

DIRECT OBSERVATION OF MICROSTRUCTURE CHANGE DURING DENSIFICATION OF SILICON NITRIDE CERAMICS WITH A NOVEL CHARACTERIZATION METHOD

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ABSTRACT

A novel characterization method is applied to study the evolution of microstructures during densification of silicon nitride ceramics. This characterization method involves an immersion liquid for making green and sintered bodies transparent, and a subsequent direct optical microscopic examination. Granules were prepared with the spray drying process and formed into green bodies by CIP. After sintering at various temperatures, the specimens were examined for microstructural evolution. Large pores were located at the center and boundary regions of granules left in the green bodies; they were not removed by densification and resulted in large pores in the sintered body, possibly forming fracture origin in ceramics.

INTRODUCTION

Defects are present in virtually all ceramics and govern various properties such as fracture strength.¹ Reduction in the concentration and size of defects is very important for the improvement of strength and reliability of high performance ceramics. To achieve this, it is necessary to fully understand the behavior of microstructural evolution during densification with particular focus on the behavior of large processing defects.

Behavior of large processing pores during densification has been a subject of both theoretical and experimental studies. Thermodynamic argument has shown that pores much larger than the surrounding grain are stable and grow during densification.² This argument was recently confirmed in alumina ceramics which were densified through the solid-state sintering process.³ It is very important to understand the behavior of processing pores in a liquid phase sintering process; since all important high strength ceramics, as well as functional ceramics, densify through the liquid phase sintering process.

This paper presents the direct observation on the behavior of processing pores during liquid phase sintering in silicon nitride. This is a representative high performance ceramic, and the formation mechanism of fracture origin is of great practical interest. Following the previous study,⁴ we have adopted the liquid immersion method for characterizing pores in green and sintered bodies. In this method, specimens were made transparent with an immersion liquid and were examined with a transmission optical microscope. This microscope provides clear, semi-three dimensional macro-and microstructural information otherwise difficult to obtain by any other method. Its characteristically large examination volume provides accurate information on features of very low concentration, such as fracture origins. The information obtained is also very objective. Mercury porosimetry and SEM observation were also applied to provide supplemental characteristics of micro-pores and high resolution images.

EXPERIMENT

Materials used in this study were all commercial grade. Silicon nitride (Ube, SNE-10) powder containing 5 wt% alumina and 5 wt% yttria as sintering additives (5 kg) and deflocculant (150 g) were mixed with pure water (3.5 kg) by an attrition mill. After adding a binder (equivalent solid content: 0.375%) and passing through a sieve (320 mesh) to remove foreign objects, the slurry mixture was spray dried to form granules. The granules

were mold pressed into pellets at 20 MPa and subsequently cold isostatically pressed at 150 MPa. The pellets were then heated ($10^{\circ}\text{C}/\text{min}$) to various temperatures and quenched. For structural examination, the granules were placed on a slide glass of the optical microscope and made transparent with a drop of immersion liquid (refractive index: 2.05, Cargille, New Jersey, USA). These transparent granules were then examined under an optical microscope in the transmission mode. In addition, the partially sintered specimens were thinned to a few tenths of a millimeter with sandpaper, then made transparent with the immersion liquid, and subjected to the same optical microscopic examination as above. Phases present in the specimens were examined by the powder x-ray diffraction method. The microstructure was examined by the conventional SEM technique. Micro-pores were examined by mercury porosimetry.

RESULTS

Figure 1 shows the structure of powder granules prepared in this study. They have a basically spherical shape and wide size distribution. A majority of granules contain deep dimples. A dimple seen from its top appears as a light small round feature in the center of a granule. The side view shows that the dimple is very deep and penetrates almost entirely through the granule. The dark circumferential region outlining each granule corresponds to the binder segregated at the surface of the granule. The binder can only be seen when viewed from the tangential direction. Small dark spots in the granules correspond to the particles of sintering additives which have a refractive index different from that of silicon nitride.

According to x-ray diffraction, the major phase in the specimen was alpha-silicon nitride at temperatures up to 1650°C and was beta-silicon nitride at 1750°C . Only beta-silicon nitride was found at 1800°C . Figure 2 shows the change in relative densities with sintering temperature. The densification started at about 1350°C . It became very rapid in the temperature range of 1450 – 1650°C and slowed down at higher temperatures. Note that the specimens were quenched immediately after reaching these temperatures. The maximum relative density of 97% was achieved by sintering for 1 h at 1800°C .

Figure 3 shows the change in microstructures with densification, which was examined by the liquid immersion technique. Pores can be observed as either light or dark parts, depending on whether air was trapped during liquid immersion; pores with air trapped appear dark, and those without air light. Except for the trapped air and/or immersion liquid, the pores were empty; they were not filled with liquid phase which is formed by the reaction between sintering additives and silicon dioxide. In the temperature range of zero shrinkage, the granules retain their spherical shape. Pores in the central region of the granules also remained in tact. With densification, the boundaries between granules became less clear and

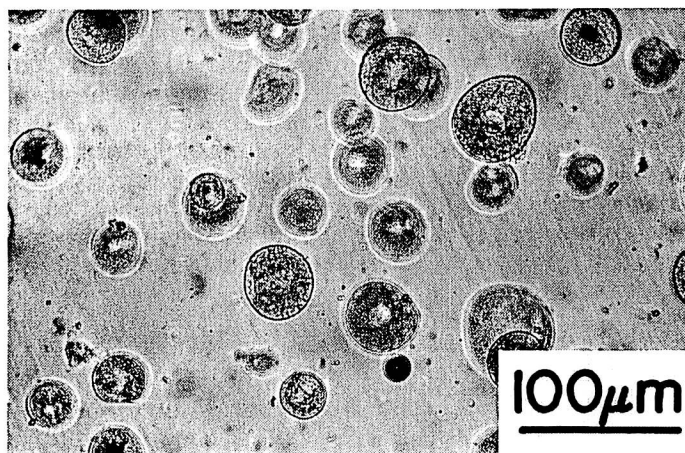


Fig. 1 Structure of powder granules examined by the liquid immersion technique.

pores at the boundaries of the granules became rounded. The pore in each granule was not removed and its shape remained almost the same during the densification process. The specimen resulted in a unique structure which is characterized by regularly arranged pores of similar size.

Figure 4 shows a SEM micrograph of a specimen sintered at 1800°C for 1 h. The structure in Fig. 3 is again present in this micrograph. Pores originated by the pores in the center of granules are arranged in the same regular manner as in the green and partially sintered bodies. The spacing between them was again approximately several tens of microns. Smaller pores were also found at the boundaries of the granules. The pore volume estimated with this micrograph was approximately a few percent, suggesting that the matrix of the specimen was fully dense except for these large pores.

Figure 5 shows the change in pore size distribution with densification. There are two groups of pores. One is centered in the submicron region and constitutes the majority of the total pore volume of the specimen. The other is large pores in the ten to a hundred micron region. The volume of large pores was so small that it was difficult to characterize them accurately in this figure. With densification, the pore volume of the first group decreased without noticeably changing the pore size while the pore volume of the second group was virtually unaffected.

DISCUSSION

Clearly the processing pores formed in the central and boundary regions of the granules cannot be removed by the compaction process nor the densification process in liquid phase sintering. The large pores at the center of the granules do not change their shape appreciably in densification. Medium-sized pores located between granules changed their shape and were rounded after densification. Small pores between primary particles can be eliminated according to mercury porosimetry. These small pores constitute the majority of pore volume in the green body, and their removal gives rise to the density increase in sintering.

These behaviors of large- and medium-sized pores are similar to what was found for alumina in solid state sintering³ where large pores were also stable and could not be removed in densification. The monotonous decrease in the volume of small pores with sintering was different from what was found in solid state sintering; in alumina, small pores grew with densification before final removal. The behavior was explained by the presence of an agglomerate. The thermodynamic argument presented in past papers also holds true for the stability of large pores; the curved solid-gas interface provides a driving force for pore growth in large pores. Likewise, a curved interface for small pores provides a driving force for pore shrinkage.² The slight difference in the behaviors of pores in alumina vs. silicon nitride can be attributed to the sintering mechanism.

The large pores were clearly empty during densification. The liquid phase formed by the reaction between the sintering additives and silicon dioxide is absent in the large pore. This

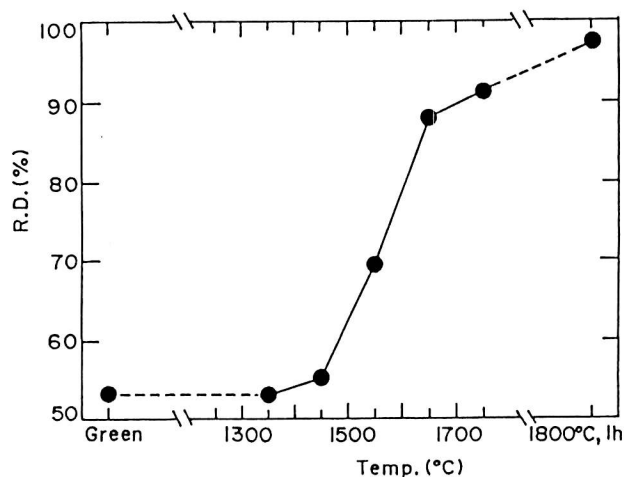


Fig. 2 Change in relative density with sintering.

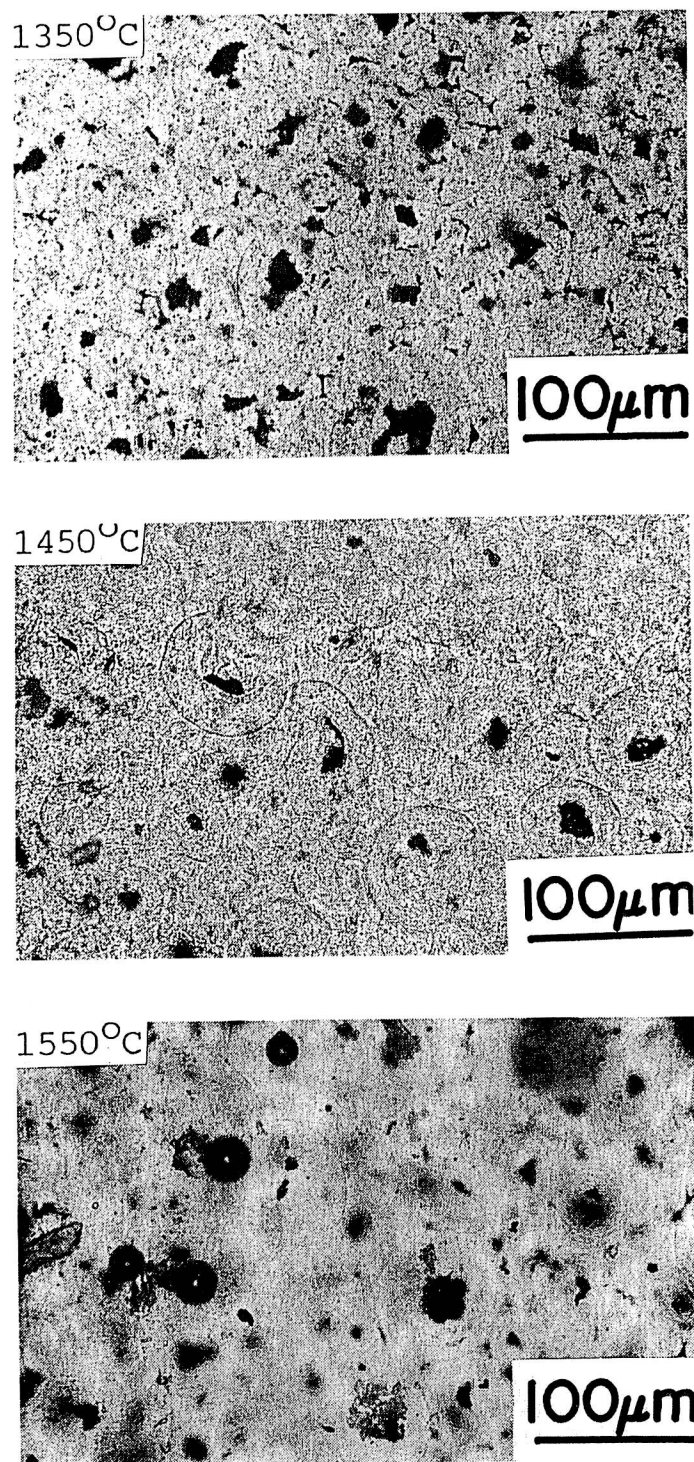


Fig. 3 Change in microstructure with sintering.

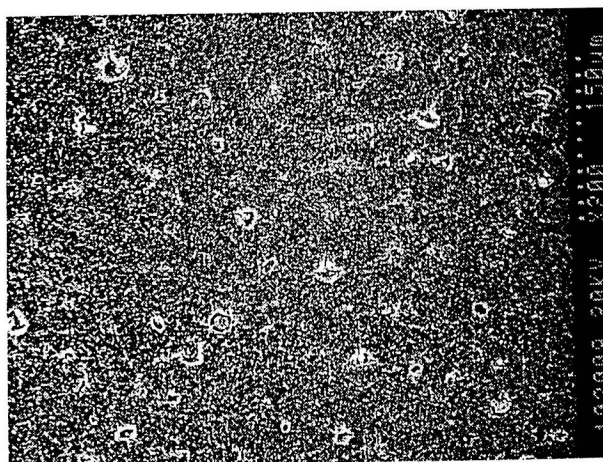


Fig. 4 Microstructure of specimen after sintering.

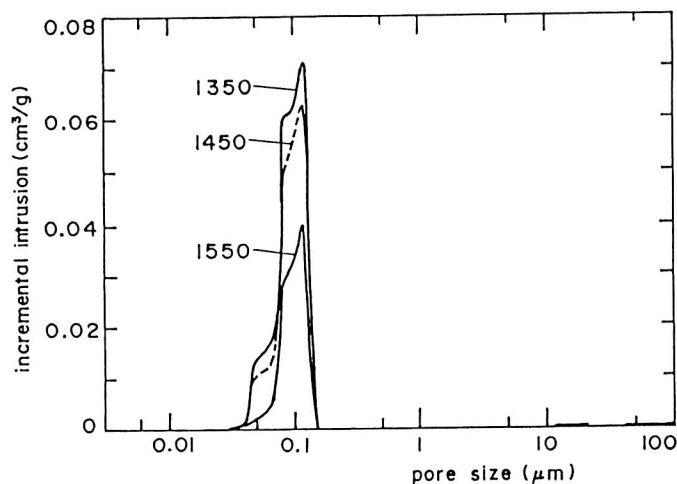


Fig. 5 Change in pore size distribution with sintering.

result is understandable when we consider the capillary force acting on the liquid; liquid is pulled into small pores since its thermodynamic stability is increased with this process if it wets the surface of the silicon nitride particle.

In the final microstructure, large scale non-uniformity originally present in the green body is preserved. Large pores in the sintered body are inherited from the large pores in the green body. The main origins of these large pores are dimples in the granules and pores formed at the boundaries of the granules. Large pores in ceramics behave as strength-limiting flaws. In the present specimen, a rather uniform strength is expected since fracture origins of similar size are uniformly distributed. The specimen is expected to have a low to medium level of strength with a high m -value in the Weibull plot. This result provides a guideline for producing high-strength ceramics. However, special efforts are needed to achieve a green body free of large scale non-uniformity.

CONCLUSION

The following conclusions were reached from examination of the microstructural evolution in silicon nitride ceramics:

- (1) Large processing pores were present at the central and boundary regions of granules in the green body, which was formed from granules containing pores.
- (2) These processing pores were stable and not removed by sintering. They remain as large pores in the sintered body.
- (3) These large pores are distributed with regular spacing in the sintered body and reduce the strength of the ceramic.
- (4) Large pores are empty; they are not filled with the liquid phase formed by the reaction between the sintering additives and silicon dioxide.

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