Evaluation of lightweight pottery using organic hallow microsphere

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The purpose of this study is to develop lightweight pottery using organic hollow microsphere and to evaluate the mechanical properties of lightweight pottery. Spherical pores about 100 μm were formed in body, and total porosity increased proportionally with the addition of organic hollow microspheres. Many pores were isolated so that open porosity is extremely smaller than total porosity. A small amount addition of microspheres drastically degraded bending strength of pottery with slight decrease in density, indicating pores act as fracture flaws. On the other hand, a decrease in bulk density degraded fracture toughness moderately. In a wide range of porosity, a bending strength σ and a fracture toughness KIC of lightweight pottery could be expressed in σ = 70.4d^0.57, and KIC = 1.27d^0.54, respectively. Here, d equals to relative density.

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Key-words : Lightweight, Pore, Bending strength, Fracture toughness, Organic hallow microsphere

1. Introduction

The most representative method for making lightweight ceramics is to create pores within the ceramics to decrease the bulk density. In order to create pores in green bodies, pore-forming agents such as organic matter or hollow inorganic matter were added to the raw material and then, molded and sintered. Another method to create pores is to create pores during the firing process. In the firing process, the addition agents decompose and combust therefore creating gases which create pores. As the high temperature pore-forming agents, carbon, hydroxyapatite, ceria and etc. are known. Pore generation during the firing process has difficulties in controlling uniform size pores with even distribution. On the other hand, creating pores in the green body during the forming stage enables pores to be evenly distributed and the size of the pores can be controlled as well. The inorganic pore-forming agents used in the casting stage do not combust even after firing process and the residual agents stay within the fired body, therefore only the hollow sphere is usable. In contrast, the organic pore-forming agents burn below 500°C, therefore allowing both hollow and non-hollow spheres to be used. The mechanical properties of the porous bodies in such ways depend on the amount and distribution of the pores created.

In this study, poly-acrylonitrile hollow microsphere was used to create the pores. The influence of pores formed by organic hollow microsphere on the sintering behavior and on the mechanical properties such as bending strength and fracture toughness of pottery was investigated.

2. Experimental procedure

2.1 Materials and preparations

The raw material 1S (Goryeo Doto, Korea Clay), widely known in Korea, was used as pottery body. Table 1 shows the chemical composition of the raw material. It is typical porcelain body composed of quartz, albite, kaolin and sericite as shown in Fig. 1 and the mean particles size was 6.7 μm. Poly-acrylonitrile Hollow Microsphere (made in Japan, hereafter designated as OHM) was used for pore-forming agent. OHM has a small deviation of size distribution and shows a uniform morphology. OHM has real spherical type and, the mean particles size was 98 μm. The most representative method for making lightweight ceramics is to create pores within the ceramics to decrease the bulk density. In order to create pores in green bodies, pore-forming agents such as organic matter or hollow inorganic matter were added to the raw material and then, molded and sintered. Another method to create pores is to create pores during the firing process. In the firing process, the addition agents decompose and combust therefore creating gases which create pores. As the high temperature pore-forming agents, carbon, hydroxyapatite, ceria and etc. are known. Pore generation during the firing process has difficulties in controlling uniform size pores with even distribution. On the other hand, creating pores in the green body during the forming stage enables pores to be evenly distributed and the size of the pores can be controlled as well. The inorganic pore-forming agents used in the casting stage do not combust even after firing process and the residual agents stay within the fired body, therefore only the hollow sphere is usable. In contrast, the organic pore-forming agents burn below 500°C, therefore allowing both hollow and non-hollow spheres to be used. The mechanical properties of the porous bodies in such ways depend on the amount and distribution of the pores created.

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2.2 Measurements

The particle size analysis of the raw material was measured using the laser diffraction method (Beckman Coulter LS13320, U.S.A). Phase analysis of the raw material was measured by XRD (X-ray diffraction, Right D/max 2500v/pc, Rigaku, Japan). The size distribution and morphology of OHM was observed and measured using SEM (JSM-6390, JEOL, Japan). OHM’s density was measured using the density measure tool (Accupyc II-1340, Micromeritics, USA). True density of pottery was measured using pulverized powders by a specific gravity bottle technique with water as liquid.

Fracture toughness was measured through SEVNB (Single-edge V-notched beam method), a method suitable for both dense ceramic and porous ceramic. The sample was prepared into 3 × 4 × 40 mm sized samples and five samples were measured and averaged. One of the samples used for measuring fracture toughness is shown in Fig. 3.

Fracture toughness \( K_{IC} \) was calculated using Eq. (1). Here, \( P \) is the fracture load and \( S \) is the distance between the supporting points. \( B \) is the thickness of the test piece, \( W \) is the width and \( a \) is the length of V-Notch. \( X \) is expressed by Eq. (2).17

\[
K_{IC} = \left( \frac{PS}{BW^{1.5}} \right) \left( \frac{3}{2} \left( \frac{a}{W} \right)^{0.5} \cdot X \right)
\]

\[
X = \frac{1.99 - \frac{a}{W} \left( 1 - \frac{a}{W} \right) \left( 2.15 - 3.93 \left( \frac{a}{W} \right) + 2.7 \left( \frac{a}{W} \right)^2 \right) \left( 1 + 2 \frac{a}{W} \right) \left( 1 - \frac{a}{W} \right)^{1.5}}{1 + 2 \frac{a}{W} \left( 1 - \frac{a}{W} \right)^{1.5}}
\]

3. Results and discussions

3.1 Sintering characteristics

The linear shrinkage rate with the addition of OHM fired at 1250°C is shown in Fig. 4. With the increase in OHM, the linear shrinkage rates increased from 12.4 to 13.1% accordingly. At heating, added OHM burned out at about 400°C and left hollow spheres in the pottery body. If added OHM particles are truly spherical and large enough, a specimen containing OHM is considered to shrink in a same rate with a specimen without addition of OHM, since an air left in hollow sphere can be easily exhausted through connected pores during viscous flow sintering. Actual OHM show a particle size distribution, therefore, the shrinkage of fired specimens gradually increases with addition of OHM.

Table 1. Chemical composition of raw material

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>K(_2)O</th>
<th>Na(_2)O</th>
<th>TiO(_2)</th>
<th>P(_2)O(_5)</th>
<th>Ig.loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass %</td>
<td>71.6</td>
<td>19.2</td>
<td>0.49</td>
<td>0.13</td>
<td>0.08</td>
<td>1.96</td>
<td>0.97</td>
<td>0.04</td>
<td>0.05</td>
<td>5.55</td>
</tr>
</tbody>
</table>
Figure 5 shows the bulk density with the addition of OHM. The increase in OHM led to an increase in pore volume in the matrix and therefore density decreased. The fired sample at 1250°C without OHM showed sufficient density of 2.368 g/cm³. With the addition of 0.6 mass % OHM, density decreased to 1.276 g/cm³, 46% lightweight compared with that of no addition.

Archimedes’ immersion technique is commonly used in order to evaluate the sintering characteristics of ceramics. Water penetrates into bodies through pores connected at boiling. The volume of open pores can be measured by the mass of water absorbed in the body. The mass ratio of absorbed water to solid body is defined as water absorption, and volume ratio of open pore to bulk solid volume is defined as apparent porosity. Apparent porosity is suitable for estimating highly porous ceramics. Apparent porosity of fired samples at 1250°C is shown in Fig. 6. Total porosity can be calculated from bulk density and true density, so the total porosity was also shown in Fig. 6. For Archimedes’ water absorption measurement by boiling in water, sample preparation condition affects the mass absorbed. Therefore, two types of sample, as-slip-casted specimens and polished specimens were used in this experiment.

Total porosity greatly increased with the increase in OHM addition, corresponding to the change of the bulk density. However, two types of apparent porosity of specimens were smaller than total porosity, since many pores were present probably isolated in the body. Especially, for as-slip-casted specimens with OHM addition of 0.45%, apparent porosity was only 0.9%. On the other hand, polished small specimens with 0.45 mass % OHM showed rather large apparent porosity.

Figure 7 shows the SEM photographs of the surface and cross section of the OHM added sample fired at 1250°C. On the as-slip-casted free surface of sample [Fig 7(a)], any large pore was not observed. This dense sintered surface layer would act as barrier and intercept the water to penetrate. On the other hand, many pores generated by OHM particles were observed [Fig. 7(b)] inside the body. Through a fraction of pores connected, water could penetrate, so that the apparent porosity increased with the increase in OHM addition. When OHM addition exceeded 0.45 mass %, many pores began to connect and apparent porosity suddenly increased.

### 3.2 Mechanical properties

The relationship between bending strength and OHM content is shown in Fig. 8. The bending strength decreased from 101 to 26 MPa with an increase in OHM, corresponding to a change of the porosity and the density in Figs. 5 and 6. Especially, only a small amount addition of OHM (0.15 mass %) drastically degraded bending strength of pottery in 43% with slight decrease in the bulk density in 11%. With the further increase in OHM, bending strength of pottery decreased gently. Therefore, the change in bending strength was not equivalent to the decrease in pore volume. Griffith flaw size C and fracture toughness $K_{IC}$ are known to affect the mechanical strength $\sigma$ as shown in a next Eq. (3). Here, $Y$, $E$ and $\gamma$ are shape factor of flaw, Young’s modulus and surface energy, respectively.

$$\sigma = \frac{K_{IC}}{Y\sqrt{C}} = \frac{\sqrt{2\gamma'E'}}{Y\sqrt{C}}$$

(3)
The fracture toughness $K_{IC}$ of samples measured is also shown in Fig. 8. While the samples without OHM had the highest fracture toughness value of 1.22 MPa/m$^{1/2}$, a decrease in bulk density degraded fracture toughness gentler than bending strength. From Eq. (3), equivalent flaw size $C$ can be obtained by:

$$C = \left( \frac{K_{IC}}{\sigma} \right)^{1/2}$$

Supposing $Y^2 = \pi$, equivalent flaw size $C$ was calculated, and the value of the specimen without OHM was about 50 $\mu$m and the value of OHM added specimens ranged from 100 to 140 $\mu$m. This large flaw size corresponded just to the size of organic hollow microspheres as shown in Fig. 2. Therefore, an addition of small amount of OHM drastically degraded bending strength of pottery.

In order to evaluate the effect of porosity on the mechanical properties, a bending strength and a fracture toughness were reexamined as a function of the relative density. Here, a relative density is defined as bulk density/true density and corresponds to $d = 1 - P$, and $P$ is a total porosity. Results are shown in Fig. 9. Many experimental equations were suggested between Young’s modulus and porosity for various ceramics materials, such as exponent, quadratic exponent, parabolic and linear equations etc. These equations include one or more empirical constants, whereas their physical meanings are frequently uncertain. On the other hand, only a few equations were reported about the relationship between fracture toughness and porosity. By J. F. Yang etc., a multimomial parabolic relationship was reported to fit a fracture toughness of porous Si$_3$N$_4$. But, a physical meaning of two empirical constants was not clarified. T. Ostrowski etc. evaluated several mechanical properties about sintered alumina, and suggested a relationship between a crack tip toughness $K_0$ and a porosity $P$ as $K_p = K_{IC0}(1 - P/P_0)^{\eta}$, then, $K_{IC0}$ and $P_0$ could be defined respectively as toughness at $P = 0$ and the porosity at which crack tip toughness reached to almost zero and was about 40% in case of alumina. Applying many mathematical equations shown in above literatures, the simplest mathematical Eqs. (5) and (6) containing only one parameter fitted well to our bending strength and fracture toughness results. Here, $d$ is a relative density of specimens, $K_{IC0}$ and $\sigma_0$ are fracture toughness and bending strength of ideally dense pottery, respectively. Exponent “$n$” is an empirical constant and can be calculated by least-squares method.

$$K_{IC} = K_{IC0}d^n$$

$$\sigma = \sigma_0d^n$$

Fracture toughness was expressed as $K_{IC} = 1.27d^{1.54}$ and the deviation was extremely small. On the other hand, the bending strength was expressed as $\sigma = 89.1d^{0.76}$ and the deviation was large and could not be ignored. Already described in previous section, added OHM acted as fracture flaw and degraded the bending strength of potteries. Therefore, further calculation by least-square method was adopted neglecting the maximum strength value of sample without OHM. As a result, bending strength as a function of relative density was expressed well as $\sigma = 70.4d^{1.57}$, and the deviation was very small.

M. Kobashi derived a theoretical relationship between Young’s modulus $E$ and relative density $d$ for porous metals having open cell structure as follows.

$$E = E_0d^2$$

Fracture energy $\gamma$ also depend on the porosity of materials, since the newly created surface area by unit crack progress is decreased by pore area. Roughly estimating the surface area as a factor $(1 - P)$, surface energy can be expressed as follows.

$$\gamma = \gamma_0(1 - P) = \gamma_0d$$

Fracture toughness $K_{IC}$ equals to $(2E\gamma)^{1/2}$ as shown in Eq. (3), so a fracture toughness of porous materials can be written as follows.

$$K_{IC} = (2E\gamma)^{1/2} = (2E_0d^2\gamma_0d)^{1/2} = (2E_0\gamma_0)^{1/2}d^{1/2}$$

A physical constant $n = 1.54$ and 1.57 in Eqs. (5) and (6) obtained for a fracture toughness and a bending strength agreed well with approximate calculation result of Eq. (9).

The microstructures of the fired body are shown in Fig. 10. From the microstructure of the sample without OHM in Fig. 10(a), any large pore was not observed, showing enough vitrification. In case for the sample added with 0.3 mass% of OHM, many pores were observed in the body as shown in Fig. 10(b). A large amount of pores were observed for the sample added with 0.6 mass% OHM in Fig. 10(c). Almost all the pores generated by OHM were spherical and the size was about 100 $\mu$m.

4. Conclusion

Poly-acrylonitrile hollow microsphere (OHM) was added as pore former to the slurry of porcelain raw material, in order to lighten and characterize the fired pottery body. With the increase
in OHM addition, the linear shrinkage rate slightly increased from 12.1 to 13.1%. It was explained as that high-temperature viscous flow of liquid phase enhanced sintering and densification. With 0.60 mass% of OHM addition, pottery density was lightened about 46% compared to the samples without OHM. Isolated spherical pores about 100 µm were formed and the density of pottery decreased linearly with an addition of OHM, whereas the bending strength drastically decreased, because the large pores combined with small cracks and acted as large fracture flaws. The relationship between relative density and bending strength of OHM added samples were expressed in equation $\sigma = 70.4d^{-0.37}$. On the other hand, fracture toughness gently degraded with a porosity. The relationship between fracture toughness and relative density was expressed in equation $K_{IC} = 1.27d^{-0.54}$.

References