Journal of the European Ceramic Society 22 (2002) 311–316

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Sintering deformation caused by particle orientation in uniaxially and isostatically pressed alumina compacts

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Received 31 January 2001; accepted 21 April 2001

Abstract

Effect of particle orientation on deformation during sintering is reported for model systems; one made with industrial grade low soda alumina, which has an elongated particle shape, and the other a special alumina with a spherical particle shape. To ensure the homogeneous packing density of particles, compacts were made by uniaxial pressing followed by cold isostatic pressing. The particle orientation was examined with a polarized light microscope and was found to be an important cause of sintering deformation. In a green body, for elongated shape of particles, the particle orientation occurred during uniaxial pressing, causing the anisotropic sintering shrinkage during sintering and thus the sintering deformation. No particle orientation nor shrinkage anisotropy was noted in the system made with the powder of spherical particle shape.

Keywords: Anisotropy; Al_2O_3; Deformation; Pressing; Sintering

1. Introduction

Anisotropic shrinkage, i.e. deformation of a green body in sintering, is a common and serious problem in the commercial production of ceramics. For reshaping the deformed body, time-consuming machining with diamond tools is required, reducing the productivity and thus considerably increasing the price of ceramics. There are two sources for the deformation. One is the particle orientation and the other the non-uniform packing density of powder particles.[1–10] The former is particularly important in ceramics made with raw powder of extremely elongated particle shape and with a forming method involving intense shear stress, such as injection moulding and tape casting.[4–10] However, this source has been believed unimportant in ceramics made through uniaxial pressing, where the shear stress during forming is minimal and the particle shape is near equiaxed. Only the latter source has been believed significant in this case. However, there is no direct evidence for this belief. There has been great difficulty in examining the particle orientation explicitly in this kind of compact. Particle orientation may also cause the deformation in this case. For improved processing of ceramics, the particle orientation and its effect on deformation must be examined explicitly for ceramics made through uniaxial pressing.

The examination of particle orientation requires a special characterization tool, since conventional tools have failed to detect the minor orientation of particles in many systems.[11] In this study, a very sensitive characterization method is applied to examine the packing structure and orientation of particles in powder compacts. It has a very high capability for detecting a minor change in packing structure of particles, and has been successfully applied to solve several difficult problems in ceramics, such as the formation mechanism of large flaws and interior stress occurring in ceramics processing.[4,5,11–18] In this technique, the compact is made transparent with an immersion liquid, and its internal structure is examined with the transmission mode of a polarized light microscope. Study with this technique may show directly and systematically the interrelation among the moulding process, microstructures of compact and sintered body, and the deformation.

The aim of this study is to clarify the particle orientation and its relevance to sintering anisotropy in a uniaxially and then isostatically pressed compact. Two

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0955-2219/01/$ - see front matter
PII: S0955-2219(01)00292-8

types of alumina powders were used for examination; one with a spherical particle shape and the other an elongated particle shape. The former is a special model material and the latter represents a typical powder of industrial grade low-soda alumina used for the commercial production of technical ceramics. The compacts are expected to have uniform density after CIP. Uniform packing of powder particles is expected in the former compact, and particle orientation in the latter. The microstructure will be examined by the novel liquid immersion method, and also by conventional characterization methods including SEM and powder X-ray diffraction analysis. In the system of elongated particle shape, particles should align with their long axis normal to the applied stress of uniaxial pressing and randomly orient within the plane normal to this direction. No specific orientation should happen in the system of spherical particles.

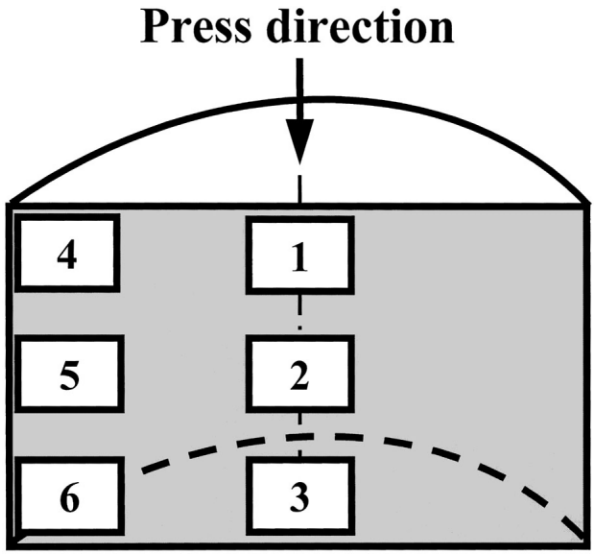

Fig. 1. Schematic diagram of location of various specimens in the large compact.

2. Experiment

Two kinds of commercial powders were used in this study, low soda alumina of industrial grade (160SG-1, Showadenko, Japan) and high purity alumina of spherical particle shape (AA05, Sumitomo Chemical Company, Japan). The slurry containing 50 mass% alumina powder was prepared by mixing it with distilled water and 2 mass% PVA (PVA105, Kuraray, Japan) in a ball mill. Spray dried alumina granules were prepared with a spray drier (Model SD13, Mitsui Kozan, Japan, inner diameter 1.3 m) with the inlet air temperature 200°C. Compacts of two sizes were prepared by uniaxial pressing (0–100 MPa) followed by CIP (100 MPa). The dimensions of large and small compacts were diameter 60 and 15 mm, and thickness 35 and 4–5 mm, respectively. Specimens (9×9×7 mm) were cut from various places in the large compacts, as shown in Fig. 1. The shrinkage during sintering was measured for two directions on these specimens and also on small specimens; parallel (H direction) and normal (D direction) to the direction of uniaxial pressing in dynamic and static conditions. A dilatometer (TMA-50, Shimadzu, Japan) was used for the dynamic measurement in the temperature region up to 1400°C at a heating rate of 10°C/min. To ensure the accuracy of the measurement, blank tests were executed many times. The errors of the present results were within the width of the line in the figure Section 3. The specimens were also heated statically at 1600°C for 2 h in an electric furnace to make sintered bodies. The shrinkage on sintering was calculated from the dimensional changes for these specimens. The relative density of green compacts was measured by mercury porosimetry (Pore Sizer 9320, Shimadzu, Japan). The liquid immersion technique, SEM and X-ray diffraction methods were used for the observation of internal structure of compacts and sintered bodies. In the liquid immersion method, samples were thinned to about 0.1 mm with sandpaper, and methylene iodide (refractive index, 1.74) was applied to make them transparent. The internal structure was observed with a polarized light microscope. In the SEM observation, samples were treated by gold sputtering. Aspect ratios of particles were measured with SEM micrographs on over 500 particles.

3. Results

Fig. 2 shows SEM micrographs for fracture surfaces of two types of alumina compacts in the H direction. The particles of low-soda alumina have elongated shapes, which is typical for this type of alumina. It should be emphasized, however, that this kind of particle shape is expressed "nearly equiaxed" in many papers of ceramics. The nominal particle size is 0.4 μm and is consistent with the micrograph. There appears no particle orientation in this micrograph. The particles of high purity alumina have nearly spherical shapes as is claimed by the manufacturer. The particle size is clearly consistent with the value provided by the manufacturer, 0.5 μm.

Fig. 3 shows a distribution histogram of aspect ratio for two types of alumina particles. The aspect ratio of particles varies widely, 1–3.4 for low soda alumina with the mean value 1.6. The alumina particles tend to be elongated in the *a–b* plane due to the hexagonal crystal structure. The aspect ratio varies only slightly for the high purity alumina, with the mean value 1.1. Clearly, these particles have a nearly spherical shape, which is a special case for alumina.

Table 1 shows green density and sintering shrinkage of specimens cut from various locations in two types of alumina compacts. The forming condition of the com-

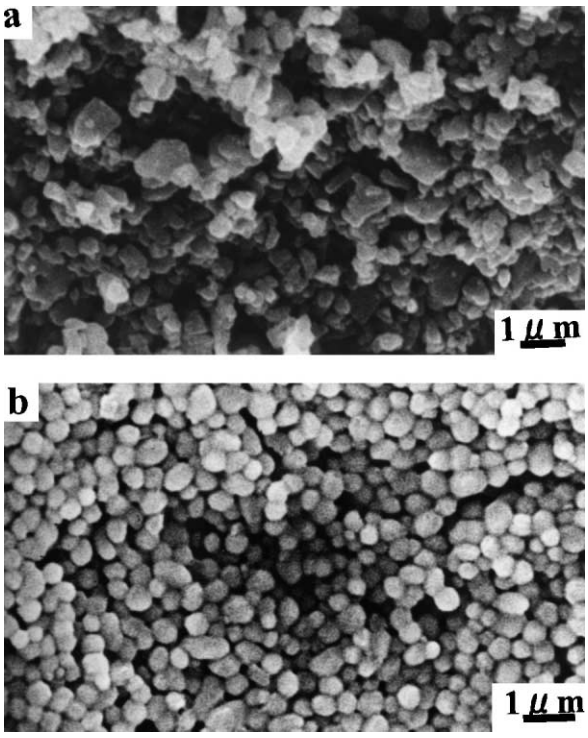

Fig. 2. SEM micrographs of fracture surfaces for (a) elongated and (b) spherical shaped powder of alumina compacts in the H direction.

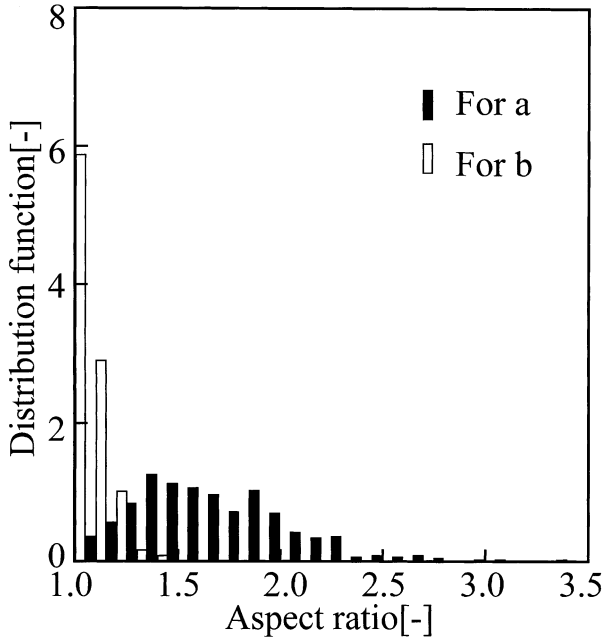

Fig. 3. Distribution histogram of aspect ratio for (a) elongated and (b) spherical shaped alumina powders.

pacts was uniaxial pressing at 40 MPa followed by CIP at 100 MPa. The density was found uniform within the experimental error (±0.3%) for both compacts. In the elongated particle system, the green densities are essentially the same for all locations in the compact, with the minimum 56.0% and the maximum 56.5%. An anisotropic sintering shrinkage occurs in this compact. The sintering shrinkage is consistently larger in the H direction than D direction; 18.0–18.1% in the former and 17.5–17.6% in the latter, respectively for all specimens. Shrinkage difference was 0.4–0.6% for two directions in all places in the compact. This is a surprising result. An opposite result should happen if we assume that non-uniformity of packing density still exists and causes the shrinkage anisotropy. Traditionally, It has been considered that the particle packing density in uniaxial pressed compact should be lower in the D direction than that in the H direction; the sintering shrinkage is larger in the former than the latter, which contradicts the present result. The packing density is uniform in the compact of spherical particles, 57.4–57.5%. No shrinkage anisotropy was found in this compact; 16.4–16.6% in H direction and 16.5–16.6% in D direction, respectively.

Table 1
Green density and sintering shrinkage of specimens cut from various locations in two types of alumina compacts

	Specimen no.					
	1	2	3	4	5	6
Elongated particle system						
Green density (%)	56.1	56.0	56.3	56.3	56.0	56.5
H direction shrinkage (%)	18.0	18.0	18.1	18.0	18.1	18.0
D direction shrinkage (%)	17.6	17.6	17.5	17.5	17.6	17.5
Shrinkage difference (%)	0.4	0.4	0.6	0.5	0.5	0.5
Spherical particle system						
Green density (%)	57.4	57.5	57.5	57.4	57.4	57.4
H direction shrinkage (%)	16.6	16.5	16.6	16.4	16.6	16.5
D direction shrinkage (%)	16.5	16.5	16.5	16.6	16.5	16.5
Shrinkage difference (%)	0.1	0	0.1	−0.2	0.1	0

Fig. 4 shows variation of sintering shrinkage with temperature for the compact, which was made with the elongated particles by uniaxially pressing at 40 MPa followed by CIP at 100 MPa. The anisotropic shrinkage was again noted in this examination. The shrinkage is slightly larger in H direction than in D direction throughout the sintering process. The difference of shrinkage for two directions increased as the sintering temperature increased. Essentially the same results were obtained for other specimens cut from various locations in the compact.

Fig. 5 shows variation of sintering shrinkage with temperature for the compact, which was made with the spherical particles by uniaxially pressing at 40 MPa followed by CIP at 100 MPa. The shrinkage of sintering was identical for two directions for all sintering temperatures in this specimen. Clearly, isotropic shrinkage happens in sintering this compact.

Fig. 6 shows the crossed polarized light micrographs for the compact made with the elongated particles by uniaxial pressing at 40 MPa and subsequent CIPing at 100 MPa. Thin specimens for examination were cut from H and D directions of the compact. The specimens

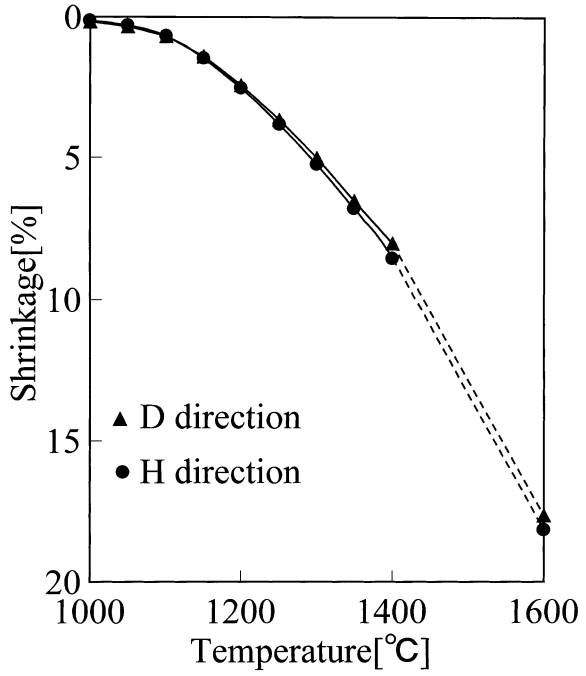

Fig. 4. Variation of sintering shrinkage with temperature in the H and D directions for compacts made with the elongated particles by uniaxially pressing at 40 MPa followed by CIP at 100 MPa.

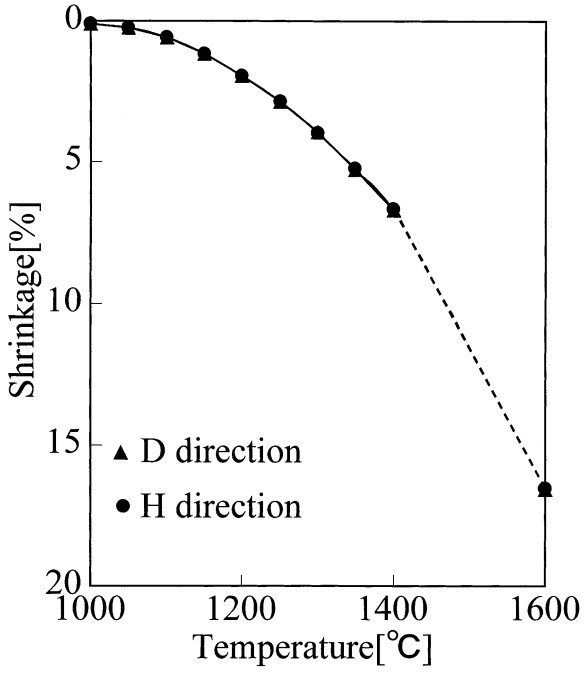

Fig. 5. Variation of sintering shrinkage with temperature in the H and D directions for compacts made with the spherical particles by uniaxially pressing at 40 MPa followed by CIP at 100 MPa.

for observation were rotated under the microscope to examine the optical anisotropy: the change of brightness shows the presence of optical anisotropy and thus the particle orientation. For the specimen cut from the H direction, the matrix showed a dark-bright change at every 45° of rotation. The matrix retained dark for all angles of rotation for the specimen cut from the D direction. The same results were noted for all the other specimens cut from various locations of this compact. Clearly, there is particle orientation in the compact. Elongated particles align with their longest axis perpendicular to the direction of uniaxial pressing within the plane parallel to the direction of uniaxial pressing and randomly orient within the plane normal to the uniaxial pressing. Spotted bright features in the micrograph are big alumina particles in the compact. They tend to align in the direction explained above. The similar particle orientation was also found in small compacts. Once the structure of particle orientation is developed during uniaxial pressing, it appears extremely difficult to eliminate it by CIP.

On the other hand, the same experiments were carried out for the compact made with the spherical particles. All field of microscope was always dark for specimens cut from the H direction and D direction in various locations of the compact. Clearly, there is no particle orientation in this compact.

Fig. 7 shows the relationship between green density and shrinkage of two directions after sintering in static condition at 1600°C 2 h in electric furnace for various compacts made with elongated particles. In compacts made with CIP only, the same shrinkage was noted for any arbitrary directions, and the relationship between green density and sintering shrinkage was linear. Whereas, in uniaxially pressed (10–100 MPa) and then CIPed specimens, the shrinkage is larger in H direction for all compacts, i.e. those compacts show shrinkage anisotropy. It is very interesting to note that green density-shrinkage curve for the specimen prepared by CIP only sits between two curves for the specimen made by uniaxial pressing followed by CIP. Traditionally, these three curves were expected to coincide, i.e. compacts with the same green density should show the same sintering shrinkage. Clearly, even the compacts of the same density show different shrinkage depending on particle orientation developed in the pressing of the initial stage.

4. Discussions

This study directly shows the importance of particle orientation on the shrinkage anisotropy in sintering for elongated particles of alumina prepared by uniaxial pressing followed by CIP. The particle orientation remains, and thus the sintering anisotropy was noted even after CIP in a specimen prepared at the lowest uniaxial pressure (10 MPa) in this study. Once the orientation is developed in the compact, its removal from the green structure appears very difficult by subsequent CIP treatment. It should be also emphasized that this study does not exclude the importance of non-uniform packing density on shrinkage anisotropy. This should be an important cause of shrinkage anisotropy in less uniform

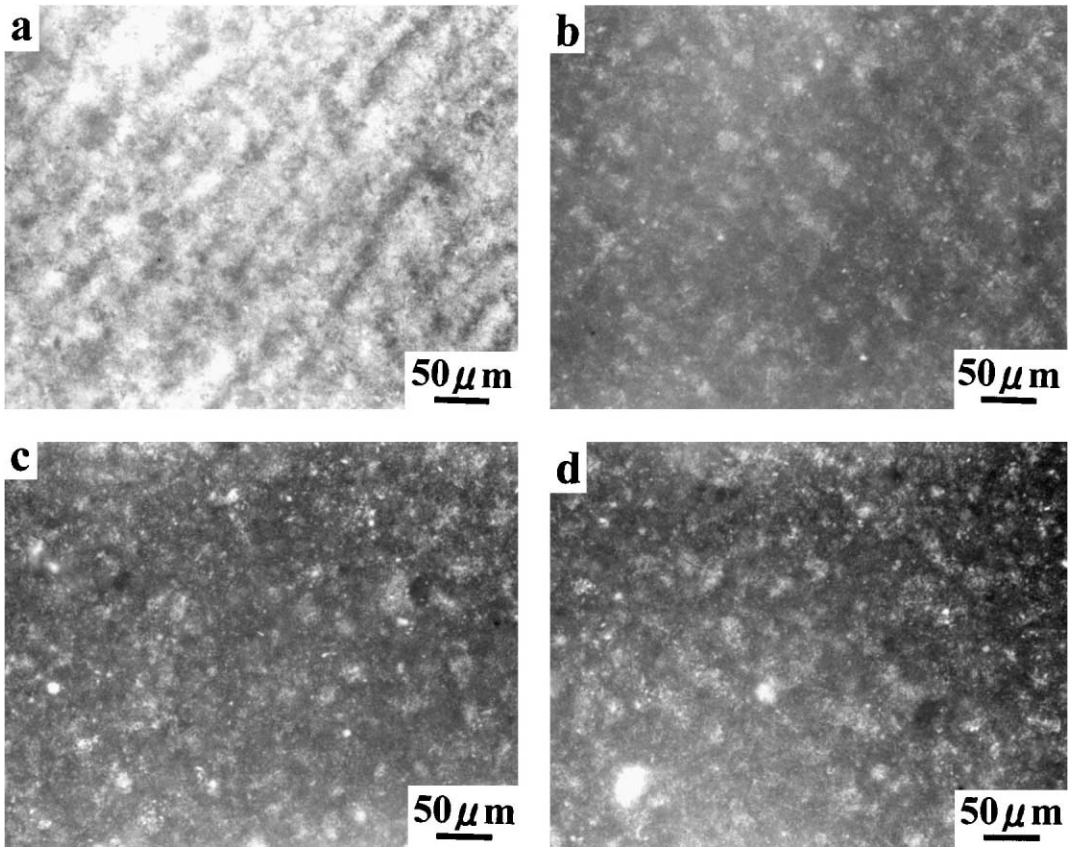

Fig. 6. Crossed polarized light micrographs of thin specimens cut from the H and D directions of the elongated particle compact: (a) H direction, at 0°; (b) H direction, at 45°; (c) D direction, at 0°; (d) D direction, at 45°.

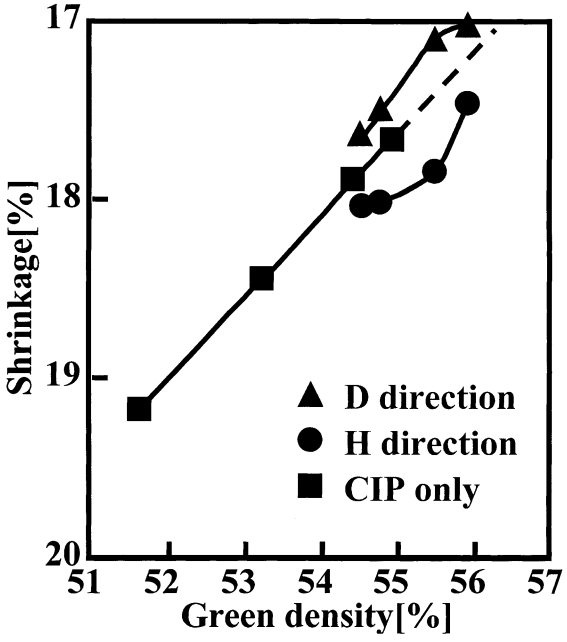

Fig. 7. Relationship between green density and sintering shrinkage of two directions for various alumina compacts made with elongated particles.

systems. In a real system, both the non-uniformity of packing density and the particle orientation cause the shrinkage anisotoropy.

Presence of particle orientation was clarified with our liquid immersion technique only. We tried repeatedly to characterize the particle orientation in those compacts with SEM and powder X-ray diffraction analysis including Rocking curve for many times,[19,20] but the efforts were unsuccessful. This indicates that orientation of elongated particles is so slight that these conventional characterization tools fail to clarify it. In our experience, a change of X-ray diffraction pattern is noticed when the retardation of polarized light through the specimen reaches 1/3 of the corresponding value of the single crystal. The sensitivity of X-ray diffraction method is too low to detect particle orientation in processing studies of ceramics.

Stress field in uniaxial pressing is clearly responsible for aligning particles of elongated shape with their longest axis perpendicular to the direction of uniaxial pressing. This structure makes the sintering shrinkage behavior to be different for directions normal and parallel to the pressing direction, causing the deformation of the sintered body. Whereas, the deformation should not happen in compact made with spherical particles, which there is not particle orientation in the compact.

With the existing theory of sintering, it is difficult to explain the higher shrinkage in H direction in uniaxially pressed compacts. Kaplan et al.[21] suggested that different

twin boundary structures result in anisotropic growth of alumina, which is related to the lack of centro-symmetry in the trigonal corundum structure. Seabaugh et al.[22] indicated that modification of diffusion in platelet-shaped alumina particle systems continuously provides material to the anisotropically growing template grains. At this stage, the high sintering shrinkage is tentatively ascribed to the larger number of particle contact per unit length in the H direction. The net shrinkage of a specimen should increase with increasing number of contacts, since each contact develops a neck in sintering and contributes to shrinkage. It is necessary to develop an adequate theory for the anisotropic sintering in a system of oriented particles.

It is difficult to identify which is responsible for the shrinkage anisotropy; the change of transport characteristics or the particle shape. They are correlated; the shortest axis of the particle corresponds to *c*-axis. The mass transport property varies with crystalline axis in anisotropic material such as alumina. The diffusion coefficient along *c*-axis may be smaller than along *a–b* plane. Unfortunately no individual diffusion datum is available for the two directions of alumina single crystal.

5. Conclusions

The orientation of particles of elongated shape is an important cause of sintering deformation in addition to the non-uniform particle packing density in uniaxially pressed alumina compacts. In a compact made of powder of elongated particle shape, uniaxial pressing produces the orientation. Subsequent CIP at higher pressure does not remove it, and the sintering shrinkage anisotropy results. There is no particle orientation in compacts made with spherical particles, and the compact shows isotropic sintering shrinkage.

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