Applying Pressure Dependence of Structural Homogeneity of Cold Isostatically Pressed and Sintered Silicon Carbide

Osami ABE*
Government Industrial Research Institute, Nagoya,
1-1 Hirate-cho, Kita-ku, Nagoya 462 JAPAN

Abstract:

Influence of applying pressure on structural homogeneity of cold isostatically pressed (CIP-ed) green compacts and sintered bodies of SiC has been studied. The compaction progressed through two processes with different pressure dependence at low and high pressure regions. Remarkable inhomogeneity was induced in the green compacts at the border applying pressure between the two processes, and resulted in the degradation of reliability of strength of sintered bodies. By applying high CIP-ing pressure, the green compacts showed a dual structure consisted of a homogeneous inner core and a high-microhardness outer shell. High reliability of strength was obtained by sintering the dense and homogeneous green compacts after removing the thin outer shell. The improved reliability was derived from preventing inhomogeneous densification and pore growth during sintering. There was a critical pore size to prevent the pore growth.

[**Key words** : Cold isostatic pressing, applied pressure, SiC, sintering behavior, mechanical properties]

1. INTRODUCTION

It is well known that dense sintered materials with excellent properties are efficiently derived from dense and homogeneous green compacts.$^{1,2)}$ Cold isostatic pressing (CIP-ing) is one of the most important forming techniques to obtain such green compacts. Some improved CIP techniques such as high-pressure CIP-ing$^{3,4)}$ and cyclic CIP-ing$^{5-7)}$ have been proposed to emphasize an advantage for forming dense compacts. However, only a few study$^{3,4)}$ have been

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* Present address : Department of Materials Engineering, Ibaragi University, 4-11-2 Nakanarusawa, Hitachi 316 JAPAN

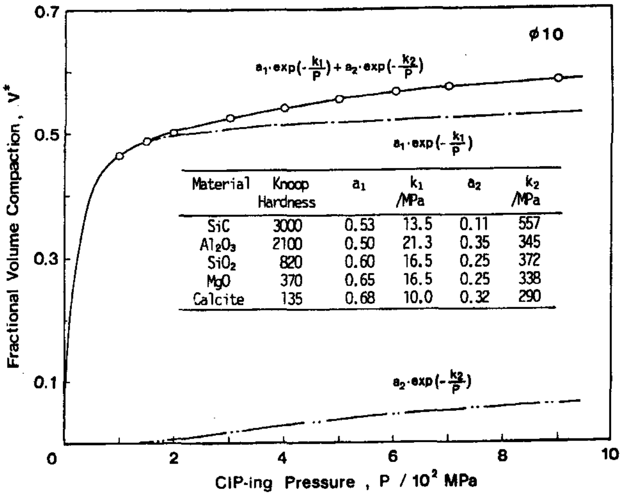
made on the other advantage of structural homogeneity on CIP-ing, although the homogeneity have frequently been referred on the fabrication processes of advanced ceramics. For CIP-ing of fine "sub-micron" ceramic powders, increased friction among powder particles would reduce the applied compaction pressure, and cause a reduction of density and inhomogeneous microstructure inside the green compacts.8) This suggests inhomogeneous densification and resultant degradation of properties of sintered bodies, especially the reliability. This kind of inhomogeneity has particularly to be taken into account for the fabrication of non-oxide ceramics for engineering applications, where the structural inhomogeneity in green compacts is apt to remain in sintered bodies and degrades the mechanical properties sensitive to defects induced because of the poorly sinterable nature.

In the present paper, structural homogeneity of CIP-ed and sintered SiC and resultant mechanical properties have been concluded. The compaction process was initially discussed from the applying pressure dependence of green density, Vickers microhardness, and pore size distribution. The structural homogeneity was estimated from density and microhardness distributions along the cross section of relatively large cylindrical compacts. The mechanical properties of sintered cylinders have also been discussed. Finally, the structure of green compacts was related with sintering behavior and microstructural development.

The powder used was high purity β-SiC (Ibiden Co., Ltd., β-UF) with the oxygen content of 0.75 wt% and the specific surface area of 21.3 $m^2\ g^{-1}$. The particles had irregular shape with the size of 0.1-0.2 μm and formed soft agglomerates dispersible by ultrasonic vibration in water. The powder with or without sintering aids was mechanically prepressed and CIP-ed (Ishikawajima-Harima Heavy Ind. Co., Ltd., CIPI-800). The detailed experimental procedure was presented in the previous papers.3,4,8-10)

2. Compaction Process of Silicon Carbide Powder

To study the compaction process, small discs ($\phi 10 \times 3^t$) were CIP-ed and analyzed by using Cooper's relation.11)



Material	Knoop Hardness	a_1	k_1 /MPa	a_2	k_2 /MPa
SiC	3000	0.53	13.5	0.11	557
Al_2O_3	2100	0.50	21.3	0.35	345
SiO_2	820	0.60	16.5	0.25	372
MgO	370	0.65	16.5	0.25	338
Calcite	135	0.68	10.0	0.32	290

Fig.1 Fractional volume compaction of o10 compacts, circles: experimental, lines: fitting to Cooper's equation.

$$V^* = a_1 \exp(-\frac{k_1}{P}) + a_2 \exp(-\frac{k_2}{P}) \qquad (1)$$

V^* : Fractional volume compaction
P : Applied pressure
a_1, a_2, k_1, k_2 : Numerical constants

Figure 1 shows the result of fitting to Eq.(1) and obtained numerical parameters. The profiles and the parameters indicated greater contribution of the initial term in Eq.(1) to the compaction ($a_1 > a_2$) and stronger pressure dependence in the second term ($k_1 < k_2$). These features were remarkable for the SiC powder more than the other ceramic powders shown in **Fig. 1**. The parameters deviated from the dependence on hardness described by Leiser et.al.,12) where k_1 and k_2 increased with hardness. The contrary low k_1 and irregularly high k_2 values for SiC in spite of the high hardness suggested a different compaction mechanism from Cooper's definition of particle rearrangement for the initial term and plastic deformation for the second term. From the increased ability for fine powders to agglomerate13,14) and the low k_1 value, it was considered that the initial term represented the compaction process through the deformation of agglomerated structure with less dependence on pressure (Process I) at the low pressure

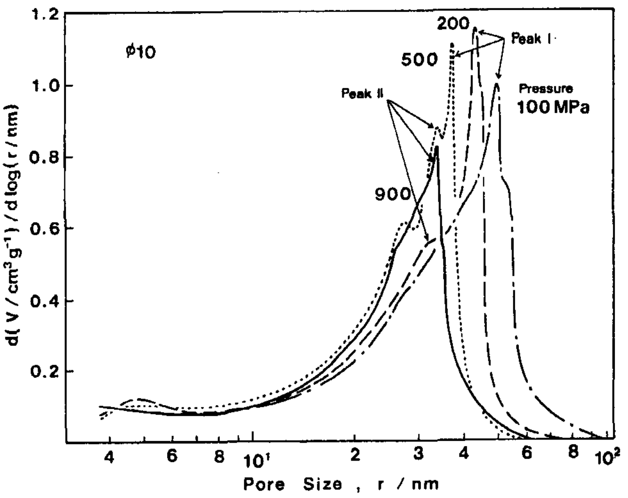


Fig.2 Pore size distribution of o10 compacts.

region. With the increase in pressure, the contribution of the initial term was saturated and the contact of hard primary particles caused the less efficiency of compaction and strong pressure dependence as indicated by the low a_2 and high k_2 values, respectively (Process II).

The pore size distribution in **Fig. 2** showed the variation supporting this consideration on the compaction process. At the low pressure region, the peak pore size decreased with the increase in pressure as indicating the deformation of soft agglomerates. Another peak around 30 nm appeared at 200 MPa, and became remarkable at 500 MPa. The pore volume reduced without decrease in the peak pore size at 900 MPa. The direct contact of hard primary particles would cause the difficulty in the reduction of pore size in Process II.

The direct contact would induce contact stress among SiC particles with high friction coefficient. The bridging and wedging would also be induced in the compacts depending on the irregular shape and size distribution of the powder. **Figure 3** shows Vickers microhardness as a function of green density. At 1000° C, where the pore size distribution was unchanged from the as-CIP-ed compacts,8) the density dependence showed a positive deviation from a linear relation. The increase in microhardness became remarkable at the pressures above 300 MPa (Process II, green density : > 59.4 %TD). By considering that hardness is a parameter indicating resistance to practically plastic deformation for green compacts identically with brittle materials as described by Tabor,[15) the increase in microhardness indicated the rise in contact stress induced by the increased density and friction in Process II. After a heat treatment at 1300° C, the microhardness values in Process I irregularly increased in contrast to the slight increase in Process II. This was caused by the inhomogeneous sintering of incompletely deformed agglomerates to form coagulates.

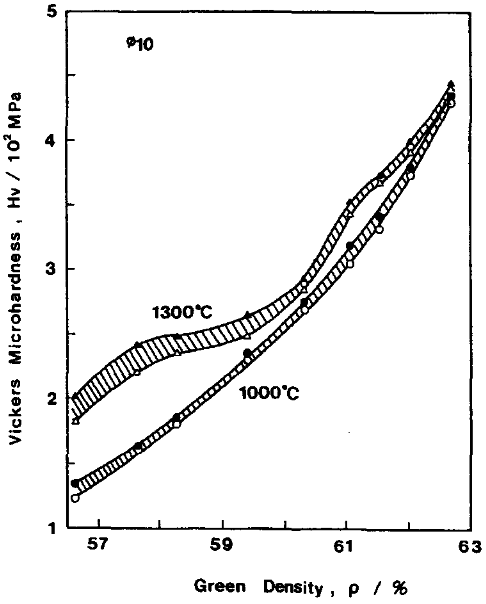


Fig.3 Green density dependence of Vickers microhardness.

3. Structural Homogeneity of Green Compacts

The continuous increase in the microhardness below 1000° C in **Fig. 3** suggested the possibility that the density distribution in compacts could be precisely estimated by measuring microhardness. **Figures 4 and 5** show the distributions of density and microhardness along the radial direction in a relatively large cylindrical compact (ϕ52x25^t) CIP-ed at 200 MPa. The microhardness distributed over the range from 152 to 258 MPa. The corresponding density range (58.1-59.3 %TD) calibrated by using **Fig. 3** agreed with the measured values in **Fig. 4**. The both density and microhardness near the surface showed gradual decreases toward the center. However, the profiles inside the compacts varied intricately and showed a disagreement at 6-12 mm inside from the surface on the center layer. It was considered that the high-density wrinkle inside the compact arose as a result of interaction between reduced compaction force and friction force induced. The radial force focusing onto the axis remarkably reduced as being close to the axis

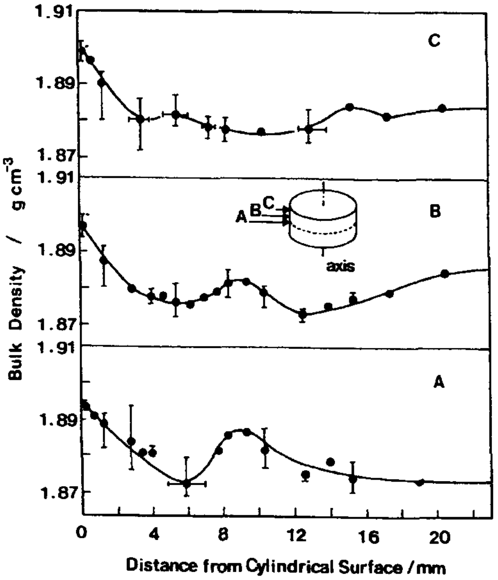


Fig.4 Density distribution in green compacts, A:center layer, B:inner layer, C:outer layer.

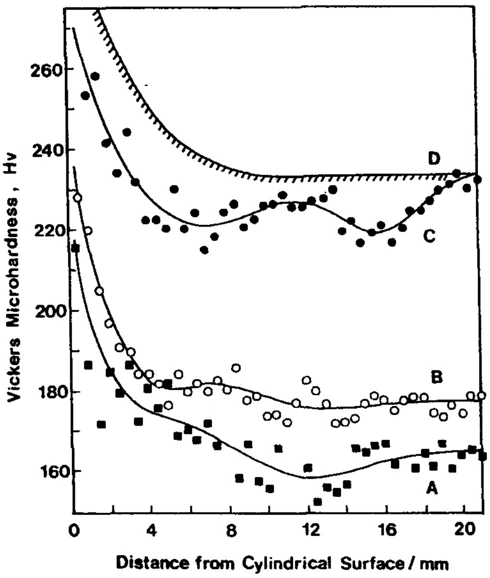


Fig.5 Vickers microhardness distribution in compacts, A:canter layer, B:5.0mm from plane surface, C:1.0mm, D:0.5mm.

and generated much friction force interacting with the axial force without focusing. Then, the inhomogeneous density profile was influenced by the outer size and shape of the compacts as described in the previous paper.$^{8)}$

The influence of applied pressure on the homogeneity was shown in **Fig. 6** as the Vickers microhardness distribution on the 1/4 cross section of ϕ52 compacts. At 100 MPa in Process I, the compact had a narrow microhardness distribution. At 200 MPa, which was the border pressure between Processes I and II, the degree of increase in microhardness was more remarkable at the surface than the center, and resulted in the high microhardness gradient. This was caused by the difference in compaction process between the inner and near-surface parts. The actual compaction pressure at the inner part was reduced to the range in Process I region, while it was almost same as the applied one near the surface. With the further increase in pressure, a homogeneous inner core with almost constant microhardness appeared at 500 MPa and was expanded at 900 MPa. As the result, the compacts CIP-ed at high applied pressure showed a **dual structure** consisting of a dense and homogeneous inner core and a thin surface

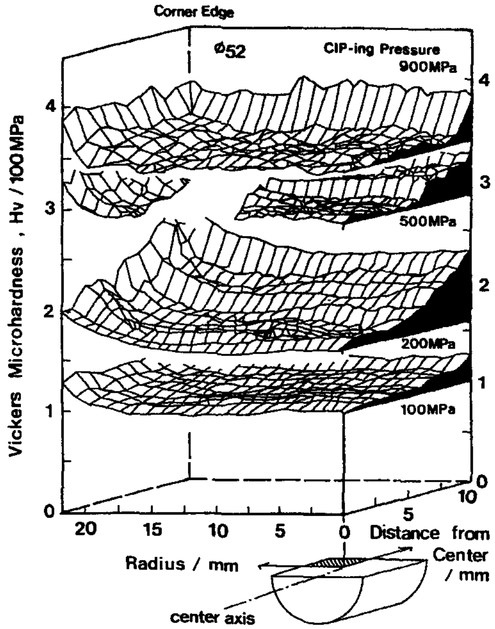


Fig.6 Vickers microhardness distribution on the 1/4 cross section of compacts.

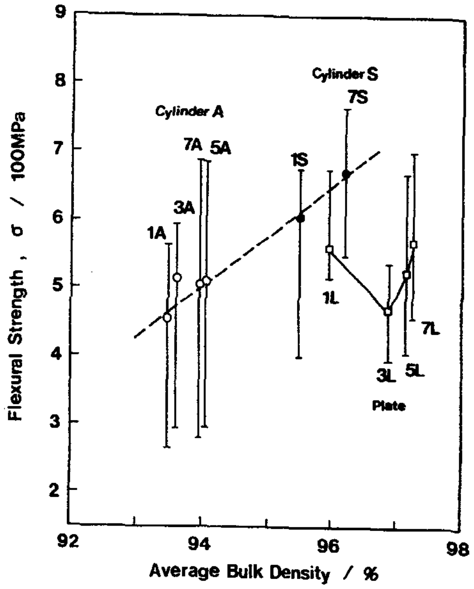


Fig.7 Flexural strength as a function of density.
1A-7A:cylinders, 1L,7L:plates, 1S,7S:cylinders sintered after removal of surface layer.

layer with high microhardness. This suggests that highly dense and homogeneous green compacts can be prepared by high-pressure CIP-ing and removal of the thin surface layer.

4. Mechanical Properties of Sintered SiC

Six CIP-ed cylinders of SiC listed in **Table 1** were sintered at 2120° C for 2h in 0.3 MPa Ar atmosphere with the additives of 6.0 wt% phenol resin and 0.5 wt% amorphous boron. Four of them were as-CIP-ed (**1A-7A**), and the other two were CIP-ed and removed the surface layer (**1S** and **7S**). Plate samples (**1L-7L**) were also sintered as the reference. JIS test bars[16) (3x4x40 mm) were cut out from the sintered bodies and examined. The average strength of sintered cylinders shown in **Fig. 7** increased with the sintered density irrespective of the removal of the surface layer. Weibull modulus as a parameter of structural homogeneity of sintered bodies decreased with the increase in CIP-ing pressure up to 500 MPa (**1A** > **3A** > **5A**) and then recovered at 700 MPa (**5A** < **7A**) as shown in **Table 1**. This order was closely corresponded to that of the structural homogeneity of green

Table 1 CIP-ing Pressure Dependence of Bulk Density and Mechanical Properties of Sintered Silicon Carbide

Sample	CIP-ing Pressure / MPa	Sintered Density / %TD			3-Point Bending Strength / MPa			Weibull Modulus	Fract. Toughness / MPa $m^{-1/2}$	
		Sur.	Center	Av.	Sur.	Center	Av.		Surface	Center
1A[*1]	100	94.4	92.6	93.5	446	495	462	7.65	2.99	3.31
3A[*1]	300	94.9	92.4	93.6	513	570	516	7.33	2.75	3.23
5A[*1]	500	95.5	92.8	94.1	459	506	511	6.17	3.00	3.14
7A[*1]	700	95.7	92.7	94.0	593	470	506	6.87	2.88	3.19
1S[*2]	100	96.0	94.6	95.4	607	446	606	7.31	3.10	3.13
7S[*2]	700	96.9	95.2	96.2	689	671	669	13.5	3.02	3.14

[*1] without removal of surface layer ($\phi 60 \mathrm{x} 26^{t}$), 30 test bars from 5 layers.

[*2] with removel of surface layer ($\phi 52 \mathrm{x} 20^{t}$), 15 test bars from 3 layers.

compacts estimated from **Fig. 6**. Additionally, the Weibull plot for **7A** showed a two-step distribution corresponding to the high-strength surface layer and the low-strength inner core.4) It was evident that the inhomogeneity induced during CIP-ing remained after sintering.

At the applying pressure of 100 MPa, where the compacts were homogeneous irrespective of the removal, the Weibull modulus for **1S** was not improved from **1A**. On the contrary, the Weibull modulus for **7S** was remarkably improved from **7A**, although the both **1S** and **7S** were homogeneous. The high green density (64.3 %TD for **7S** to 56.4 %TD for **1S**) was required in addition to the homogeneity to fabricate sintered SiC with reliable strength. The fracture toughness were almost constant and the size and shape of grains were identical to each other irrespective of the CIP-ing pressure and the removal.4) Then, the green structure did not influenced on the grain morphology but on the size and location of defects. The strength of sintered plates (1L-7L) showed an analogy to the Weibull modulus of cylinders (not to the average strength). The inhomogeneity in green compacts reflected to the strength directly because of the thin thickness, and was expanded to some specimens in larger sintered bodies.

5. CIP-ing Pressure Dependence of Sintering Behavior

The densification process, microstructural development, and

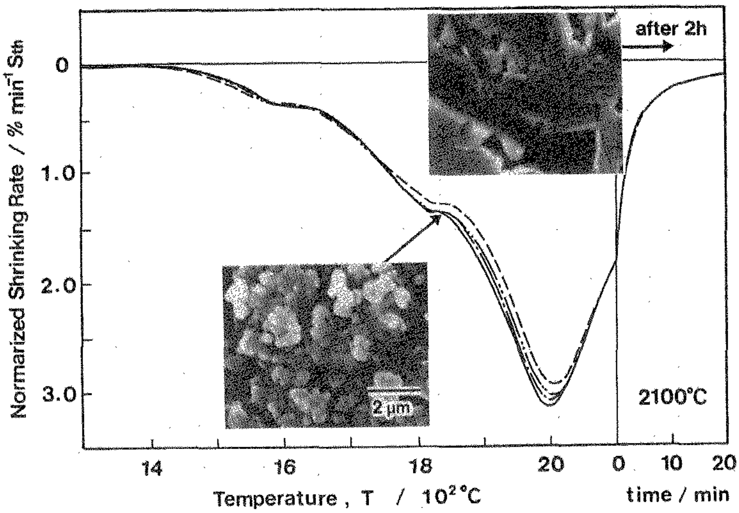


Fig.8 Normarized shrinking rate as a function of temp.
CIP-ing : ——100, —·—300, —··—500, ---- 700MPa (photos.:500MPa)

pore growth behavior was discussed to correlate the properties of green and sintered bodies. **Figure 8** shows the temperature dependence of relative shrinking rate normalized by the theoretical shrinkage. The shrinking rate showed three characteristic peaks. The initial two peaks at 1600 and 1800°C were related with the formation of partially sintered coagulates with the similar size to the aggregates. The incompletely deformed aggregates would shrink to form the coagulates, and made the microhardness increase. The other peak at 2000°C was accompanied with β/α transformation of SiC and grain growth including elongation of plate-like grains. The formation of coagulates and elongated grains was the factor not only disturbing densification but also inducing defects such as residual pores in the sintered bodies. The increased CIP-ing pressure promoted the relative shrinking rate above 1700°C, although the coagulates and plate-like grains formed and grew up.

In the intermediate densification process around 1800-2000°C, plate-like grains generated inside irregularly shaped domain-like structure with the size of several micrometers.[17)] If large pores formed among the domains, it became difficult to fill them by diffusion in the poorly sinterable SiC, and the pores might grow up accompanying with the grain elongation. **Figure 9** shows the influence of

CIP-ing pressure on temperature dependence of maximum pore size (MPS).4) The increase in MPS up to 1800° C was remarkable for high CIP-ing pressure. However, the MPS for high CIP-ing pressure decreased above the temperature, while that for low CIP-ing pressure increased furthermore. The border CIP-ing pressure between the increasing and decreasing MPS at high temperatures was about 200 MPa identically with that in the two CIP-ing processes. This means that pore growth can be prevented for the green compacts containing pores with less size than a critical, although the coagulates formed below 1800° C. The critical pore size for this SiC powder was about 60 nm at the border applying pressure. The improved mechanical properties were derived from preventing pore growth.

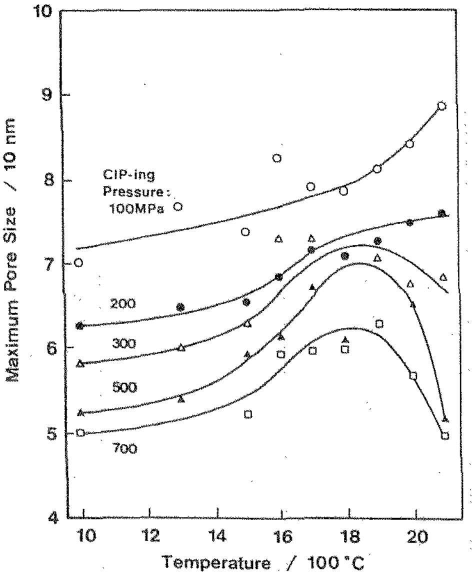


Fig.9 Temperature dependence of maximum pore size.

5. Conclusion

Structural homogeneity in CIP-ed compacts was discussed in relation with the compaction mechanism, powder properties, sintering behavior, and mechanical properties of sintered bodies. The compaction process of fine powders with high ability to agglomerate progressed in two processes. Remarkable inhomogeneity induced in the compacts remained in the sintered bodies to degrade the strength and the reliability. The reliability was improved for highly dense and homogeneous green compacts CIP-ed at high pressures and removed the thin surface layer. The continuous pore growth in the poorly dense compacts induced large defects in the sintered bodies, while the pore size reduced at high temperatures in the highly dense compacts. There was a critical pore size to obtain defect-less sintered bodies.

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