Some properties of the early Arita celadon

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Old celadon samples produced at four early Arita sites in the 1640–1650’s were used for the macroscopic, microscopic, compositional, and color studies of glaze and body using XRD, SEM, XRF and colorimeter. Molar ratio of SiO2/Al2O3 of the early Arita celadon glaze was 8.4–9.3, and the glaze and body had 1.68–3.95 and 1.07–2.21 wt % Fe2O3, respectively. The total amount of MgO and CaO in the glaze was 12.2–14.9 wt %. The celadon color of the early Arita celadon was influenced by a small amount of Fe2O3 in the glaze and body. The body was mainly composed of α-quartz, mullite, and glass, and the average particle size of α-quartz was 17–30 µm and 2–3 times larger than that of the modern celadon. Some characteristics were compared with those of the early Korean Koryŏ celadon reported in some literatures.

Key-words : Archaeometry, Celadon, Glaze, Color, Arita, Korean Koryŏ

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1. Introduction

Japanese white hard porcelain was first developed by Korean potters in Arita, Saga, Japan in 1616 using Izumi-yama pottery stone. The basic production technology of celadon was completed in 1620–1630’s. The technologies of the early Arita celadon were probably influenced by those of ancient Chinese and Korean celadon, e.g., Chinese Song Dynasty (A.D. 960–1278) and Yuan Dynasty (A.D. 1279–1368), Korean Koryŏ Dynasty (A.D. 918–1392). It is well known that the color produced by adding a small amount of iron oxide (Fe2O3) to a base glaze fired in reduction is called celadon. However, the resulting glaze color gives yellow, tan, grey, grey-green, light-green, olive-green and blue green. Traditional Korean jade-green glaze makes celadon color clearer and almost perfectly transparent (in some cases, crystal phase and microscopic bubbles make it less transparent). The color of celadon is strongly dependent on the amount of iron oxide, the ratio of Fe2+/Fe3+ in glaze, the chemical composition of base glaze and body, the color of body, the thickness of glaze, the presence of crystalline phases in glaze, innumerable small entrapped bubbles in glaze, the firing temperature and the kiln atmosphere etc. Many scientific and archeological researches focused on the ancient or traditional Chinese and Korean celadon were widely reported. However, there are no scientific reports on the early Arita celadon. It is very important to study scientifically the early Arita celadon from the standpoint of the transmission of celadon technology from China and Korea to Japan, the difference of celadon technology among three countries, and to obtain basic information for the development of new Japanese celadon color.

In this study, the effect of the chemical composition, crystal and internal structure of the early Arita celadon glaze and body on some properties was investigated, and some properties were compared with those of the early Korean Koryŏ celadon.

2. Experimental

2.1 Early Arita celadon samples

Five celadon shards produced in A.D. 1640–1650’s in Arita area were provided from Arita Folk and History Museum, and the morphology of shards is shown in Fig. 1. These shards were archeologically excavated from four tunnel type kiln sites (Tengudani, Yanbeta, Maruo and Tatara no moto kiln) on a hill with terraced chambers. From Tatara no moto kiln, two celadon shards with different colors were collected from the different chambers.

![Fig. 1. As-collected some early Arita celadon shards produced in 1640 to 1650’s. (a) Tengudani-kiln, (b) Yanbeta-kiln, (c) Maruo-kiln, (d) Tatara no moto-kiln(A), and (d)-(2) Tatara no moto-kiln(B).]
2.2 Properties of the early Arita celadon

The chemical composition of body and glaze was analyzed by a point focus X-ray fluorescence analysis (XRF, model ZSX, focus size: 3 mm, Rigaku Co., Japan). The surface of the glaze and polished cross section of the body were separately investigated. Bulk density of the body was measured by the Archimedes’s method in water at 20°C. The crystal phase was characterized by a powder X-ray diffraction (XRD, model X’Pert-MRD, PANalytical Co., Japan). The thickness and pore morphology in the body and glaze were observed by a field emission scanning electron microscopy (FE-SEM, model JCM-6700F, JEOL, Japan). The particle size of α-quartz in the body was observed after etching glass phase around α-quartz in the polished body using 4.6% HF at 15°C for 10 min. The color value of celadon glaze with body was measured by a color and color difference meter (model X-Rite 528, Nippon Lithograph, Co., Japan) based on the L* (lightness), a* (hue), and b* (saturation) test. Some properties of the early Arita celadon were compared with those of the modern Arita celadon which was commercially produced in Arita at 1300°C under 2% CO gas atmosphere by a gas kiln. Typical glaze powder of the modern Arita celadon was prepared from Masuda feldspar, New Zealand kaolin, α-quartz and lime stone, and commercial α-Fe2O3 powder as a reference. The chemical composition of the final glaze powder is SiO2: 70.76, Al2O3: 12.38, Fe2O3: 2.19, TiO2: 0.01, CaO: 8.99, MgO: 0.02, K2O: 4.09, and Na2O: 1.58 wt%, respectively.

3. Results and discussion

3.1 Chemical composition of the early Arita celadon

Table 1 shows the chemical composition of glaze and body of the early Arita celadon and a modern Arita celadon. The chemical compositions of the early Arita celadon are SiO2(68.74–76.23), Al2O3(17.75–21.07), Fe2O3(1.07–2.21), TiO2(0.06–0.09), MgO(0.22–0.36), CaO(0.24–0.76), K2O(3.66–6.08), and Na2O(0.46–0.97 wt%) for the body, and SiO2(62.08–77.96), Al2O3(13.56–17.75), Fe2O3(1.07–2.12), TiO2(0.06–0.17), MgO(1.29–1.76), CaO(10.74–13.69), K2O(3.55–6.80), and Na2O(0.71–1.76 wt%) for the glaze, respectively. The chemical compositions of the body and glaze on some early Korean Koryŏ celadons produced in early 9th century investigated by G. In. Gang14 are SiO2(73.90–75.76), Al2O3(15.85–17.44), Fe2O3(2.04–2.70), TiO2(0.29–0.94), MgO(0.35–0.92), CaO(0.28–0.59), K2O(2.61–3.98), and Na2O(0.54–1.20 wt%) for the body, and SiO2(57.32–61.40), Al2O3(13.56–14.62), Fe2O3(1.55–2.39), TiO2(0.49–0.97), MgO(1.48–3.83), CaO(9.77–16.95), K2O(1.75–3.32), and Na2O(1.59–2.51 wt%) for the glaze, respectively. The molar ratio of the early Arita and Korean Koryŏ celadon body are 5.5–7.3 and 7.2–8.1, respectively. The early Arita celadon bodies have higher Al2O3, and Na2O + K2O than those of the early Korean Koryŏ celadon body. As for the glaze, the molar ratio of the early Arita and Korean Koryŏ celadon are 8.4–9.6 and 7.1–7.4, respectively. The content of Fe2O3 in the early Arita celadon body was 1.07–2.21 wt% and lower than that of the early Korean Koryŏ celadon (1.97–2.7 wt%).

White pottery stone was discovered in Arita in early 17th century, and is still mined and used for some modern ceramic wares without another mineral additive. It is composed of α-quartz, sericite (K2O·3Al2O3·6SiO2·2H2O), microcline feldspar (K2O·Al2O3·6SiO2), kaolinite (Al2O3·2SiO2·2H2O), and a small amount of iron sulfide (FeS), and the chemical composition of this clay after crushing and refining treatment is Loss.Ig: 4.87, SiO2: 74.04, Al2O3: 17.01, Fe2O3: 0.37, TiO2: 0.04, CaO: 0.09, MgO: 0.16, K2O: 2.9, and Na2O: 0.59 wt%, respectively. In the Arita area, pottery clay with low iron oxide content has historically been used for the production of white porcelain for around four hundred years. Many kinds of ceramic wares have been produced by using colorful over- and under glaze decorations.

The molar ratios of SiO2/Al2O3 of the early Arita celadon and Korean Koryŏ celadon glazes were 8.4–9.3 and 7.1–7.4, respectively. The early Arita celadon glaze had higher Fe2O3 (1.68–3.95 wt%) but lower MgO + CaO (12.2–14.9 wt%) content compared with those of Korean Koryŏ celadon (Fe2O3: 1.55–2.39 wt%, MgO + CaO: 13.6–18.43 wt%). It is supposed that higher content of MgO + CaO in both glazes was derived from wood ashes, however, the kinds of raw mineral and wood ashes and their composition used for the glaze of Korean Koryŏ are not well known. In the Arita area, some glaze stones which were mined have been traditionally used for celadon base glaze with wood ashes. These glaze stones are composed of α-quartz, α-cristobalite, albite (Na2O·Al2O3·6SiO2), orthoclase feldspar (K2O·Al2O3·6SiO2), and anorthoclase (Na2O·K2O·Al2O3·6SiO2), and have low refractoriness (SK13, 14, 17). The average chemical composition of glaze stones which are commercially used for many kinds of celadon glazes in the Arita area is Loss.Ig: 2.25, SiO2: 77.96, Al2O3: 13.22, Fe2O3: 0.45, TiO2: tr., CaO: 0.05, MgO: 0.05, K2O: 4.53, and Na2O: 1.35 wt%, respectively. By using these glaze stone and wood ashes, the early Arita celadon-like glaze can be produced in a gas kiln. From these results, it was suggested that the substitutions in molar ratio of SiO2/Al2O3 and the total amount of CaO and MgO...
in glaze were derived from glaze stone and wood ashes. These affected some properties of glazes in both the early Korean Koryō and the early Arita celadons. Usually, Japanese wood ashes contain 47–56 wt % CaO, 2–6 wt % MgO, and 2–4 wt % P2O5, and these oxides have many effects on the properties of the celadon glaze. In this study, the effect of P2O5 on the color of the glaze was not investigated.

### 3.2 Structure of the early Arita celadon

Figure 2 shows the polished cross section of five samples of the early Arita celadon and one modern celadon fired at 1300°C. The bulk density of body, thicknesses of glaze layer, the size distribution and average sizes of pores included in glaze and body were shown in Table 2. Bulk density, average pore sizes of glaze and body of a modern celadon were 2.41 g/cm³, 50 and 4 μm. The bulk density of five early Arita celadon bodies is 2.15–2.23 g/cm³ due to larger pores in the body compared with that of a modern celadon body. Average pore size and pore size distribution in glaze layer of early Arita celadon and a modern celadon were 59–170 and 13–275 μm, respectively. Some rounded large pores were observed in all bodies of the early Arita celadon. These pores were due to bloating by the generation of O2 or the expansion of air in the pores during the over-firing at higher temperature.16) The difference in pore size in

<table>
<thead>
<tr>
<th>Celadon sample</th>
<th>Bulk density of body</th>
<th>Pore distribution</th>
<th>Average pore size</th>
<th>Pore distribution</th>
<th>Average pore size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tengudani-kiln</td>
<td>2.15 g/cm³</td>
<td>6–138 μm</td>
<td>26 μm</td>
<td>25–250 μm</td>
<td>125 μm</td>
</tr>
<tr>
<td>Yanbeta-kiln</td>
<td>2.26</td>
<td>5–88 μm</td>
<td>17 μm</td>
<td>25–275</td>
<td>96 μm</td>
</tr>
<tr>
<td>Maruo-kiln</td>
<td>2.28</td>
<td>2–50 μm</td>
<td>7 μm</td>
<td>13–175</td>
<td>59 μm</td>
</tr>
<tr>
<td>Tatara no moto-(A)</td>
<td>2.21</td>
<td>6–63 μm</td>
<td>21 μm</td>
<td>20–260</td>
<td>115 μm</td>
</tr>
<tr>
<td>Tatara no moto-(B)</td>
<td>2.15</td>
<td>5–75 μm</td>
<td>25 μm</td>
<td>25–270</td>
<td>170 μm</td>
</tr>
<tr>
<td>Modern gas kiln</td>
<td>2.41</td>
<td>0.5–18 μm</td>
<td>4 μm</td>
<td>20–80</td>
<td>50 μm</td>
</tr>
</tbody>
</table>

Fig. 2. Polished cross-section of some celadon shards. (a) Tengudani-kiln, (b) Yanbeta-kiln, (c) Maruo-kiln, (d) Tatara no moto-kiln(A), (e) Tatara no moto-kiln(B), and (f) modern gas kiln.

Table 2. Some properties of Arita celadon
the body of the early and modern Arita celadon mainly depends on the forming method and firing temperature. However, in case of Maruo-kiln celadon, average pore size in body and glaze layers were 7 and 59 \( \mu \text{m} \) and similar to those of a modern Arita celadon.

Figure 3 shows the morphology of \( \alpha \)-quartz in the bodies. All samples were treated in HF solution to dissolve glass around \( \alpha \)-quartz. Average particle size were 16.9 \( \mu \text{m} \) (Tengudani kiln), 24.1 \( \mu \text{m} \) (Yanbeta kiln), 19.7 \( \mu \text{m} \) (Maruo kiln), 25.8 \( \mu \text{m} \) (Tatara no moto kiln-A), 29.3 \( \mu \text{m} \) (Tatara no moto kiln-B), and 10.7 \( \mu \text{m} \) (modern Arita celadon), respectively. The particle size of \( \alpha \)-quartz is very important factor to produce porcelain wares without crack and deformation of the body under heating and cooling treatment. Form the analysis of the early Arita celadon, it is speculated that ancient potters tried to prepare fine clay powder with traditional processes as much as possible.

Figure 4 and Table 3 show the crystal structure and a qualitative mineral analysis of the early Arita celadon body by XRD. Five Arita celadon bodies mainly consisted of \( \alpha \)-quartz, mullite and glass, and showed difference in the mineral composition. Samples from Tengudani-, Tatara no moto-(A) and -(B) kiln were composed of mullite, \( \alpha \)-quartz, and glass. A small amount of \( \alpha \)-cristobalite was also detected in the celadon body from Yanbeta- and Maruo-kiln. Relative mineral content of these samples was calculated from the intensity ratio of X-ray peaks for each crystal phase. In case of a modern Arita celadon, the relative crystal content of mullite, \( \alpha \)-quartz, \( \alpha \)-cristobalite, and glass was 3.3:100:0:2.3. The composition of raw minerals of each early Arita celadon body was not known, however, the increased crystal growth of mullite was confirmed in bodies from Tengudani-, Yanbeta, and Tatara no moto-kiln compared to a modern celadon.

3.3 Color of the early Arita celadon

Table 4 shows the color values of some celadon glazes. Color was light yellow-green, yellow-green, dark-green, and blue-green, and all samples had transparent glaze layer. L* of Tengudani-, Yanbeta-, and Tatara no moto-kiln(A) celadon glazes
were 63.3, 65.3, and 60.8, and these shards displayed bright tones compared with those of Maruo- and Tatara moto(B) kiln. a* of shards of Tengudani- and Maruo-kiln was −8.3 and −6.9, and showed more green-like color tone. Furthermore, Yanbeta-kiln celadon glaze showed a brighter blue-like color tone than other samples. There were not the differences in in \( L^* \), a* and b* of five celadon glazes. The color of the celadon glaze was mainly influenced by the amount of Fe\(_2\)O\(_3\), and it changed from light blue green below 2 wt% Fe\(_2\)O\(_3\) to dark green over 4 wt% Fe\(_2\)O\(_3\). The early Arita celadon glaze had higher molar ratio of SiO\(_2\)/Al\(_2\)O\(_3\) and lower MgO and CaO content than that of Korean Koryō celadon from Tables 1 and 2. It is expected that higher molar ratio of SiO\(_2\)/Al\(_2\)O\(_3\) tends to create a transparent glaze. From the chemical compositions of glazes shown in Table 1, the color change of five early Arita celadon glazes is proposed to be mainly influenced by the small amount of Fe\(_2\)O\(_3\) in glaze and body, the thickness and bubbles in glaze layer. The study of effect of Fe\(^{3+}\)/Fe\(^{2+}\) ratio in glaze layer and the firing temperature of the early Arita celadon on the celadon color is currently in progress.

4. Conclusion

In this paper, some properties of the early Arita celadon produced at four old kiln sites in 1640–1650’s was investigated. The main results are as follows:

1. The bulk density of the early Arita celadon body was 2.15–2.23 g/cm\(^3\) due to large pores (7–26 \(\mu\)m), and thickness of glaze layer and the size of bubbles in glaze of the early Arita celadon were 350–680 \(\mu\)m and 59–170 \(\mu\)m, respectively.

2. Main minerals in five Arita celadon bodies were \(\alpha\)-quartz, mullite and glass, and the mineral composition was different. Average particle size of \(\alpha\)-quartz was 16.9–29.3 \(\mu\)m, and it was 2–3 times larger than that of the modern celadon body produced by a gas kiln.

3. Molar ratios of SiO\(_2\)/Al\(_2\)O\(_3\) of the early Arita celadon glazes were 8.4–9.3, and these values were higher than those of Korean Koryō celadon glazes (7.1–7.4).

4. The color of the early Arita celadon body was white or white gray due to the use of pottery stone with lower Fe\(_2\)O\(_3\) content. The celadon glaze had higher Fe\(_2\)O\(_3\) but lower MgO and CaO contents compared with those of some traditional Korean Koryō celadon. The glaze was transparent and color of the celadon was mainly influenced by the amount of Fe\(_2\)O\(_3\), it changed from light blue green below 2 wt% Fe\(_2\)O\(_3\) to dark green over 4 wt% Fe\(_2\)O\(_3\).

Acknowledgement The authors wish to thank Mr. Nobuyuki Murakami, Arita Folk and History Muesum, Arita-machi, Saga, for providing the early Arita celadon shards. This study was supported by the Memorandum concerning Research Exchange between Saga Ceramics Research Laboratory and Korea Institute of Ceramic Engineering & Technology.

Reference