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Influence of Pore Structure in Green Compacts on the Densification of $SiC–Al_2O_3–Y_2O_3$

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Abstract: Pore size, pore size distribution (PSD), and the resultant densification behavior of α-SiC granular compacts, which were shaped under the uniaxial compaction pressure of 6.8–154 MPa, were investigated. Three kinds of SiC granules were used, namely Powder R (as-received spray-dried granules), Powder C (after classification of the Powder R), and Powder G (after grinding of the Powder R). Experimental results showed that at low compaction pressures, the green compacts derived from Powder R and Powder C exhibit a bimodal PSD, which is primarily caused by the presence of intergranular porosity. At relatively high compaction pressures, all of the green compacts display a roughly similarly unimodal PSD and exhibit a similar densification behaviour regardless of the starting granule characteristics. The green compacts with a narrow and unimodal PSD can be easily densified to a high-density sintered body and this behaviour was particularly pronounced for the green compacts derived from the ground granules even when the applied compaction pressure is relatively low. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

In the consolidation of ceramic powders, it is well-known that the characteristics of powders strongly influence their consolidation behaviour and the resulting green compact microstructure. The microstructure of the powder compacts has a profound effect on the subsequent sintering behaviour and on the resulting microstructure homogeneity of the final sintered body. A conventional technique for the fabrication of high-density and high-quality ceramic body is colloidal processing.[1] However, in industry production, dry-pressing is probably the most widely-used technique in the consolidation of powders, in spite of its disadvantages for the fabrication of high-reliability ceramics compared with the colloidal processing route.[2]

Densification of consolidated powders is an essential process of removal of voids within the green compacts. Hence, the size and spatial distribution of the pores should be considered as two important indicators for the green microstructure homogeneity and subsequent sintering behaviour. A number of investigations have indicated that a homogeneous pore size distribution in green compacts is responsible for the resulting microstructure homogeneity.[3–5] Recently, Galakchov and Shevchenko[6] have pointed out the significance of pore structure inhomogeneity on the strength and reliability of sintered ceramics. They indicated that the presence of intergranular porosity in the green compacts is the major cause of strength degradation for the sintered body. In this investigation, experiments were carried out to elucidate the pore structure inhomogeneity and the related densification behaviour in a $SiC–Al_2O_3–Y_2O_3$ ceramic, which has recently been reported to exhibit prominent mechanical properties,[7,8] by using three kinds of starting SiC granules consolidated under different uniaxial compressive pressures.

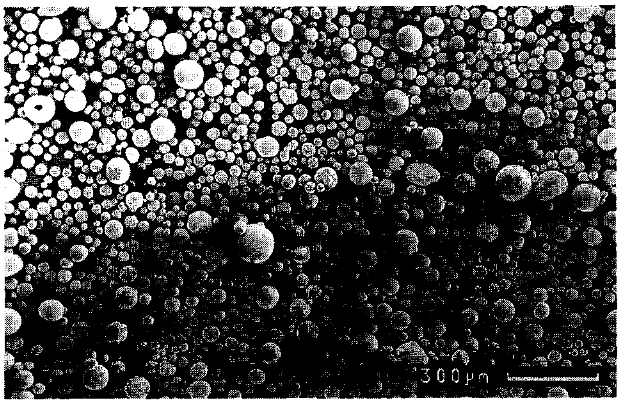

Fig. 1. SEM image of the spray-dried SiC granules, namely Powder R.

2 MATERIALS AND PROCEDURES

Three kinds of SiC granules, which consisted of 90% α-SiC (Showa Denko, Japan), 6.2% Al_2O_3, and 3.8% Y_2O_3, were employed. Each kind of granule has its own morphology; the first is the spray-dried granule (Fig. 1) which has a spherical appearance but was wide-spread in size fractions (from 120 to 400 mesh), namely Powder R. The second one was obtained by classification of the Powder R into a narrow size fraction of 150–180 mesh, namely Powder C. The third one was obtained by vigorous hand-grinding of the Powder R (Fig. 2), namely Powder G. These granules were consolidated separately into green compacts using a conventional single-acting die-pressing method with varying compaction pressures from 6.8 MPa to 154 MPa.

Mercury penetration porosimetry (Autopore, Model 9220) was used to detect the pore size and pore size distribution of the green compacts. To calculate the pore size distribution, a mercury surface tension of 485 dyn/cm and a contact angle of 130° were assumed. Part of the green compacts were sintered at 1900°C for 2 h, then the temperature was increased to 2000°C for 30 min in Ar atmosphere. Three to five specimens were used to determine the sintered density of SiC by means of the Archimedes' principle.

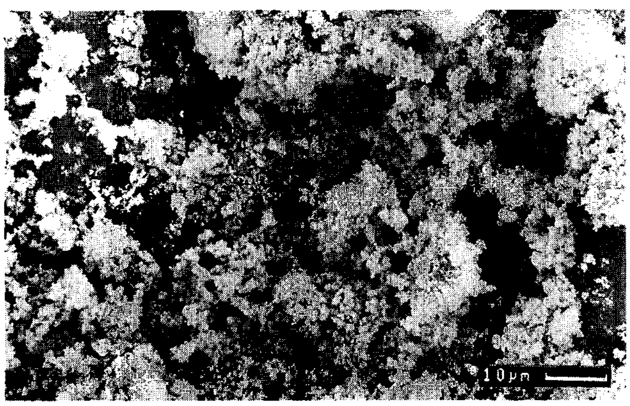

Fig. 2. SEM image of the ground SiC powders, namely Powder G.

3 RESULTS AND DISCUSSION

Figures 3(a)–(c) show the pore diameter–incremental volume of mercury profiles of the green

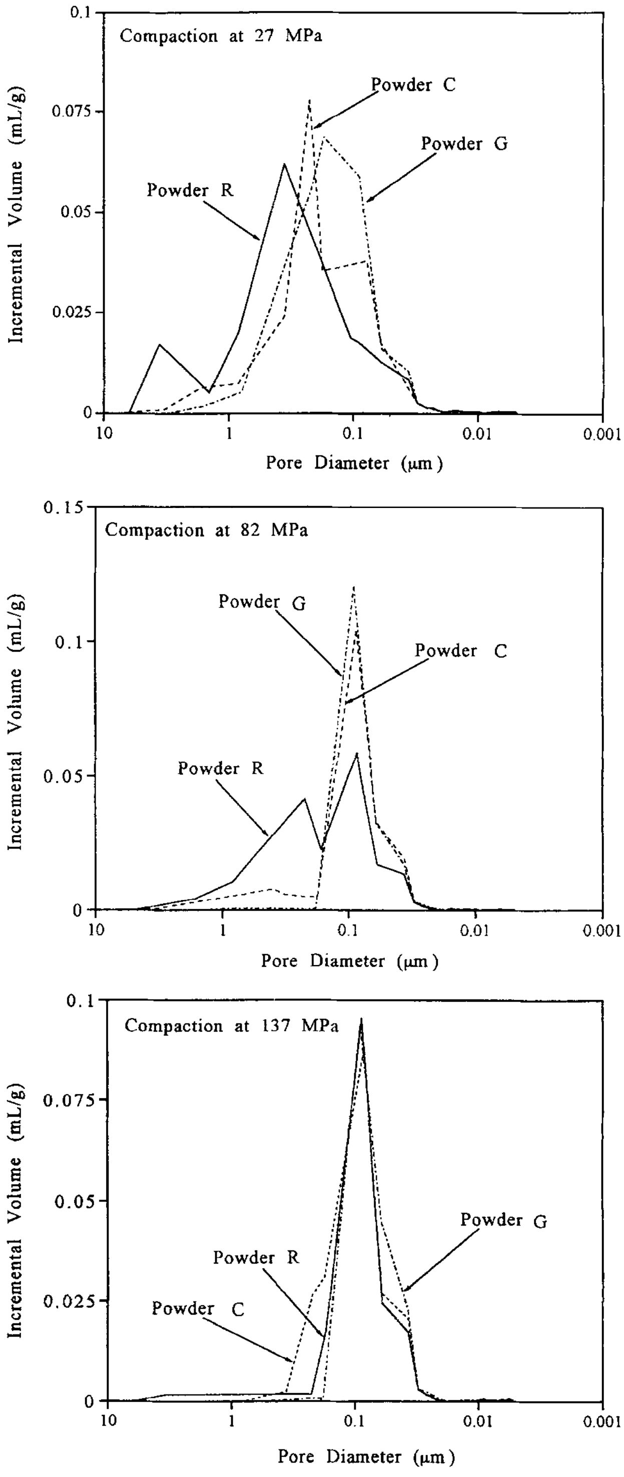

Fig. 3. The pore size distribution of the green powder compacts consolidated at (a) 27 MPa, (b) 82 MPa, and (c) 137 MPa for different types of SiC granules.

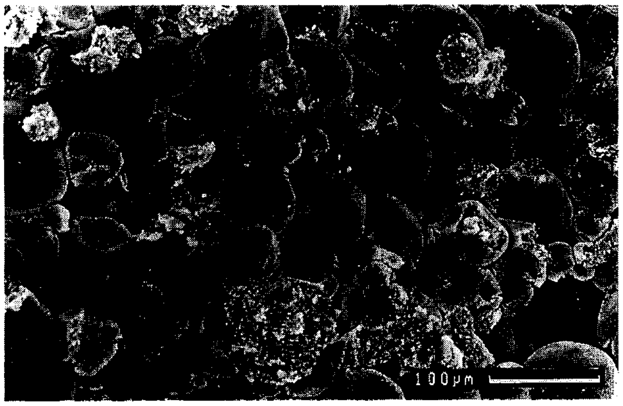

Fig. 4. Intergranular voids exist at lower compaction pressure.

compacts derived from different starting granules under compaction pressures of 27 MPa, 82 MPa, and 137 MPa, which are defined here as low, intermediate, and high compaction pressures, respectively. Obviously, the pore size distribution (PSD) of the green compacts is a function of the starting granule characteristics at a fixed compaction pressure. At low pressure, i.e. 27 MPa, both the unclassified (Powder R) and classified granule (Powder C) compacts reveal a bimodal PSD but the pore size frequency is different. The former compact contains a greater population of larger pores, here defined as pores > 1 μm, than the latter one. The large pores within the green Powder R compacts are primarily intergranular pores, particularly for those interstices among undeformed and/or unfractured granules (Fig. 4). The population of pores lying between 0.1 μm and 1 μm may arise from the interstices among deforming or slightly fracturing granules, or the voids among particle agglomerates in each single granule. Such particle agglomerates probably originated from an initially not well-dispersed ceramic slurry. The pores with a much smaller size, e.g. a pore diameter $\leqslant 0.1$ μm, are intragranular or interagglomerate pores. However, although the classified granular compacts (Powder C) also show a bimodal PSD, the large pores defined earlier are barely found, instead, the most frequent pore size is approximately 0.3 μm. This is because granules with a narrower size distribution and relatively larger size crush more easily at a given compaction pressure than the same kind of granules with a broader size distribution.[9,10] Therefore, in the green Powder C compact, most of the intergranular pores are removed by granular deforming and fracturing mechanisms,[11] resulting in a greater population of small pores. Although it shows a unimodal PSD, the ground granular (Powder G) compact exhibits a broad PSD indicating the interparticle distance is still relatively large. It also suggests the existence of some particle agglomerates within the compacts.

Increase of the compaction pressure to 82 MPa, the Powder C and Powder G compacts show a unimodal and narrow PSD, suggesting that the intergranular voids (for Powder C) have disappeared and the raw particle packing and interparticle distance in these compacts are similar. The most frequent pore size in the PSD is reduced with increasing pressure indicating the decrease of the interparticle distance. The majority of the pore sizes are approximately 0.1 μm. In comparison, the green compacts derived from the unclassified granules (Powder R) show a bimodal PSD; with a main peak at 0.09 μm and a subpeak at 0.2 μm. The formation of the subpeak in the PSD suggests that some granules with substantial difference in size may deform or fracture only slightly leaving the presence of small voids.

At relatively high pressure, the PSD of the green compacts is almost similar (Fig. 3(c)) irrespective of the initial difference in the granule characteristics. The most frequent pore size of these green compacts is roughly the same, i.e. 0.09 μm, which is close to the size observed in Fig. 3(b) for the ground and classified granule compacts. If a pore size equal or below 0.09 μm corresponds to a narrow packing of the raw particles, Fig. 3 suggests that most of the particles are packed closely at low pressures for the ground and classified granules, but a much higher pressure is needed for compaction of the unclassified granules in order to achieve a dense particle packing configuration.

The median pore diameter was calculated automatically by a computer by assuming a contact angle of 130° in the Washburn equation. The median pore diameter decreases linearly with increasing compaction pressure, Fig. 4, for both classified and unclassified granules. This linear dependence of the median pore diameter–compaction pressure behaviour closely resembles that observed in the compaction of spray-dried alumina.[9] Although the compaction of dry ceramic powders is rather complex in its detail, this gross behaviour appears to be simple and is consistent with the well-established mechanics of the compaction of granular media. However, a non-linear median pore diameter–pressure dependence results in the compaction of the ground granules. The reason for such a non-linearity is not well understood at present. The difference in the compaction mechanism between the ground granules (they are actually in the form of raw particles) and the well-defined granules (i.e. powder in its granule form) may be one of the possibilities.[11]

After sintering of the green compacts, the resultant fired densities of the ceramics were determined (Table 1). Clearly, an increase of the compaction

Table 1. Influence of compaction pressure and granule characteristics on the densification of $SiC–Al_2O_3–Y_2O_3$ ceramic. Densities are expressed by % of theoretical density, 3.25 g/cm^3

Granules	16 MPa	27 MPa	83 MPa	137 MPa
Powder R	92.9 ± 1.3	95.0 ± 2.0	96.8 ± 2.3	97.3 ± 1.5
Powder C	92.6 ± 1.9	95.1 ± 2.2	96.9 ± 1.6	97.0 ± 0.9
Powder G	97.7 ± 1.6	97.8 ± 1.6	98 ± 2.1	97.9 ± 1.1

pressure increases the green density of the compacts, and consequently enhances the fired density for both Powder C and Powder R compacts. However, for the Powder G compacts, the compaction pressure appears to have no influence on the fired density. A fired density of approximately 98% of theoretical can be obtained easily for the ground granular compacts, even under compaction pressure as low as 16 MPa.

Since the densification is primarily a process for the removal of voids or pores in the green compacts, the size as well as the size distribution of the pores in the green microstructure play critical roles in the sintering process. Zheng and Reed [12] have reported that the micropores can be completely eliminated but the size of the larger pores increases during sintering. A comparison between Table 1 and Fig. 3 suggests that the lower fired densities at lower compaction pressures for both the classified and unclassified granular compacts are primarily the result of the presence of intergranular porosity as observed by Galakchov and Shevchenko.[6] Therefore, it may generally be concluded by a direct examination of the PSD in the green compact that SiC ceramic with a high sintered density can hardly be obtained if the green microstructure contains a bimodal or broader PSD, even with the aid of a liquid-phase sintering mechanism.[7] In contrast, a green microstructure containing a narrower PSD and small-sized pores is primarily responsible for obtaining a $SiC–Al_2O_3–Y_2O_3$ ceramic with high sintered density.

4 CONCLUDING REMARKS

The influence of pore size and pore size distribution on the densification of an SiC ceramic was investigated using SiC granules with different granular characteristics. For the classified and unclassified spray-dried granules, a bimodal PSD, primarily due to both intergranular and intragranular pores can frequently be observed at lower compaction pressure. This leads to a lower sintered density. Increase of compaction pressure yields green compacts with an improved homogeneity of the green microstructure, resulting in higher sintered density. However, for the ground granular compacts, the compaction pressure shows little or no influence on the sintered density and seems to be a result of the pore structure homogeneity.

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