High-pressure Cold Isostatic Pressing of Ultra-fine Oxide Powders†

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Abstract

Fine Al_2O_3 , MgO and SiO_2 powders of various sizes were consolidated into a dense and uniform structure by high-pressure cold isostatic pressing. Although the average particle diameter was less than 21 nm, Al_2O_3 , MgO and SiO_2 powder compacts were compressed to 60% of their theoretical density by cold isostatic pressing at 1 GPa, because the open and strong aggregate structure collapsed under the cold isostatic pressure. The pore size of these compacts decreased below the primary particle size. Especially, in the case of MgO powders, the maximum relative density increased to 80% and the ratio of pore size to primary particle size was less than 20%. However, in the case of Al_2O_3 powders, whose size was more than 100 nm, a slight increase in relative density and decrease in pore size in the compacts occurred with an increase in isostatic pressure up to 1 GPa. In the case of particles larger than 100 nm and high-hardness materials, high cold isostatic pressure was not effective in increasing the packing density.

The mean vertical force and compressive stress at the contact point between particles in compacts and the maximum tensile stress in a particle during isostatic pressing were estimated using Rumpf's and Hertz's equation. Because these stresses were smaller than the hardness and tensile strength of Al_2O_3 or MgO materials, no viscous deformation or fracture of particle took place during compacting. The relations between the ratio of mode pore diameter to particle diameter and the relative density of Al_2O_3 , MgO and SiO_2 compacts agreed with those of spherical and monosized particle beds. The main mechanism of densification of compacts during isostatic pressing was the collapse of aggregates and rearrangement of particles.

1. Introduction

To improve the sintering qualities of inorganic type powders used in ceramics etc., and to obtain ceramics with a fine structure at low sintering temperatures, the reduction of particle size of raw material powders, and the increase in the physical activities of non-crystal or of particles without complete crystallization are effective⁵⁾. However ultra-fine particles with a particle size of 0.1 μm or less readily form a strong and coarse aggregate structure in general and compacting of a dense, uniform structure is difficult. Therefore refinement and high activation of particles does not necessarily lead to obtaining dense sintered compacts under low temperature conditions.

It is believed that pH control in water and colloid scientific methods using surface active agents are effective in collapsing and dispersing the strong aggregate structure of ultra-fine particles^{7,13,15)}. However with ultra-fine particles of less than 100 nm, the dispersion of aggregates by these methods is extremely difficult and this has not been successful except for cases of particles with special surface conditions such as SiO_2 fine particles, formed from metallic alkoxide⁶⁾. Another effective method to collapse aggregate structures of ultra-fine particles is by compacting using ultra high pressure. Gleiter et al^{4,8)} compacted a gaseous phase ultra-fine particle to several nm particle diameter formed under a very high vacuum of 10^{-6} torr by applying a maximum of 5 GPa uniaxial pressure, and succeeded in producing a dense bulk body (nanocrystalline) with a crystal particle size of several nm without sintering. However this method used by Gleiter et al requires a large scale apparatus

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involving high costs and since it is by uniaxial compacting, a uniform structure cannot be obtained. Therefore, as reported previously⁶⁾, the authors produced a granulated powder resembling a closely packed structure by the spray drying method from spherical mono-dispersed silica fine particles of not more than 0.1 μm , formed from metallic alkoxides by isostatic pressing at 1 GPa, and obtained a Green body with a maximum relative density of 78%.

Furthermore, the authors heat treated mullite precursor ultra-fine particles of not more than 10 nm, synthesized from metallic alkoxide at not more than 1000°C by which the amorphous phase remains and the particle size hardly increases, then conducted isostatic pressing at 1 GPa⁵⁾. As a result, a Green body with a relative density of 60–70% was obtained, and at a sintering temperature less than the liquid phase formation temperature of 1,500°C which is lower by 200°C than normal, the density was increased to 98% and above to obtain a mullite sintered compact with an average crystal particle size of not more than 100 nm. High activity ultra-fine particles were prepared and using a method to collapse the aggregate structure by a high pressure of 1 GPa, a ceramic (nano structure sintered compact) having an ultra-fine structure, sintered and densified at a relatively low temperature was produced. However the ultra-fine particles synthesized from metallic alkoxide possessed better dispersion qualities in water compared with particles produced by other methods and even though made of ultra-fine particles, they aggregate very much. In this report, to study whether the aggregate structure of ultra-fine particles made by other methods or from other materials would collapse by isostatic pressing and whether improvement

of densification or sintering qualities of compacts could be obtained, ultra-fine particles of oxides with various diameters, made by various methods and from raw materials other than metallic alkoxides were used. Then the particle size and particle material which affect the densification process of compacts following an increase in isostatic pressure were studied and a quantitative study of the densified structure was attempted.

2. Experiments

Three kinds of oxide type fine particles, Al_2O_3 , MgO , and SiO_2 were used. Their specific surface area (S_W), density (ρ_T), specific surface area converted diameter (d_B) calculated using Eq. (1) and crystal structure are summarized in **Table 1**.

$$d_B = 6000/(S_W \rho_T) \quad (1)$$

The specific surface area was measured by the BET method by nitrogen adsorption while the crystal structure was measured by an X ray analysis method (XRD method). Al_2O_3 (I) is $\alpha\text{-Al}_2\text{O}_3$ (Made by Showa Denko, AL160SG) made by de-alkalizing the powder obtained by the Bayer method, while Al_2O_3 (II) to (IV) are high purity Al_2O_3 (Made by Daimei Chemical, TM-D, TM-100, and TM-300) obtained by thermal decomposition of $\text{NH}_4\text{AlCO}_3(\text{OH})_2$. I and II whose specific surface area equivalent particle diameters (d_B) are not less than 100 nm, are $\gamma\text{-Al}_2\text{O}_3$ (trigonal system) while III and IV of 12.2, and 5.6 nm are $\gamma\text{-Al}_2\text{O}_3$ (cubic system). It has been confirmed that $\gamma\text{-Al}_2\text{O}_3$ is rearranged by differential thermal analysis to $\alpha\text{-Al}_2\text{O}_3$ at a temperature of around 1150°C. Ob-

Table 1 Powder properties of raw materials.

(A) Al ₂ O ₃					
Sample No.	S _W [m ² /g]	ρ _T [g/cm ³]	d _B [nm]	purity [%]	phase
I	5.6	3.98	269	99.4	Trigonal (α – Al ₂ O ₃)
II	14.0	3.98	108	99.99	Trigonal (α – Al ₂ O ₃)
III	134	3.67	12.2	99.99	Cubic (γ – Al ₂ O ₃)
IV	290	3.67	5.6	99.99	Cubic (γ – Al ₂ O ₃)
(B) MgO					
Sample No.	S _W [m ² /g]	ρ _T [g/cm ³]	d _B [nm]	purity [%]	phase
I	8.4	3.58	199	99.9	Cubic
II	18.0	3.58	94	99.9	Cubic
III	37.0	3.58	45	99.9	Cubic
IV	168	3.58	10	99.9	Cubic
(C) SiO ₂					
Sample No.	S _W [m ² /g]	ρ _T [g/cm ³]	d _B [nm]	purity [%]	phase
I	128	3.20	21	99.9	amorphous
II	284	3.20	9.6	99.9	amorphous

servation by an electron microscope shows that all the particles are aggregated but the primary particle sizes are relatively uniform.

MgO were all particles obtained by vapor oxidation of magnesium (Made by Ube Kosan, 2000A, 1000A, 500A, and 100A) with particle size controlled by the reaction conditions¹⁰). Observations by an electron microscope confirmed that MgO (I) consisted of a mixture of particles of around 0.1–0.5 μm formed into a cubic shape and fine particles of several 10 nm. Even with MgO (II) and (III), the particle diameters are smaller than those of MgO (I) but cubic shape particles were observed¹⁰). MgO (IV) did not contain cubic particles and consisted only of fine particles and a relatively uniform particle size distribution was observed. The particle size distribution is fairly widespread compared with Al_2O_3 but the specific surface area converted diameter (d_B) was taken as representative of the particle diameter.

SiO_2 was made by hydrolysis in oxyhydrogen flame of a volatile silane compound (Made by Nippon Aerosil, AEROSIL-130, 380). The specific surface area equivalent particle sizes were 21, 9.6 nm and the fine particles were amorphous. Seen by an electron microscope, they were similar to Al_2O_3 (III), (IV) and MgO (IV) in that they were ultra-fine particles with a relatively uniform particle size.

The raw material powders were put in a metal mold of 20 mm and preparatory uniaxial compacting was performed for 3 minutes at 6.2 MPa. Then under conditions ranging from 0.05 to 1 GPa, isostatic compacting was conducted for 3 minutes. The powder density and pore size distribution of the compacts were evaluated by the mercury press method.

3. Results

3.1 Changes in compact density by isotropic high pressure compacting

Figs. 1(a) and (b) show the relation between the isostatic compacting pressure and the relative density after compacting (ρ_G/ρ_T). Out of the four types of Al_2O_3 particles, Al_2O_3 (I) and (II) whose particle diameters were not less than 100 nm reached a relative density of 46.7% in the uniaxial compacting stage ($p_C = 0 \text{ GPa}$). However the increase in density accompanying an increase in pressure was slight and even when a pressure up to 1 GPa was applied, a density increase of only around 10% compared with the case of metal mold forming was observed. On the other hand, with $\gamma\text{-Al}_2\text{O}_3$ III and IV with a particle size of 12.2 and 5.6 nm, the relative density at

Fig. 1 Change in the relative density of compacts with cold isostatic pressure. Uni-axial pre-pressing pressure (p_U) was 6.2 MPa.

60% was reached, roughly comparable to that of (I) and (II). With any of the powders, the relation between the relative density (ρ_G/ρ_T) and the compacting pressure was linear on a semi-logarithmic graph like the following equation using constants a and b .

$$\rho_G/\rho_T = a \log(p_C) + b \quad (2)$$

The slope with (I) and (II) was about 0.05 but with (III) and (IV), it was about 0.25 or fivefold more. In the Figure, the results on SiO_2 of particle diameters 21, 9.6 nm are also shown and they roughly coincide with the results of Al_2O_3 (III) and (IV).

In the case of Al_2O_3 (I) and (II) for which the particle size was not less than 100 nm, the application of pressure was not very effective in increasing the density of compacts. Even with SiC and the like which are non-oxide particles, results with which isostatic pressures up to 900 MPa were applied have been reported^{1,2)}, but since the particle size was around 100 nm and above, a notable density increase following the application of pressure was not observed. However with fine particles of 2, 30 nm and less, the application of isostatic pressure was extremely effective in increasing the compact density, not only for Al_2O_3 but for SiO_2 and for those shown in Fig. 1(b) such as MgO. Even with a pressure of 1 GPa, the density increase limit was not reached and with a pressure increase above 1 GPa, further densification can be expected.

Also with MgO, the slope was the steepest in the relation between the relative density of the smallest particle size MgO (IV) and pressure (Fig. 1(b)). Also, it roughly coincides with the relation between compact pressures of Al_2O_3 (III), (IV), SiO_2 and their relative density, while for particle sizes of not more than 21 nm, the effect of material was hardly observed in the relation between the compact pressure and the relative density (ρ_c/ρ_T). On the other hand, when the particle size was 45 nm (III), although not as conspicuous as with Al_2O_3 , the slope compared with that of (IV) became somewhat flatter. With MgO (I) and (II) with an even larger particle size, the slope hardly changed. As the particle size became larger, the relative density following uniaxial compacting became higher and the slope did not become flat as much as that for Al_2O_3 and therefore, under a pressure condition of 1 GPa, the maximum relative density of MgO (I) reached 80%. In the case of MgO, even with a particle size of 100 nm and above, the slope in the relation between the relative density and pressure, as with Al_2O_3 , was of a mechanism where as it did not become flatter compared with that of ultra fine particles with particle size of 21 nm and less, and the following 2 points are conceivable for this mechanism. The first is that for MgO (I) to (III), the particle size distribution is widespread and therefore the mechanism where small particles intrude into the space of large particles effectively functions even in high pressure stages. Secondly, the hardness of MgO

is lower compared with that of Al_2O_3 and MgO is more liable to plastic deformation whereby deformation develops at the particle contact points under high pressure conditions. When the densification mechanisms of compacts in the pressurizing process change following a rearrangement of particles to the second mechanism which is a deformation of particles, a change is seen in the slope of Equation (2) and it was reported that it could not be approximated by one straight line¹¹⁾. However within the stress scope of the present study, no change was observed in the slope even under high pressure conditions near 1 GPa and both slopes of MgO and Al_2O_3 were approximated by a single straight line. Consequently, in the densification mechanism, the rearrangement of primary particles is dominant within the stress scope of the present study and it can be presumed that densification by plastic deformation of particle contact points is not dominant. The particle distribution of MgO (I) – (III) compared with that of Al_2O_3 (I), (II) is more widespread and it is believed that because the mechanism of small particles intruding into the space of large particles functions effectively, the relative density increases. To observe these mechanisms, attention was focused on the pore size distribution to study the changes in the compact structure during isostatic pressure application.

3.2 Changes in pore size distribution in compacts during pressure application

Figs. 2(a) and (b) show changes of pore size distribution accompanying the increase in isostatic compacting pressure of Al_2O_3 (II) and (III). During the metal mold forming stage, ($p_c = 0$ GPa), pores larger than the primary particle size ($d_p = 108$ nm) were present in Al_2O_3 (II) but by applying a low isostatic compacting pressure of only 0.05 GPa, pores larger than the primary particle size became hardly observable (Fig. 2(a)). Even by increasing the compacting pressure, not only the pore volume but the pore diameters were not appreciably reduced. With powders having a particle size of 100 nm or larger, almost all aggregate structures collapse under a relatively low pressure and a dense compact structure is acquired. Since a dense primary particle arranged structure already exists in the low pressure stage, rearrangement of particles is minimal even with an increase in pressure. It is thought that the near completion of particle rearrangement in the low pressure stage which is the densification mechanism of compacts, is the reason for the flat slope angle of Al_2O_3 (I) and (II) in Fig. 1(a).

On the other hand, with Al_2O_3 (III) having ultra-

Fig. 2 Pore size distribution in compacts of Al_2O_3 powders measured by mercury porosimetry

fine particles with primary particle size of 12.2 nm, pores with sizes 10 times larger than the primary particle size exist in the low pressure stage, indicating that aggregate structures have not collapsed (Fig. 2(b)). However with an increase in pressure, the pore diameters decrease and at 0.3 GPa, the pore diameters become about the same as the primary particle diameters. Then under high pressure conditions of 0.6 GPa and above, the pore diameters become smaller than the primary particle diameters. Aggregate structures of ultra-fine particles of around 20 nm and smaller do not collapse under low pressures but with an increase in pressure, they collapse and become deformed. At 1 GPa, the mode pore size is smaller than 6 nm which is the measurement limit set for the mercury pressure fitting method adopted in this report, and reaches a size 60% or

less of the primary particle diameter (d_B) which does not differ much from the ratio between the d_B in the case of Al_2O_3 (I) and (II) particles 100 nm or bigger and mode pore size. Consequently, it is thought that the arranged structures of primary particles of 12.2 nm and 108 nm are approximately the same under high pressure conditions of 1 GPa.

Also in the case of MgO (I), the pore diameters are roughly smaller than the primary particles' diameters and are of a dense structure in a relatively low pressure stage (Fig. 3). Although the powder is of a relatively large particle size of 200 nm compared with Al_2O_3 (I), the mode pore size is conspicuously reduced with an increase in pressure. Also with MgO (II) and (III), the pore diameters become smaller in proportion with an decrease in particle size but a tendency similar to that of

Fig. 3 Pore size distribution in compacts of MgO powders measured by mercury porosimetry. Estimated mean particle size was 200 nm

MgO (I) was obtained. With MgO (IV), as with Al₂O₃ (III), pores with diameters several times larger than the primary particles' diameter are present under low pressure conditions but the pore diameters decrease with an increase in pressure and at 1 GPa, open pores larger than 6 nm are hardly observable.

In regard to powders on which experiments were made, the ratio between the mode pore size (D_m) and the primary particle size (d_B) under various pressure conditions was obtained and the relations with the compacting pressure are shown in **Figs. 4(a)** and **(b)**. With Al₂O₃ (I) and (II) ($d_B = 269, 108$ nm), in which the compact relative density does not change much with high pressure applications, a reduction down to around $D_m/d_B = 0.6$ was seen under low pressure conditions of 0.05 GPa. However even by applying a higher pressure of 1 GPa, D_m/d_B drops only to 0.4, indicating that the packed structure of particles does not change much (**Fig. 4 (a)**). On the other hand, with Al₂O₃ (III) or SiO₂ (I), (II) and MgO (IV), which consist of fine particles of 100 nm and less, $D_m/d_B \gg 1$ at a low pressure stage but from around 0.3 GPa, the mode pore size became smaller than the particle size and at 1 GPa, it reached the same level as that of Al₂O₃ (I) and (II) ($d_B = 269, 108$ nm) of $D_m/d_B = 0.4$. The relation between D_m/d_B and the compacting pressure also was approximated by a nearly straight line on a logarithmic graph and compared with Al₂O₃ (I) and (II), the slope of fine particles of around 10 nm particle size was about 5 times steeper. Also in the relation between the compact density and pressure shown in **Fig. 1**, the slope differed by about 5 times, roughly coinciding with the above. In the case of MgO (I), (II) and (III), the

(a) Al₂O₃ and SiO₂ powders

(b) MgO powders

Fig. 4 Ratio of mode pore size in powder compacts to mean particle diameter with cold isostatic pressure.

mode pore size decreased with an increase in pressure and the slope indicated in the Figure by a straight line shows an intermediate value between that of Al_2O_3 (I), (II) and Al_2O_3 (III). As a result, D_m/d_B at 1 GPa decreased down to 0.2 or less.

Since a correlation is observed between the iso-static compacting pressure and the mode pore size as well as the compact density, the relation between the relative density (p_G/p_T) and D_m/d_B is shown in Fig. 5. Under low pressure conditions with a relative density not exceeding 0.3, some dispersion of D_m/d_B values may occur depending upon the particles but when high pressure is applied and the relative density becomes 0.5 or more, hardly any difference between particles is observed and the relation can be approximated by a straight line of slope -2 as shown in the Figure.

This result was compared with the packed structure of spherical mono-dispersed particles. It was assumed that the diameter of spheres which are in the air gap formed by the respective particles and which come into contact with each particle corresponds with the pore mode diameters. Table 2 summarizes the ratios (D/d) between the particle diameters of each structure and the diameter of spheres which inscribe each particle as well as the relative densities. When the results in Table 2 overlapped with those of Fig. 5, the experiment values roughly coincided with the pore diameter/particle diameter ratio up to the packed model structure and the compact relative density. The slope gradient became approximately -2 and the spherical mono-dispersed particles D/d coincided with the fine particles D_m/d_B used in this study. The specific area converted particle size and mode pore sizes were both affected by the particle size distribution. However since both the converted particle size and the pore diameters were about the same, the effect due to the particle size distribution was offset and it was thought that they roughly coincided with the case of spherical mono-dispersed particles. Also in the case of MgO (I) where the relative density reached a maximum of 80%, approximation was made by the straight line in the Figure. If it is to be assumed that densification progressed by mechanisms such as the deformation of primary particles, it can be presumed that the distribution

Fig. 5 Relations between ratio of mode pore size in powder compacts to mean particle diameter and relative density of powder compacts. Results of model packed bed using spherical and monosized particle were added

would divert from this straight linerelation. Therefore it is thought that densification progresses through a particle rearrangement mechanism.

The study on compact structure was organized by focusing on mode pore size and next, the mode pore size distribution was studied. As shown in the example given in Fig. 6, the pore size distribution can be approximated by Gauss distribution (Eq. 3) and not by the kind of particles or compacting conditions.

$$\nu = k_1 \exp \{ (D - D_m)^2 / k_2 \} \quad (3)$$

Here, k_1 is the pore volume frequency (ν) when the pore diameter (D) is equivalent to D_m and corresponds to the height of the peak value of the pore diameter distribution while k_2 indicates the spread of distribution. To study the correlation between the respective parameters, the parameters were estimated from the pore diameter distribution of compacts obtained in this study and Fig. 7 shows the results of the relations between k_2 and the mode pore size (D_m). The relation between the two is roughly a proportional relation and can be approximated by the straight line ($k_2 = 0.2 D_m$) in the Figure. Especially in the case of MgO, a good straight line relation exists and with changes in pore size distribution form

Table 2 Ratio of pore channel diameter to particle size and relative density of model packed beds for monosized spherical particles

Packing structure	Simple cubic	Body-centered cubic	Hexagonal close packing
Relative density	0.524	0.605	0.741
D/d	0.732	0.414	0.225

Fig. 6 Examples of curve fitting results for pore size distribution in compacts by Gauss distribution function (Eq. 2)

Fig. 7 Relations between parameter k_2 Eq. (2) and mode pore size in compacts

Fig. 8 Change in the ratio of parameter k_2 in Eq. (2) to mode pore size in Al_2O_3 powder compacts with increase of cold isostatic pressure

during the process of compacting with a slight pressure increase, only the mode pore size decreases, resulting in densification.

On the other hand, with Al_2O_3 , the mode pore size (D_m) and k_2 are not necessarily proportional and as shown in **Fig. 8**, with Al_2O_3 (III) which consists of ultra-fine particles, k_2/D_m decreased with the application of compacting pressure and the distribution form changed. Also with Al_2O_3 (IV), the pore sizes reached 6 nm or less with a pressure of 0.2 GPa or higher and although this is not shown in **Figs. 7** and **8**, a change in pore size distribution form was conspicuous. It is believed that with ultra-fine particles of Al_2O_3 , the aggregate structure remaining from the low pressure stage gradually collapses

during the pressurizing process and therefore changes in the pore size distribution form could be seen.

4. Discussion

In regard to the densification mechanism produced by isostatic high pressure compacting of ultra-fine particle packed beds, the rearrangement of particles following the collapse of the aggregate structure or elastic deformation at the particle contact point and collapse of the particles themselves can be considered. From the results shown in **Fig. 5**, it can be presumed that the rearrangement of particles is dominant in the densification mechanism but by computing the compression stress at the particles' contact point

as well as the tensile stress inside the particles during the pressure application process and by comparing the hardness of the particles with the collapsing strength, a quantitative study on the possibility of particle deformation and collapse was made. When isostatic stress (p_C) is applied on particle compacts, the force (P) generated at the particles' contact point may be obtained using the following equation if the packed bed is a uniform and isotropic random bed^{12,16}.

$$P = p_C d_B^2 \varepsilon / (1 - \varepsilon) \quad (4)$$

Where, ε is the air gap ratio of the compact and from Fig. 1, the compact density is proportional to the logarithm of the isotropic stress (p_C); therefore ($\log p_C = 1 - \varepsilon = a \log p_C + b$). Equation (4) can be rewritten as Equation (5) using constants a and b .

$$P = p_C d_B^2 \{1 - (a \log p_C + b)\} / (a \log p_C + b) \quad (5)$$

In the case of ultra-fine particles, aggregate bodies may be present and the assumption of a uniform isotropic random structure may not be satisfied. However, from the measurement results of pore size distribution in Fig. 3, it can be seen that aggregate structures are nearly collapsed under high pressure conditions of 0.2 GPa and above, and there is a difference in force between the inside and the surface of the aggregate structure even in the low pressure stage but by assuming that P of Equations (4) and (5) is an average value, it is believed that such assumption is justified. Fig. 9 shows the results obtained by deriving the constants a and b for each powder of Fig. 1 and converting the force which acts on the contact points. As the particles become larger, the contact points in the compacts become fewer and therefore the force that acts on the contact points becomes greater. Also, the slopes in the Figure have all a gradient smaller than 1 and the forces applied as compacting pressure and at contact points are not proportional. Also with Al_2O_3 (III) and (IV) and MgO (IV) in which the primary particle sizes are not larger than 15 nm, the force acting on the contact points hardly changes at pressures of 0.03 GPa or less and it can be seen that the force which was applied by rearrangement of particles is dispersed.

Next, the average stress generated at the particle contact point by force (P) was estimated^{9,14}. Assuming a spherical particle, the particle contact point is subject to an elastic deformation due to force (P) as

Fig. 9 Estimated mean force at contact point between particles in compacts according to Rumpf's equation (Eq. 3)

shown in Fig. 10(a) and the elastic displacement (Δ) is expressed by the following equation using Hertz formula.

$$\Delta = \{9P^2 (1 - \nu^2)^2 / (2 d_B Y^2)\}^{1/3} \quad (6)$$

Where, ν is Poisson's ratio and Y is Young's modulus. To evaluate the elastic deformation characteristics of the particle from its hardness, the area (A) of the osculating circle following elastic deformation is obtained geometrically using the following equation.

$$A = \pi r^2 = \pi (\Delta d_B / 2 - \Delta^2 / 4) \quad (7)$$

The displacement amount at the contact point is calculated using Equation (6) and the results of the calculation of P/A as the simplified mean stress at the contact point by applying Equations (5) and (7) of P/A is given in Fig. 10 (b). For Poisson's ratio and

(a) Scheme of contact point between particles.

(b) Estimated mean compressive stress at contact point by Equation (5) and (7).

Fig. 10 Estimation of elastic deformation and mean compressive stress at contact point between particles.

Young's modulus, $\nu = 0.25$, $Y = 420$ MPa for Al_2O_3 , and $\nu = 0.25$, $Y = 248$ MPa for MgO were used³⁾. The mean stress at the particle contact point differed somewhat depending on the type and size of particles, but it remained within the range of 4 GPa to 20 GPa. Since the hardness of particles is around 25 GPa for Al_2O_3 and 15 GPa for MgO ³⁾, P/A had about the same value as the hardness value or was slightly lower. Although the contact points may be plastically

broken down locally, the stresses at the contact surfaces were nearly the same as the hardness and an occurrence of a plastic deformation larger than the value of Δ obtained from the elastic displacement is inconceivable. **Table 3** shows the ratio between the displacement amount Δ at 1 GPa for each powder obtained from Equation (6) and the particle size. The deformation amount at a contact point was estimated to be about 3% of the particle size at the most. With a plastic deformation of this magnitude, it is thought that the effect of the deformation of a particle contact point on the pore size between particles, on the increase in compact density, or on making the pore size finer is slight.

Finally, the effect due to fracture of particles was studied. By applying a compression force (P) to the particle contact points, the tensile stress (σ_T) generated near the particle contact point was obtained using the following equation¹⁴⁾.

$$\begin{aligned}\sigma_T &= \{(1 - 2\nu)/3\} \{3P/(\pi r^2)\} \\ &= \{(1 - 2\nu)/2\} (P/A)\end{aligned}\quad (8)$$

The tensile stress generated near the particle contact point obtained using this equation was $(1 - 2\nu)/2$ times the mean compression stress and when $\nu = 0.25$ was used, it became 1/4 times. In **Table 3**, the tensile stresses of the corresponding powders at 1 GPa, obtained using Equation (8), are shown but they are within a range of 2.5 – 5 GPa. This value, compared with the theoretical strength of alumina monocrystals, ($\sigma_{th} = E/10 = 42$ GPa)¹⁷⁾ or with the actual measured value (15 GPa)¹⁷⁾ of the tensile strength of alumina monocrystal whiskers, is sufficiently small. The tensile stress obtained using Equation (8) is generated within a depth range of about twice the contact radius r of the particles from the particle contact surface and rapidly decreases inside the particle¹⁴⁾. The contact radius r at a compact pressure of 1 GPa was obtained geometrically using the following equation and the calculated results are shown in **Table 3**.

$$r = (\Delta d_B/2 - \Delta^2/4)^{1/2} \quad (9)$$

In either case, the contact radius r is about 10% of the particle diameter and even with Al_2O_3 which has the largest particle size, it is 28 nm. From the Weibull theory¹⁷⁾ in which the material strength is dominated by the maximum defect in the material, the maximum defect length c which is concerned with fractures near the particle contact point due to the generated tensile stress σ_T is assumed to be equivalent to a range of about $2r$ within which the maximum tensile

Table 3 Estimated deformation of particle, tensile stress and tensile strength at contact point. Isostatic pressure was equal to 1 GPa.

Samples	Al ₂ O ₃				MgO			
d_B [nm]	269	108	12.2	5.6	200	94	45	10
Δ/d_B [%]	2.2	2.4	2.6	2.6	1.8	2.3	2.7	3.3
σ_T [GPa]	4.9	5.0	5.3	5.3	2.6	2.9	3.2	3.5
r [nm]	28	12	1.4	0.63	19	10	5.2	2.7
σ_e [GPa]	10	15	42	42	12	17	23	32

strength is generated. From this assumption, the fracture strength σ_e near the contact point was estimated from the following equation.

$$\sigma_e = K_{IC} c^{1/2} / 1.26 \quad (10)$$

Where, K_{IC} is the critical stress intensity factor for brittle materials and the value differs depending on the literature and measuring method but since a value of around 2 ~ 4 MNm^{3/2} for Al₂O₃, and 3 MNm^{3/2} for MgO was obtained, 3 MNm^{3/2} was used. **Table 3** shows the results of the calculation of the fracture strength near the contact point σ_e with $c = 2r$. For Al₂O₃ (III) and (IV), since $\sigma_e > \sigma_{th}$ was obtained, $\sigma_e = \sigma_{th}$ was used. From this result, it can be estimated that the strength near the fine particle contact point of 1 μ m and less used in this report was not lower than 10 GPa which is close to the theoretical strength. Consequently, it can be considered that with a generated stress of several GPa, fracture of particles hardly occurs.

Observations of compacts using an electron microscope were made on compacts of Al₂O₃ (II) and MgO (I) which are of relatively large particle size. Their particle shapes were maintained even under isostatic high pressure compacting conditions of 1 GPa and no notable particle fracture or deformation was observed. The relation between the relative density shown in **Fig. 5** and the mode pore size/particle size coincided with the model packed structure of spherical mono-dispersed particles and in consideration of this, there was little possibility of substantial plastic deformation or particle fracture occurring at contact points even under high pressure conditions. It is thought that densification occurred by rearrangement of primary particles following the collapse of aggregate structures.

5. Conclusion

Using ultra-fine particles of Al₂O₃, MgO, and SiO₂ of various particle sizes, isostatic high pressure compacting under pressures of up to 1 GPa was

conducted and from the results obtained through evaluation and analysis of the compacting characteristics and compact structures, the following conclusions were reached.

- 1) Isostatic high pressure of 1 GPa is extremely effective for the densification of ultra-fine particle compacts with particle sizes of 15 nm and less, irrespective of the type of powder. Strong and coarse aggregate structures completely collapse under high pressure, and the relative density increased up to a maximum of 60%. It was also possible to make the pore size inside the compact smaller than the primary particle size.
- 2) With Al₂O₃ powders of 100 nm and a larger particle size, the density and pore size did not change appreciably with an increase in pressure. High pressures of 0.6 GPa or above were not very effective for the densification or for making air gaps in compacts smaller. On the other hand, with MgO powders, even for particle sizes of 100 nm and above, increased densification and reduction in pore size were seen with an increase in pressure and a maximum relative density of 80% and a reduction to 20% or less of the mode pore size with respect to the specific surface converted diameter were achieved.
- 3) The relation between the mode pore size/primary particle size ratio and the compact relative density was roughly approximated by a single straight line on a semi-logarithm graph. Also, by estimating the force applied at the particle contact points, the generated stress, and the maximum tensile stress generated inside the particles, and by making comparisons with the particle strength and the particle fracture yield value, it was confirmed that no notable plastic deformation or particle fracture phenomena at the contact points had occurred. Consequently, within the experiment scope of this study, densification was enhanced by the primary particle rearrangement mechanism following the collapse of aggregate structures.

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Nomenclature

A	= area of contact circle between particle	[nm ²]
a	= parameter in Eq. (3)	[—]
b	= parameter in Eq. (3)	[—]
c	= maximum flow length in contact area of particle	[nm]
D	= pore diameter in compacts	[nm]
d	= particle diameter	[nm]
d_B	= mean particle diameter estimated from specific surface area by BET method	[nm]
D_m	= mode pore diameter in compacts	[nm]
k_1	= parameter in Gauss equation	[cm ³ /g]
k_2	= parameter in Gauss equation	[m ²]
K_{IC}	= critical stress intensity factor for brittle material	[MNm ^{-2/3}]
P	= force at contact point between particles in compacts	[N]
p_C	= cold isostatic pressure	[GPa]
p_U	= pressure of uni-axial pre-pressing	[GPa]
r	= radius of contact circle between particles	[nm]
S_W	= specific surface area by BET method	[m ² /g]
ν	= pore volume frequency	[cm ³ /g]
Y	= Young's modulus	[MPa]
Δ	= deformation at contact point between particles	[nm]
ε	= porosity in powder compacts	[—]
ν	= Poisson's ratio	[—]
σ_e	= estimated tensile strength of contact area of particle	[Pa]
σ_T	= tensile stress in particle	[Pa]
σ_{th}	= theoretical tensile strength of materials	[Pa]
ρ_G	= density of powder compacts	[kg/m ³]
ρ_T	= powder true density	[kg/m ³]

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