In this paper, mineral and sintering properties of high alumina-containing clay (Yamase clay) derived from a weathered granite stone were investigated, and compared with those of low alumina-containing clay derived from a weathered sandstone (Hobashira clay) for the ancient Karatsu ware. Content of Al$_2$O$_3$ in Yamase clay was 30.8–33.1 mass %, and showed higher than that of Hobashira clay (13.1–15.8 mass %). Yamase and Hobashira clay had a mineral composition of kaolinite (64.3), α-quartz (10.6), muscovite (11.9), albite (10.3), and microcline (2.9 mass %), and kaolinite (12.9), α-quartz (52.9), muscovite (23.4), albite (6.9), and microcline (3.9 mass %), respectively, by the Rietveld analysis. Bulk densities of Yamase clay heated at 1200, 1300, and 1400°C were 1.99, 2.15, and 2.35 g/cm$^3$, and Yamase clay had a higher refractoriness than Hobashira clay. After heating Yamase clay at 1300–1400°C, the heated body was composed of fine needle-like mullite (49.8) and glass (50.2 mass %) without the bloating of the body.

1. Introduction

Karatsu ware (Karatsu-yaki) is one of the Japanese traditional potteries and its basic production technology by using the potter’s wheel, the climbing kiln and some ash glazes was transformed from the Korea peninsula to Karatsu in 1580’s. The ware design, the color of body and glaze of the ancient Karatsu wares are very similar to those of the ancient Korean ceramic ware (Puncheong) produced in the 15–16th century.

Archeologically, some ancient kilns (Handou, Hobashira, Kojukanja, Saraya, Hiramatsu, Handoukame, Yamase, etc.) were operated in Karatsu area in the 1580’ to 1590’s, and Yamase kiln was geologically only located on the granite zone, and another kiln was located on the sandstone zone. It was reported that ancient Karatsu wares produced at Yamase kiln had a porous body and the inside of their foot showed small cracks starting from the center and moving towards the outside, like the spokes of a bicycle wheel.

In our previous studies, the chemical and mineral properties of some sedimentary clays derived from the weathered sandstone and granite were investigated. In this paper, the properties of some shards of Karatsu ware excavated from ancient kilns, and the sintering properties of Yamase clay derived from a weathered granite stone and Hobashira clay derived from the weathered sandstone was studied.

2. Experimental

Two clays (Yamase clay and Hobashira clay) were mined from near the ancient Yamase and Hobashira kilns located in Karatsu-shi, Saga, Japan. These clays were treated by an usual elutriation in water to remove coarse particles (<100μm), and then dried at 60°C. Clay powder was mixed with water (18 mass %), and well pugged. The pugged clay was pressed in a gypsum mold (10 × 20 × 20 mm) to form a clay plate. Some shards of ancient Karatsu wares excavated from ancient kilns were contributed from the Ko-Karatsu Research and Exchange Association, Karatsu-shi. The chemical composition of treated clays was analyzed by X-ray fluorescence analysis (XRF, model ZSX, Rigaku Co., Japan), and the crystal phase was characterized by a powder X-ray diffraction (XRD, model X’Pert-MRD, PANalytical Co., Japan). The glaze layer on ancient shars was removed by a micro-cutter. Quantitative analysis of mineral phase composition of two clays was performed by a Rietveld method using the Fullprof program. The diffraction profiles were fitted with a pseudo-Voigt peak function and manually selected background points. The refinement quality is indicated through the minimization and convergence of terms: R-pattern ($R_p$), R-weighted pattern ($R_wp$), R-expected ($R_e$), and goodness-of-fit ($\chi^2 = R_wp^2/R_e^2$). The reliability factors for the Rietveld quantitative phase analysis are $R_p = 12.0\%$, $R_wp = 16.0\%$, $R_e = 9.70\%$, $\chi^2 = 2.72$ for Hobashira clay and $R_p = 9.88\%$, $R_wp = 13.8\%$, $R_e = 9.96\%$, $\chi^2 = 1.93$ for Yamase clay, respectively.

The morphology of clay was observed by a transmission electron microscopy (TEM, model 2010, JEOL, Japan). Clay plates were heated at 1100–1400°C in air using an electric furnace with heating rate of 100°C/h to investigate the sintering property. The composition of mullite and glass in the heated clay plate was measured by a chemical etching of glass phase using 4.6 vol %...
The bulk density and mineral phase composition of the heated clay plates were measured by the Archimedes’s method in water at 20°C and XRD, respectively. Furthermore, the polished internal structure and mullite crystal in the heated body and ancient shards were observed by a field emission electron microscopy (SEM, model JSM-6700F, JEOL, Japan) and a digital microscope (model VW-6000, KEYENCE Co., Japan).

3. Results and discussion

3.1 Chemical composition and mineral phase of shards of ancient Karatsu ware

Table 1 shows the average chemical composition and bulk density of shards of ancient Karatsu wares excavated from some ancient kilns. Number of samples for the analysis was 8. Alumina content of ancient shards from Kojuukanja, Hobashira, Ohtani, Handoukame, and Hiramatsu kiln which were built on the weathered sandstone zone was 12.5–17.7 mass %, and these values were very similar to that of ancient Arita pocelains. However, alumina content of ancient shards from Yamase kiln was 35.9 mass %, and it was suggested that high alumina-containing raw material which was derived from the weathered granite was used only at Yamase kiln in 1580’s in Karatsu. The content of Na2O + K2O in shards from Yamase kiln was 2.4 mass %, and it was lower than that of another kilns (2.6–4.8 mass %).

The internal structure of body of ancient shards from Yamase and Hobashira kilns was shown in Fig. 1. Many pores of 15–140 μm in diameter were observed in ancient shards from Yamase kiln, and its bulk density (1.91 cm3/g) was lower than those of bodies of Kojuukanja, Hobashira, Ohtani, Handoukame, and Hiramatsu kiln (2.1–2.3 cm3/g).

Figure 2 shows XRD patterns of ancient shards from Hobashira and Yamase kilns. The strong diffraction peak of α-quartz, and weak peaks of mullite and cristobalite were observed in the shard from Hobashira kiln, and the peak intensity ratio of minerals was very similar to those of shards from another ancient kilns in Karatsu-shi. However, the formation of mullite in the shard from Yamase kiln was only promoted than that of the shard from Hobashira kiln, and the XRD intensity ratio of mullite to α-quartz and bulk density of ancient shards from Yamase kiln were very similar to those of shards with 31–39 mass % of Al2O3 which were produced at the south regions of the Korea peninsula at the 15–16th century.

3.2 Chemical and mineral composition of Yamase and Hobashira clay

Table 2 shows the chemical composition of Yamase and Hobashira clay mined from near the ancient Yamase and Yobashira kiln. Clay samples for the chemical analysis were mined from different three points near the ancient two kilns. Alumina content in Yamase clays was 30.8–33.1 mass %, and higher than that of Hobashira clay (13.1–15.8 mass %). Ignition loss of Yamase and Hobashira clays were 10.7–12.8 and 3.9–4.8 mass %, respectively. From these results, Yamase clay was composed of high-alumina containing mineral. Average content of Na2O + K2O in Yamaase and Hobashira clay were 2.7 and 3.6 mass %, these values were similar to those of shards excavated from ancient Yamase and Hobashira kiln. Typically, Hobashira-1 and Yamase-1 clays shown in Table 1 were used for the following experiments.

Figure 3 shows the XRD Rietveld refinements results for Yamase and Hobashira clays, and Table 3 shows the mineral composition of two clay samples. Two clays were composed of α-quartz (SiO2), kaolinite [Al2(Si2O5)(OH)4], muscovite

Table 1. Average chemical composition (mass %) and bulk density of body of ancient shards excavated from some kilns operated in the 1580–1590’s in Karatsu-shi

| Kiln name | SiO2 | Al2O3 | Fe2O3 | TiO2 | CaO | MgO | K2O | Na2O | B.D. (cm3/g) |
|-----------|------|------|-------|------|-----|-----|-----|------|-------------|
| Yamase    | 56.81| 35.90| 2.62  | 0.61 | 0.25| 0.90| 2.11| 0.31 | 1.9         |
| Kojuukanja| 74.92| 17.73| 1.21  | 0.60 | 0.12| 0.65| 3.01| 0.60 | 2.3         |
| Hobashira | 71.91| 21.44| 3.73  | 1.11 | 0.62| 0.64| 1.07| 1.93 | 1.5         |
| Ohtani    | 81.35| 15.00| 1.41  | 0.60 | 0.11| 0.44| 2.90| 0.71 | 2.5         |
| Handoukame| 75.62| 16.81| 1.70  | 0.81 | 0.24| 0.65| 2.81| 0.97 | 2.1         |
| Hiramatsu | 74.78| 15.91| 2.52  | 0.70 | 0.23| 0.86| 3.21| 1.61 | 2.3         |

Fig. 1. The internal structure of ancient shards excavated from (a) Yamase kiln and (b) Hobashira kiln.

Fig. 2. XRD patterns of ancient shards excavated from (a) Yamase kiln and (b) Hobashira kiln. m: mullite, q: α-quartz, c: cristobalite.
[K(Al2.9Si3.1O10)(OH)2], albite [Na(AlSi3O8)], and microcline [K(AlSi3O8)]. From this result, Yamase clay had about 5 times higher content of kaolinite than Hobashira clay.

Figure 4 shows TEM images of two clays. Fine platy crystals of 100–600 nm in width were observed in Hobashira clay, and needle-like crystals of 200–400 nm in length and around 50 nm in width were observed in Yamase clay. It was supposed that platy crystals were muscovite, and needle-like crystal was kaolinite from XRD and TEM observation.

### 3.3 Sintering property of Yamase and Hobashira clay

Plates prepared from Yamase and Hobashira clays were heated at 1100–1400°C in air. Figure 5 shows the bulk density of the heated plates. The bulk density of the heated plate from Yamase clay increased with the heating temperature, and reached 2.19, 2.29 and 2.35 cm³/g at 1250, 1300 and 1400°C, respectively. The bulk density of the heated plate from Hobashira clay reached 2.21 and 2.40 cm³/g at 1250 and 1300°C, respectively. The sintering was promoted at temperature from 1250 to 1300°C, but it abruptly fell to 1.95 cm³/g at 1400°C by the bloating phenomenon in the body. It was supposed that platy crystals were muscovite, and needle-like crystal was kaolinite from XRD and TEM observation.

Figure 6 shows the XRD patterns of two clay plates heated at 1100–1400°C. The formation of mullite crystals in Hobashira clay started at 1200°C, the XRD relative intensity (mass %) of mullite (hkl = 210 at 2θ = 26.27°) + quartz (hkl = 101 at 2θ = 26.27°) was 5.5 at 1200°C, 12.9 at 1300°C, and 18.2% at 1400°C. The final

| Clay sample | SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | MgO | K₂O | Na₂O | Ig. loss |
|-------------|------|------|------|------|-----|-----|-----|------|---------|
| Yamase-1    | 50.13| 31.45| 2.52 | 0.49 | 0.29| 0.86| 0.71| 2.17 | 11.01   |
| Yamase-2    | 48.51| 33.08| 2.18 | 0.34 | 0.22| 0.53| 0.65| 1.81 | 12.78   |
| Yamase-3    | 51.35| 30.78| 2.98 | 0.44 | 0.32| 0.71| 0.69| 2.05 | 10.68   |
| Hobashira-1 | 71.98| 15.77| 2.02 | 0.81 | 0.06| 0.78| 0.46| 2.93 | 4.76    |
| Hobashira-2 | 75.91| 13.08| 1.56 | 0.61 | 0.13| 0.43| 1.11| 3.45 | 3.94    |
| Hobashira-3 | 74.79| 14.65| 2.15 | 0.41 | 0.09| 0.56| 0.34| 2.56 | 4.41    |
mineral phase of the heated plates at 1300–1400°C was α-quartz, cristobalite, mullite and glass phase, but the formation of mullite crystals was not promoted at higher temperatures. The formation of mullite in Yamase clay started at 1100°C and promoted with increasing heating temperature. The heated plate at 1350–1400°C was composed of mullite and glass with a very small amount of α-quartz. The XRD relative intensity ratio of mullite crystal was 54.1 at 1200°C, 75.4 at 1300°C, 97.8 at 1350°C, and 98.7% at 1400°C. From the XRD relative intensity ratio of mullite and α-quartz in ancient shards and heating clays shown in Figs. 2 and 6, it is supposed that the ancient Karatsu wares produced at Yamase and Hobashira kilns were fired around 1250°C by using similar raw clays mined from near those ancient kilns at that time.

Figure 7 shows the polished internal structure of the Yamase and Hobashira clays heated at 1400°C. Pores of 8–150 μm in diameter were observed in the heated Yamase clay. However, Hobashira clay bloated at 1400°C and had a biscuit-like porous structure with large pores of 15–460 μm in diameter, and the growth of large pores by the connecting of small pores in the body was confirmed. It was supposed that the formation of large pores was caused by the rapid expansion of the gas which was derived from the incorporated air during the forming of raw clay and the additional O2 gas which were formed by the thermal decomposition of 1.6–2.5 mass % of Fe2O3 (3Fe2O3 → 2Fe3O4 + 1/2O2) in the clay at 1400°C.8) From Figs. 5 and 6, the bloating phenomenon was not observed in Yamase clay heated at 1400°C, and this clay had a higher refractoriness and a lower sintering property than that of Hobashira clay as expected.

Figure 8 shows the morphology of mullite crystals in the heated plate at 1300°C. The average size of mullite crystals from Yamase and Hobashira clay were 1–5 μm in length and 0.3–0.8 μm in width, and 1–2 μm in length and 0.1–0.3 μm in width. Large needle-like mullite crystals were formed in the clay heated at 1300°C, and were very similar to mullite crystals from NewZealand kaolin heated at 1400–1500°C.7) 49.8 mass % of

![Fig. 5. The bulk density of the Hobashira clay and Yamase clay heated at 1100–1400°C in air.](image)

![Fig. 6. XRD patterns of (a) Yamase clay and (b) Hobashira clay heated at 1100–1400°C for 1 h in air. m: mullite, q: α-quartz, c: cristobalite.](image)

![Fig. 7. The polished internal structure of the heated body at 1400°C in air for 1 h. (a) Yamase clay, (b) Hobashira clay.](image)
mullite crystal and 50.2 mass % of glass were formed in Yamase clay heated at 1300–1400°C.

4. Conclusion

In this study, the properties of some shards of Karatsu ware excavated from ancient kilns, and the chemical, mineral and sintering properties of Yamase clay derived from a weathered granite stone and Hobashira clay derived from the weathered sandstone was studied. Alumina content of ancient shards of Karatsu wares excavated at Yamase kiln which were operated in the 1580 to 1590’s was 35–38 mass %. Alumina content and the mineral phase composition of the ancient shards were very similar to those of ceramic wares produced in the 15 to 16th century in Korea.

Yamase clay was composed of α-quartz (10.6), kaolinite (64.3), muscovite (11.9), albite (10.3), and microcline (2.9 mass %), and this clay had a higher alumina content than Hobashira clay. The formation of mullite from Yamase clay was enhanced at 1100°C, and the final composition was mullite and glass over 1300°C. The bulk density of Hobashira clay reached 2.40 cm³/g, but abruptly fell to 1.95 cm³/g at 1400°C by the bloating phenomenon. The bulk densities of the heated Yamase clay were 1.99, 2.15, and 2.35 g/cm³ at 1200, 1300, and 1400°C, respectively, and Yamase clay had a higher refactoriness than Hobashira clay.

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