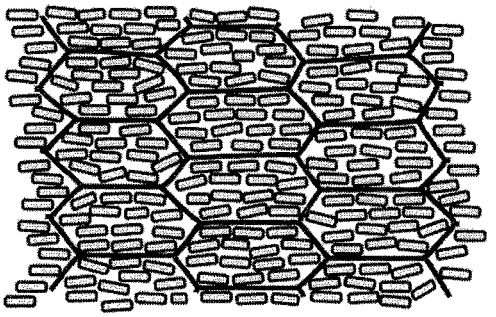


Figure 4 Particle orientation

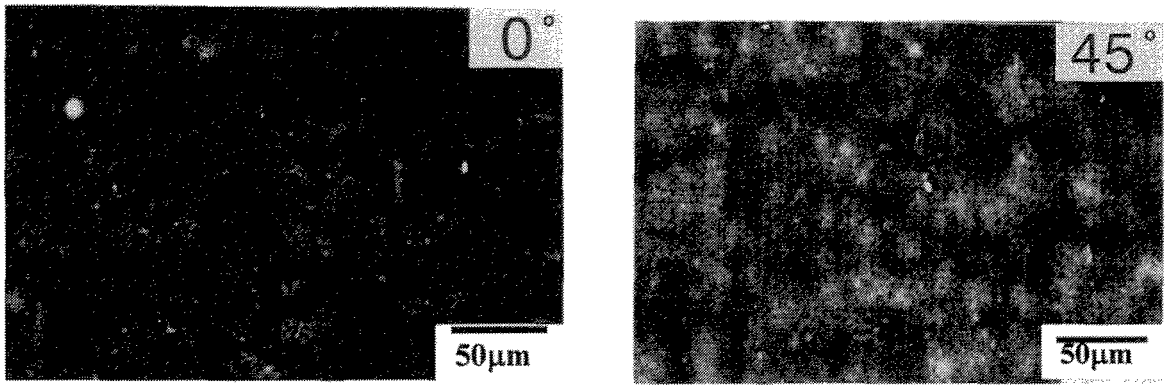


Figure 5 Crossed polarized light micrograph

3.3 Orientation of particles

Crossed polarized light microscopy is used to examine the particle orientation in a compact made of optically anisotropic material such as alumina, in which the particle shape is also anisotropic.

Fig. 3 shows the alumina particles which was used to produce the alumina compact, the liquid immersion micrograph of which was already shown in Fig. 1. Clearly, the particles are slightly elongated. In the uniaxial pressing, they may orient with their longest axis normal to the pressing direction in the compact as schematically shown in Fig. 4.

Fig. 5 shows the crossed polarized light micrograph of the same green compact, the internal structure of which is shown in Fig. 1. The micrograph clearly showed the dark-bright change of optical image. This result is understandable if one recall the polarized light micrograph of a single crystalline alumina. The green compact consisting of small oriented crystal should have the similar optical properties as that of single crystal. The result is consistent to the packing structure of Fig. 4.

Fig. 6 and 7shows another example of particle orientation in alumina green body made by injection molding process [6]. The expected structure is shown in Fig. 6(a). This structure of particle orientation is developed by the strong shear stress in the molding process. Alumina particles of slightly platelet shapes, which are typical for industrial grade low soda alumina, are aligned with their largest face parallel to the die wall due to strong shear stress near the wall. In the center region, the particles are randomly aligned, since no shear stress is present in this region.

These polarized light micrographs is consistent to this expectation. Large particles of elongated shape are aligned parallel to the surface of the body . The micrograph taken at the low magnification (Fig. 7) is consistent to the structure expected and deduced above. The dark cross is noted in the micrograph. The direction of cross was kept the same when the specimen is rotated under the microscope. This is understandable, since no change of structure should happen in the cross section of the specimen, which has the structure as shown in the schematics. The optical image should be the same for the same structure.

Two points should be emphasized. One is that the sintered structure is consistent to the green structure [7]. In the sintering period, the structure is emphasized and the particle alignment is more clear in the sintered body. Another point is that the alumina powder contains a small fraction of large particles. Their size appears very large relative to the average particles size. They may develop extremely large particles in the sintered body and may reduce the properties.

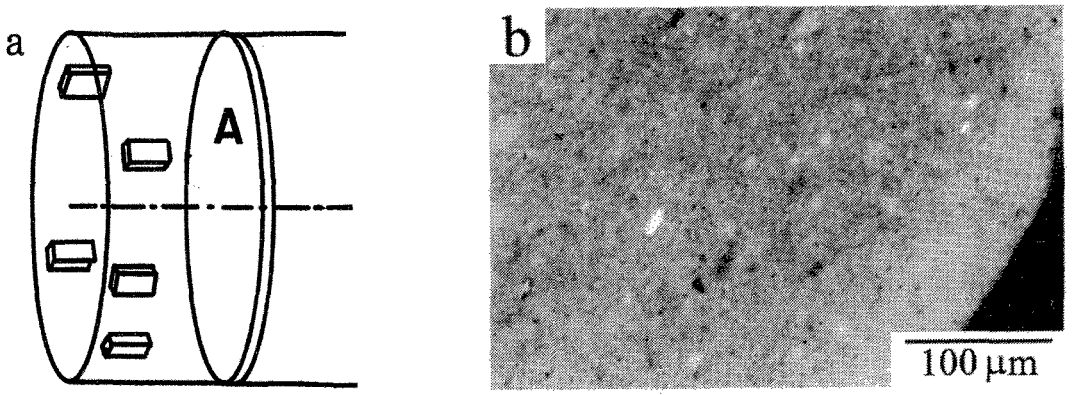


Figure 6 Structure of alumina body made by injection molding
(a) schematic structure, (b) structure near the rim examined by liquid immersion polarized light microscopy

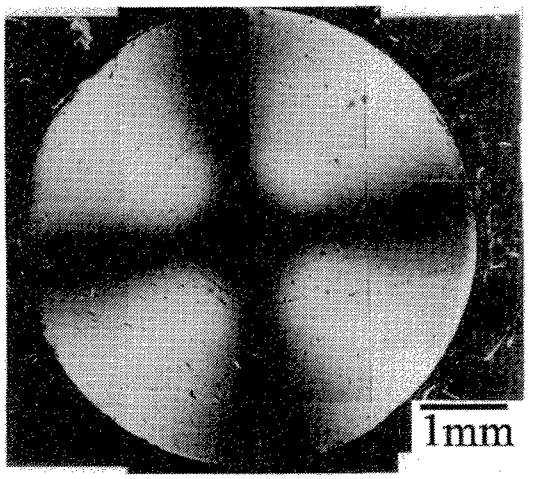


Figure 7 Crossed polarized micrograph of alumina made by injection molding

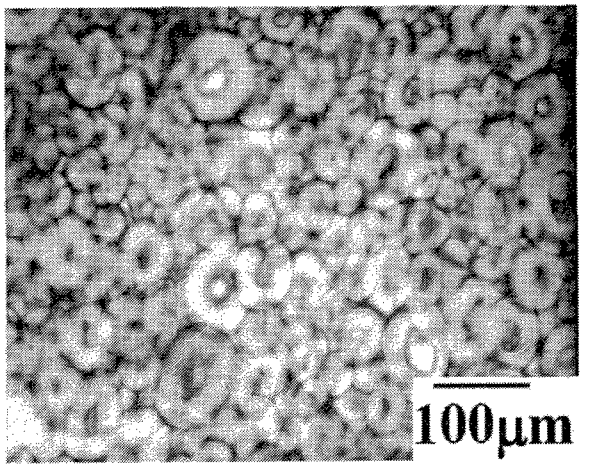


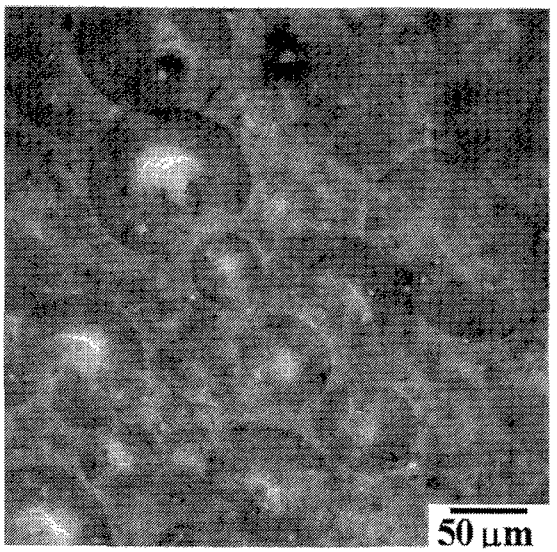
Figure 8 Infrared micrograph of silicon nitride compact

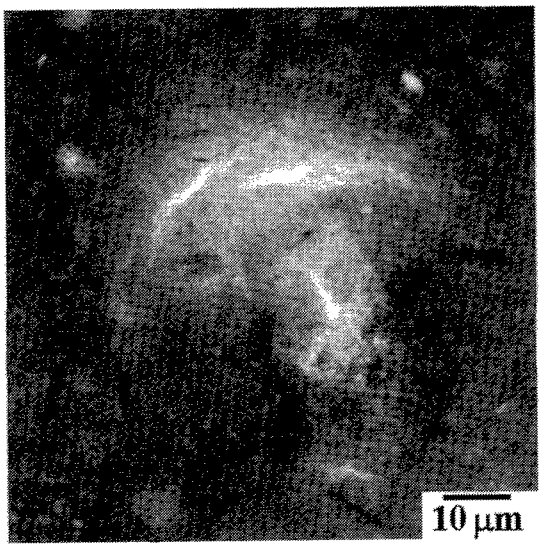
3.4 Infrared light microscopy for silicon nitride powder compact

Fig. 8 shows the infrared micrograph of silicon nitride compact made by uniaxial pressing [8]. This micrograph is much clearer than the corresponding micrograph taken with the normal optical microscope (not shown here). The transmission of infrared light is much higher than the visible light for the present system, where the refractive index is high and the particle size is comparable to the wave length of visible light. The structure observed in this micrograph is very similar to that of alumina. Cleary, the structure of compact made by pressing method is very similar regardless of the material. Another merit of IR microscope is that thick specimens can be examined [9]. This may open a new way for non-destructive evaluation of green compact.

3.5 Confocal Laser Scanning Fluorescent Microscopy

Fig. 9 shows the CLSFM micrograph of alumina compact[10]. The specimen is similar to that shown in Fig. 2. The structure is noted much more clearly and detailed. The cracks at the center of compacted granules are visible. The difference of brghtness at various regions in the microstructure shows the difference in the packing density of powder particles. In this microscopy, the brightness decreases as the packing density of powder particles increases. Cleary, the packing density is non-uniform in this green compact.





(a) (b)

Figure 9 Confocal Laser Scanning fluorescent micrograph of alumina compact

(a) Overall structure, (b) detailed structure for cracks

5. SUMMARY

Various kinds of microscopy were developed to examine the structure of ceramic green compacts. They have very high potential for detailed analysis of structure and are capable of revealing various kinds of structures in compacts for the first time. The detailed structure analysis directly shows that there are much to be controlled in the current processing of ceramics. Better control of processing can lead to production of better ceramics.

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