Infrared Microscopy as a Powerful Tool for the Examination of Internal Microstructure of Nano-Powder Compact
——Yttria Stabilized Zirconia as a Model——

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Abstract: Infrared (IR) light microscopy with liquid immersion technique was applied to examine the internal structure of granules and green compact of ZrO2 nano-powders, whose refractive index is 2.14. Internal structure could be easily observed despite the high refractive index by IR microscopy. This high transparency of the compact to IR light was ascribed to an increased ratio between the particle size 0.1 μm and wavelength λ=1.3 μm. Granule deformation is directly observed with this method for green bodies compacted under various pressures. IR microscopy combined with the liquid immersion technique is very effective for understanding the internal structure of compacted nano-powders.

Key-words: Infrared light, Microscope, Internal structure, Granule, Green body, Zirconia, Nano-powder

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1. Introduction

The internal microstructure in green compacts must be fully understood, because large defects in green bodies develop fracture origins in sintered body, and govern the mechanical properties of ceramics.1,2 We have examined the development of large defects in the processing of alumina ceramics with a unique evaluation method called the liquid-immersion microscopy (LIM).3-7 The compact is made transparent with an adequate immersion liquid in this microscopy and its internal structure is observed in the transmission mode of an optical microscope. That transparency of the compact was attained by suppressing the light scattering at interface of particle and liquid through a matching of the refractive indices for relevant phases. The needs for an adequate liquid limited the application of this characterization method. The LIM techniques could not be applied to ceramics with high refractive index for which no immersion liquid was available.8

Recently, this limitation of the LIM was removed by using an infrared (IR) light microscope with wavelength 1.3 μm for Si3N4 (refractive index = 2.04, particle radius).9 Long wave light can penetrate the specimen much more easily than visible light.9,10 Similarly, high light transmission should be also accomplished in a powder compact with the particle size much smaller than the wavelength. The infrared light microscope can be an effective tool for examining the internal structure of green compacts consisting of nano-powders with high refractive index.

This study explores wide application of the IR-LIM technique for examining the internal structure of green compacts made of nano-powders with high refractive index. The material subjected for the present study is yttria stabilized zirconia ceramics, which has excellent mechanical properties including superplastic deformation.11,12 It has a higher refractive index (n=2.15) than Si3N4, but has a very small particle size.

2. Experimental

The raw material used in this study was commercial zirconia (TZ 3YS, Tosoh Co., Ltd., Tokyo, specific surface; 8 m2/g) of nanometer size particles. Compact were formed by die pressing at pressures of 10, 30 and 100 MPa and heated at a temperature of 900°C for 1 h, for binder removal and also for enhancement of strength needed for handling. A thin sample of 70 μm thick was prepared by grinding a small piece of specimen with fine sandpaper (No. 1000) for observation. The immersion liquid used was a saturated solution of sulfur in diiodomethane, with the refractive index 1.79. This is a non-toxic liquid. The thin specimen was immersed in the immersion liquid and was evacuated for 5 min. The commercial IR microscope (Model BX50-IR, OLYMPUS, Tokyo) with IR camera (Model C2741, Hamamat Electronics, Hamamatsu) was used for observation. The maximum operating wavelength of IR camera was 1.8 μm. A filter was used to exclude light with λ < 1.3 μm. The structures of the granules and the compact were also observed by scanning electron microscope (SEM).

3. Results and discussion

Figure 1 shows SEM micrographs of the nano-powders of yttria stabilized zirconia. The primary particle size was about 100 nm or less. The particles have near equi-axed shapes. The primary particles appear to form secondary particles of the size a few tenth of micrometer.

![SEM micrographs of the nano-powders of yttria stabilized zirconia.](image)
Figure 2 shows SEM and IR–LIM micrographs for granules of yttoria stabilized zirconia. The granules have sizes under 100 μm and near spherical shapes. The spherical shape is often observed in granules made from flocculated slurry.\textsuperscript{10,11} The internal structure is observed for the granules with radius under \( \sim 50 \) μm in IR–LIM. Each granule appears solid without a big void with the infrared light microscope. Clearly the infrared light is effective for examining the internal structure of the granules consisting of nano-powders with high refractive index. The large ratio of wavelength of the infrared light to the particle size contributes to this high transparency of the granules. There is a large mismatching of refractive indexes of the particle and the immersion liquid.

Figure 3 shows SEM and IR–LIM micrographs of green body made with the above granules. These micrographs are taken from the direction perpendicular to die pressing. The fracture mode of the green body is mixed; trans- and inter-granular fracture were noted in the SEM micrograph. The structure is non-uniform; boundaries of granules are visible in some places. In the infrared light micrograph, the granules are clearly visible in the green compact. The granules remained in the spherical shape without fractured at 10 MPa in the compact. The inhomogeneous structure containing partially fractured granules will cause inhomogeneous densification in sintering, producing defects at interstices of granules. The structure in the present zirconia system is similar to those observed in alumina\textsuperscript{2,3,4,10} and silicon nitride systems.\textsuperscript{5,11}

Figure 4 shows the internal microstructure of the compact pressured at 30 MPa and 100 MPa. Again, the interstices between granules remain as black lines in the sample pressed at 30 MPa. The granules have elongated shapes in the compact. The granules look deformed more in the green body pressed at 100 MPa. The shape of granule is still noted and is more clearly seen than in the compact pressed at 10 MPa. Clearly, the transmittance of light through the compacts and thus the visibility of structure increase with increasing pressure. This result can be explained by the scattering of light caused by the pores at the interfaces of particles rather than the particles themselves. The suppressed pore
size and/or pore volume reduces the scattering. The IR-LIM is a powerful tool for observation of internal structure in the green body consisting of nano-powder.

4. Conclusions

Infrared light microscopy with liquid immersion technique has high potential to study the internal structure in the green compact with nano-powders. Even internal structure of high refractive index materials, internal structure in the green compact with nano powders was obtained by using infrared light. Change of granule deformation in the green compact with pressures is clarified with this method. This technique will be widely used to examine the internal structure of the nano-powder compacts.

References