Characteristics of Clays from the Westerwald Deposits in West Germany (Part 2)

—Comparison of the Densification Process with Respect to That of a Feldspatic Body—

Hideki ISHIDA and Osamu WATANABE

(Ceramic Research and Development Laboratory, INAX Corporation, 3-6, Koiehonmachi, Tokoname-shi, Aichi 479)

Using the isothermal method and press softening measurements, the densification process of clays from the Westerwald deposits in West Germany was compared with that of a feldspatic body prepared from Japanese raw materials. The clays from the Westerwald deposits completed the densification at around 120°C lower than that of the feldspatic body and showed high deformation resistance as well, the softening deformation being 1/3 that of the feldspatic body. This is closely related to the fact that 90% of the illite which is flux component and 22% of the quartz particles are concentrated in the range lower than 2 μm. In addition, it is believed that the composition of mullite is different, as judged by the marked difference in the shape of the crystallized mullite.

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Key-words: Westerwald clay, Kibushi clay, Illite, Densification, Mullite, Softening deformation

1. Introduction

Westerwald is the biggest clay deposit in West Germany, and the clay there is widely utilized domestically as well as overseas as the raw materials for ceramics for building construction, sanitary ware and table ware. The mineral assemblage of Westerwald clay features the kaolinite-illite-quartz system. 1) This is quite different from Kibushi clay developed in the Tertiary System in the Seto and Tajimi areas which are representative clay supplying areas in Japan for pottery. However, comparison and evaluation as ceramic raw material seem not to have been carried out sufficiently.

This clay can be formed by itself and has excellent firing stability. Its extrudability, an important aspect in pottery forming, has already been reported. 2) In this paper, the densification behavior and the press deformation resistance of Westerwald clay before the vitrification point have been studied by comparing it with a feldspatic body prepared with domestic materials. The latter is a common preparation for building ceramics.

2. Experiment

2.1 Specimen

The same clay from the Westerwald deposits (I-Body), as in the previous report, 2) was used. The Yakusa Kibushi clay used as the specimen for comparison in the previous report requires, by itself, high temperatures for densification and is therefore not useful for comparison industrially. For this reason, feldspar and quartz were added to it so as to make the feldspatic body (F-Body). The chemical composition and mineral assemblages of each body are shown in Table 1.

2.2 Forming

The test specimens were prepared by an auger type extruder. The forming pressure was adjusted to 2 MPa, assuming the medium forming pressure for the ceramics for building construction. The water content at forming was determined to be 22.9% for the I-Body and 23.2% for the F-Body.
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According to the evaluation method of extrusion reported previously, the gradient and the intercept of the extrudability line were $6.36 \times 10^{-2}$, $-3626$ for the I-Body and $10.68 \times 10^{-2}$, $-6362$ for the F-Body. The test was performed after drying the specimens at 80°C for 48 h. The packing ratios of the dried bodies were 72% for the I-Body and 71% for the F-Body.

Table 1. Chemical compositions (in mass %) and mineral assemblages for I-Body and F-Body.

<table>
<thead>
<tr>
<th></th>
<th>I-Body</th>
<th>F-Body</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>67.3</td>
<td>70.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21.5</td>
<td>18.6</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>CaO</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>MgO</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>tr.</td>
<td>1.4</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Ig-loss</td>
<td>6.3</td>
<td>4.8</td>
</tr>
<tr>
<td>Total</td>
<td>100.8</td>
<td>99.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Quartz</th>
<th>Quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assemblage</td>
<td>Kaolinite group</td>
<td>Kaolinite group</td>
</tr>
<tr>
<td>Rutile</td>
<td>Feldspar</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of the apparatus used for measuring pressure softening. 1: specimen, 2: electric furnace, 3: alumina rod, 4: weight, 5: differential transformer, 6: thermocouple, 7: electric furnace controller, 8: amplifier, 9: recorder.

Fig. 2. Relation between the reciprocal absolute temperature and the logarithmic holding time at the vitreous point.

2. Evaluation of the densification behavior

The isothermal method was employed, using two electric furnaces. One being kept at the soaking temperature and the other being kept at the scheduled temperature. The relation between the temperature and the time necessary for the vitrification was obtained by transferring the specimens quickly between the two furnaces. The soaking temperature was set at 1000°C for 48 h. The packing ratios of the dried bodies were 72% for the I-Body and 71% for the F-Body.

2.3 Evaluation of the densification behavior

The isothermal method was employed, using two electric furnaces. One being kept at the soaking temperature and the other being kept at the scheduled temperature. The relation between the temperature and the time necessary for the vitrification was obtained by transferring the specimens quickly between the two furnaces. The soaking temperature was set at 1000°C based on the result of preliminary tests and the vitrification point was taken as the point of 1% of water absorption. Details of the experimental method have been reported.

2.4 Evaluation of press softening behavior

Figure 1 shows the laboratory-made press softening measuring unit used for this test. Displacement can be measured directly by the differential transformer. The differential type is intended to eliminate the error due to the thermal expansion of the alumina rods. The size of the specimens was 30×100×6 mm, the span was 84 mm and the load 0.7 N. Measurement was carried out under 10 deg/min heating rates, 1250°C maximum temperature and 1 h holding time.

3. Experimental results

3.1 Densification behavior

Figure 2 shows the experimental results. Both bodies show good linear relationship between the temperature (T) and the time (t) necessary for vitrification, which can be expressed by the following equation.

$$\ln t = A/T + C$$

Compared to the F-Body, the I-Body has a larger gradient, resulting in it being more susceptible to temperature changes. But it is evident that the vitrification temperature of the I-Body is approximately 120°C lower than that of the F-Body, and also that the I-Body can be densified at a much lower temperature than the temperature predicted from the chemical composition.

3.2 Press softening behavior

The degree of press softening is considered to be closely related to the densification of the body. The softening deformation should be expressed with respect to the degree of the densification and not the temperature. Since Eq. (1) can be applied to both bodies, the degree of vitrification V at the isothermal heating and cooling state can be calculated using the following equations.
under the assumption of $V=1$ at the vitreous point.

Isothermal period

$$V = \exp\left[-\frac{A}{T} + C\right] \cdot t \quad (2)$$

Heating and cooling period

$$V = \frac{A}{a} \exp\left[-C\right] \left[\exp\left(-\frac{x}{x^2}\right) F(x)\right]_{x=A/T}$$

$$F(x) = 1 - \frac{2}{x} + \frac{3}{x^3} - \ldots \quad (3)$$

Where $V$ is the degree of vitrification, $A$ and $C$ are the constants for each body, $T$ is the absolute temperature (K), $t$ is the holding time (min), $a$ is the heating or cooling rate (deg/min) and $x = A/T$ respectively.

Figure 3 shows the relation between the degree of vitrification calculated by replacing $A$ and $C$ in Eqs. (2) and (3) by the experimentally determined values for both bodies, and the softening deformation. The softening deformation of the I-Body at the vitreous point is very small, being only $1/3$ that of the F-Body. In addition, its softening deformation doesn't change significantly in the over-fired state. The I-Body retains high deformation resistance.

4. Discussion

According to the results of X-ray diffraction analysis, the constituent phases of the both bodies at $V=1$ were mullite, quartz and glass phase. Figure 4 shows the relation among the amount of constituent phase of the well densified bodies and the bodies before firing, and their particle size distribution. Assuming that the constituent minerals are based on the theoretical composition, Norm calculation was used for the bodies before firing and the X-ray internal standard method was applied for the calculation of the fired bodies. The chemical composition of the glass phase was also calculated based on this assumption.

The amount of mullite determined from the phase diagram showed close correspondence with the results of measurement I-Body 29% and F-Body 19%. This indicates that mullite was
crystallized also from mica group (illite\textsuperscript{2}) of I-Body, and from Norm calculation, the total amount of mica group changed into mullite and glass phase. In addition, mica group in F-Body consists mainly of muscovite from the results of optical microscope analysis, and also it is not so closely related to the crystallization of mullite from Norm calculation. Figure 5 shows the changes of the amount of mullite measured by X-ray diffraction analysis. Mullite increases its formation speed between 1050\degree-1150\degree C, but there is no difference of the formation speed due to kinds of minerals. Figure 6 shows scanning electron microscope (SEM) photographs of the formed mullite. Etching treatment was carried out by hydrofluoric acid, I-Body and F-Body require different concentration of the acid and time for the treatment (10\%, 30 min and 5\%, 20 min respectively). This indicates that the characteristics of the two glass phases are quite different. The mullite in F-Body shows inhomogeneous formation with a large aspect ratio, over 1\,\mu m in length. In contrast, the mullite in I-Body is formed homogeneously with a small aspect ratio and mostly under 1\,\mu m in length. From the above, it appears that the mullite component may be Al\textsubscript{2}O\textsubscript{3} rich\textsuperscript{6} or may not it may contain other components such as TiO\textsubscript{2}.\textsuperscript{7} It is evident that the amount of quartz changed significantly before and after firing, indicating that it melts easily. This is because that 22\% of the amount of quartz in the I-Body is under 2\,\mu m, whereas almost all the quartz in the F-Body is in the form of accessory minerals of the feldspar.

Fig. 5. Relation between mullite forming volume in mass \% and firing temperature. Specimens were soaked for 1 h at each temperature and forming volume was measured by X-ray diffraction analysis.

Fig. 6. SEM photographs of the fired body (1150\degree C) after etching by hydrofluoric acid. (A) F-Body (5\% solution for 20 min), (B) I-Body (10\% solution for 30 min).

Fig. 7. SEM photographs of the fired body (1150\degree C). (A) F-Body, (B) I-Body.
group, and almost all the quartz doesn’t melt because it is concentrated in the over 2 µm range when ordinary wet milling by ball mill is carried out. Figure 7 shows SEM photographs of the two bodies at 1150°C. F-Body shows many pores due to a melt of feldspar.

This phenomenon was remarkable from 1120°C. In contrast, it is not observed in I-Body. The amount of open pores in I-Body and F-Body at 1150°C is approximately 0.3% and 10% respectively. From Fig. 5, considering that the mullite crystallization of the two bodies are almost completed, I-Body completes its densification almost at the same time when mullite is crystallized, whereas I-Body requires further diffusion of the liquid phase. Comparing to I-Body, this is one of the reasons that F-Body necessitates a lot of energy in order to have densification. At the same time, it can also be considered the fact that with regard to the flux component, 90% of mica group particles in I-Body are below 2 µm in size, the densification speed is accelerated.

It is expected that the liquid phase (glass phase) in I-Body mainly consists of SiO₂ rich component after the crystallization of mullite and part of quartz, and F-Body consists of feldspar as the flux component. In another words, the glass phase of I-Body is SiO₂ rich, whereas Al₂O₃ rich glass phase in the F-Body. The amount of glass phase in the two bodies, as it is shown in Fig. 4, is nearly the same. Since the glass phase composition, which is considered to influence greatly on the press softening, differs significantly, viscosity calculation was carried out. The calculation followed the Fulcher's equation using the Lakatos et al. and Knapp constants. Since the constants of TiO₂ and Fe₂O₃ have not been ascertained with clarity, they were eliminated from the calculation. Figure 8 shows the results. Although many assumptions were included in carrying out the calculations, it is estimated that the viscosity of the glass phase in I-Body is higher than that of the glass phase in F-Body. This difference gets larger if V (degree of vitrification) is employed at the horizontal axis, considering that the difference in viscosity of the glass phase is influencing the degree of the press softening of the two bodies.

From the above, comparing to F-Body, I-Body completes the densification at lower temperature, and in addition, softening deformation is 1/3 that of F-Body. The main reasons are considered as follows. The particle size of the flux component in I-Body is small and particles disperse homogeneously, and the densification is possible without accompanying a significant move of the liquid phase. Mullite is formed from lower temperature and disperses homogeneously. The amount of the formed mullite is about 2 times that of F-Body. There is no remarkable difference in the amount of the glass phase, but I-Body retains high viscosity.

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