Mechanical strength and local structure of ‘new’ Hagi porcelain investigated by $^{57}$Fe-Mössbauer spectroscopy

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Abstract. A relationship between the local structure and mechanical strength of ‘new’ Hagi porcelain ‘A’ and ‘B’ prepared by sintering two types of iron containing aluminosilicate soils under oxidizing and reducing atmospheres were investigated by means of $^{57}$Fe-Mössbauer spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), as well as three point bending test. The largest mechanical strength ($\sigma$) value of 64.3±3.1 MPa was estimated from the three-point bending test of reductively sintered Hagi porcelain ‘A’. The Mössbauer spectrum was composed of two paramagnetic doublets due to tetrahedral Fe$^{II}$ and Fe$^{III}$ with the isomer shift ($\delta$) values of 1.13±0.02 and 0.31±0.01 mm s$^{-1}$. On the other hand, a paramagnetic doublet and a magnetic sextet with the $\delta$ values of 0.30±0.01 and 0.35±0.02 mm s$^{-1}$ were observed from the Mössbauer spectra of other samples. It can be concluded that the mechanically strengthened Hagi porcelain was successfully fabricated by choosing soil ‘A’ and by sintering under a reducing atmosphere.

1. Introduction
Hagi porcelain is known as one of the most famous Japanese traditional porcelains. It originates from the end of the 16th century; a Korean craftsman started their fabrication at Hagi district, Yamaguchi prefecture, west Japan. Hagi porcelain has a characteristic cracking structure, which causes a change of color due to tea component, being known as a popular ‘Seven-color’ change of Hagi porcelain.
However, the cracking structure observed in Hagi porcelain is not always favourable for common use at schools, restaurants, etc., because the crack causes a weak mechanical strength.

In order to overcome this problem, new composition and new fabrication condition have been studied. A relationship between the local structure and mechanical strength was investigated by means of $^{57}$Fe-Mössbauer spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and three-point bending test.

2. Experimental

Hagi porcelain ‘A’ and ‘B’ were prepared by a conventional sintering method. Weighed amount of porcelain clay ‘A’ or ‘B’, 30-40 vol.% of water and 0.3-0.4 mass% of dispersing agent were well mixed and poured into a gypsum mold. When the dried mixture was sintered at around 1230 °C under a reducing or an oxidizing atmosphere, opaque white cylindrical samples were obtained. In order to achieve a reducing atmosphere, propane gas was flown in the electric muffle furnace. For Mössbauer measurement, enriched isotope of $^{57}$Fe$_2$O$_3$ ($^{57}$Fe = 95.54 %) was used in the sample preparation. Mössbauer spectra were recorded by a constant acceleration method with a source of $^{57}$Co(Rh) and with a reference of $\alpha$-Fe. X-ray fluorescence (XRF) analysis was carried out by a conventional glass-bead method. A transparent medal-like bead was prepared by melting the pulverized mixture of Hagi porcelain (0.4 g) and lithium tetraborate (4.0 g) at 1100 °C for 10 min. The XRD pattern was conducted from 2$\Theta$ = 10 to 90° at a scanning rate of 6 degree min$^{-1}$, using the Cu-K$_\alpha$ X-rays generated by setting the tube voltage and the current to 40 kV and 40 mA, respectively. SEM image was taken by energizing 10 kV of electric voltage under the magnification of 30 to 10$^4$ using gold-coated samples. Three-point bending test was carried out for 20 pieces under the head speed of 1 mm min$^{-1}$ and 50 mm span.

3. Results and Discussion

The mass percent of Hagi porcelain ‘A’ was determined to be SiO$_2$ (57.9 %), Al$_2$O$_3$ (26.1 %), Fe$_2$O$_3$ (8.75 %) and others (7.25 %), while that of Hagi porcelain ‘B’ to be SiO$_2$ (63.1 %), Al$_2$O$_3$ (28.6 %), Fe$_2$O$_3$ (2.2 %) and others (6.1 %) from the XRF analysis. This result shows that the both Hagi porcelains were mainly composed of iron containing aluminosilicates.

The mechanical strength ($\sigma$ in Pa) was estimated by the following equation;

$$\sigma = \frac{8PL}{\pi d^3}$$ (1)
where \( P \), \( L \) and \( d \) are breaking load (in N), span (in m) and diameter (in m), respectively. The \( \sigma \) values of Hagi porcelain ‘A’ prepared under a reducing and an oxidizing atmospheres were estimated to be 64.3±3.1 and 60.1±2.8 MPa, whereas those for Hagi porcelain ‘B’ were 43.1±1.9 and 37.2±1.9 MPa. These results show that the mechanically strengthened Hagi porcelains were successfully fabricated because the \( \sigma \) value of conventional Hagi porcelain was reported to be 25 MPa [1]. It should be noted that the \( \sigma \) value of the porcelain ‘A’ was larger than that of the porcelain ‘B’ by 20 MPa, and that the \( \sigma \) value of reductively prepared porcelains were larger than that of oxidatively prepared ones by 5 MPa. It is considered that the Hagi porcelain with the highest mechanical strength can be fabricated by sintering soil ‘A’ under a reducing atmosphere.

The obtained \( \sigma \) value was utilized for Weibull analysis, i. e.,

\[
\ln \left\{ \ln \{1-(n/20)\} \right\} = m \ln \sigma + \text{const.} \quad (2)
\]

where \( n \) and \( m \) respectively show ranking number and Weibull index. \( \ln \left\{ \ln \{1-(n/20)\} \right\} \) vs. \( \ln \sigma \) plot of Hagi porcelains were shown in Figure 1. Weibull index, a slope value of each fitted line, for Hagi porcelain ‘A’ and ‘B’ prepared under a reducing and an oxidizing atmospheres were respectively calculated to be 23.7, 25.6, 25.1 and 22.5. These values indicate that the homogeneous porcelains were fabricated because the \( m \) values of traditional ceramics are reported to be 5-20 [2].

SEM photographs of Hagi porcelains were shown in Figure 2. Particles with the size of about 1 \( \mu m \) can be seen in the photographs of Hagi porcelain prepared under a reducing atmosphere (figure 2 (A-a) and (B-a)), while those with the size of around 2-3 \( \mu m \) can be observed in the Hagi porcelains prepared under an oxidizing atmosphere (figure 2 (A-b) and (B-b)). These results shows that the enhancement of mechanical strength was occurred due to the compaction of the porcelain surface when the Hagi porcelain was reductively sintered.

XRD patterns of the Hagi porcelains were represented in Figure 3. A precipitation of Mullite \((Al_6Si_2O_13)\) phase was confirmed from JCPDS card for all Hagi porcelains. In addition, specific peaks attributed to Cordierite \((Mg_2Al_2Si_5O_18)\) and Sekaninaite \((Fe_2Al_2Si_5O_18)\) were detected at \( 2\theta = 10.1, 21.6, 28.2 \) and 29.2 ° in the XRD patterns of Hagi porcelain ‘A’ (figure 3 (A-a) and (A-b)). On the other hand, peaks for Cordierite and Sekaninaite were absent from those of Hagi porcelain ‘B’. The mechanical strength of Hagi porcelain ‘A’ is about 1.5 times larger than that of Hagi porcelain ‘B’.
from the three-point bending test; thus the precipitation of Cordierite and/or Sekaninaite enhances the mechanical strength of the Hagi porcelain.

Mössbauer spectra of Hagi Porcelain ‘A’ sintered under a reducing or an oxidizing atmosphere were shown in Figure 4. Due to tetrahedral Fe$^{\text{II}}$ and Fe$^{\text{III}}$ with the isomer shift ($\delta$) values of 1.13±0.02 and 0.31±0.01 mm s$^{-1}$, two paramagnetic doublets were observed in the spectra of the reductively sintered porcelain ‘A’ (figure 4(a)). While a paramagnetic and a magnetic Fe$^{\text{III}}$ species with $\delta$ values of 0.30±0.01 and 0.35±0.02 mm s$^{-1}$ were observed for the Hagi porcelains prepared under other conditions. These results indicate that the precipitation of magnetic Fe$^{\text{III}}$ resulted in the decrease of mechanical strength of Hagi porcelain prepared under an oxidizing atmosphere. Because of less precipitation of magnetic Fe$^{\text{III}}$, the weakening of mechanical strength was restrained when sintered under a reducing atmosphere.

4. Summary
A relationship between mechanical strength and local structure of the newly fabricated Hagi porcelain was investigated. The largest mechanical strength of 64.3±3.1 MPa was estimated from the three-point bending test of Hagi porcelain ‘A’ prepared under a reducing atmosphere. Precipitation of Cordierite (Mg$_2$Al$_4$Si$_5$O$_{18}$) and Sekaninaite (Fe$_2$Al$_4$Si$_5$O$_{18}$), were confirmed by the XRD pattern. Due to tetrahedral Fe$^{\text{II}}$ and Fe$^{\text{III}}$ with the isomer shift ($\delta$) values of 1.13±0.02 and 0.31±0.01 mm s$^{-1}$, two paramagnetic doublets were observed from the Mössbauer spectra. It is concluded that less precipitation of magnetic Fe$^{\text{III}}$ in the matrix restrain the decrease of mechanical strength.

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References
[1] METI Chugoku 2008 Hagiyaki no Huai wo ikasita jittuyouteki na ko-kyodo tei-kyusuisei touki no kaihatsu (a fabrication of Hagi porcelain with high mechanical strength and low water absorption ability) A report of the research project on regional resources the Ministry of Economy, Trade and Industry, Japan (in Japanese)
[2] Okada A 1998 Ceramics no hakai-gaku (Tokyo: Uchidarokakuho) p 45 (in Japanese)