Magnetic properties of Hagi ware

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Hagi ware originally consists of a mixture of two raw materials: Daido clay and Mishima clay. During its firing process, we observed a change in the magnetic properties of the iron oxide, Fe_2O_3. The magnetic moment of the Daido clay (which only contains a small amount of the Fe_2O_3 γ-phase) attains a maximum at a firing temperature of approximately 600°C, where a minor amount of the poorly crystallized Fe_2O_3 temporarily changes to the ferromagnetic γ-phase. Furthermore, the magnetic moment of the Mishima clay (which contains a large amount of the Fe_2O_3 γ-phase) decreases as the firing temperature increases, whereas the coercive field rapidly increases at firing temperatures above 1000°C. The magnetization curve of the Mishima clay that was fired at temperatures above 1200°C is characteristic of a two-component system consisting of a minor γ-phase and a major α-phase. The above-mentioned phenomena were also confirmed by XRD analyses. A series of experiments indicated that the firing of Hagi ware can be characterized as a transformation from the γ-phase of Fe_2O_3 to the α-phase of Fe_2O_3. This transformation is considered to contribute to the change from soft magnetism to hard magnetism of Hagi ware.
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1. Introduction

In addition to Fe_3O_4, the iron oxide Fe_2O_3 is one of the most common magnetic materials,[1]–[3] and it is generally classified into four phases, namely, the α, β, γ, and ε-phases.[4]–[8] The α-phase and the γ-phase are abundant in the natural world, but the β- and ε-phases are rare and are therefore artificially synthesized.[8] The α-phase (termed hematite) has a rhombohedral crystal structure, and it exhibits weak ferromagnetism at temperatures between −13 and 672°C[9] as a result of the Dzyaloshinskii-Moriya interaction.[10],[11] The coercive field (H_c) can have a value as great as 1 kOe, and the color of the hematite powder is red. The β-phase exhibits paramagnetism at room temperature and transforms into the α-phase at a temperature of 500°C. The cubic γ-phase (termed maghemite) exhibits ferrimagnetism. The basic crystal structure is the inverse spinel structure with some vacancy sites, and it theoretically has a saturation moment (M_s) per unit cell of $20\mu_B$ (experimentally $17.36\mu_B$).[12] Its magnetic transition temperature, T_C, is between 1093 and 1259°C, because the γ-phase transforms into the α-phase at temperatures above 400°C.[4] Its coercive field, H_c, is one-tenth that of the α-phase, and the γ-phase is representative of a soft magnet. The color of

the maghemite powder is brown. Finally, the ε–phase does not naturally exist; however, its chemical synthesis, detailed structure and magnetic properties have been investigated recently.[8] Thus, Fe_2O_3 is not only the subject of fundamental research but also has many possibilities for industrial applications. One of the applications of native Fe_2O_3 includes its use in the production of reddish-brown earthen-ware termed "Hagi ware".

Hagi ware is one of the most famous ceramics in Japan, and it has an exceptional high amount of Fe_2O_3. We therefore considered that from a scientific viewpoint, Hagi ware is a good candidate to study natural iron oxides. Hagi ware consists of a mixture of light gray Daido clay [**Fig. 1**(a)] and bay Mishima clay [Fig. 1(b)]. The ratio of Daido clay to Mishima clay is usually 5:1 in the mass ratio. Both clays contain SiO_2, Na_2O, Al_2O_3, and Fe_2O_3, in addition to volatile constituents (mainly water), as seen in **Fig. 2**. The ratio of the volatile constituents within Hagi ware (the mixture of the Daido and Mishima clays) depends on the firing temperature. The percentage of volatile constituents within the Hagi ware is 11.6% in the dried state, 1.39% in the biscuit-fired state, and 0.00% in the glost-fired state.[13] It is known that the water, which is mainly restricted to SiO_2 and within the crystal structure, is extracted at temperatures above 200°C and between 600 and 800°C, respectively. The distinct difference in the chemical compositions of the two clays can be explained by their ratios of Fe_2O_3. Mishima clay has seven times the amount of Fe_2O_3 as compared to Daido clay. Indeed, the reddish-brown color is characteristic of Hagi ware, and it is recognized that Mishima
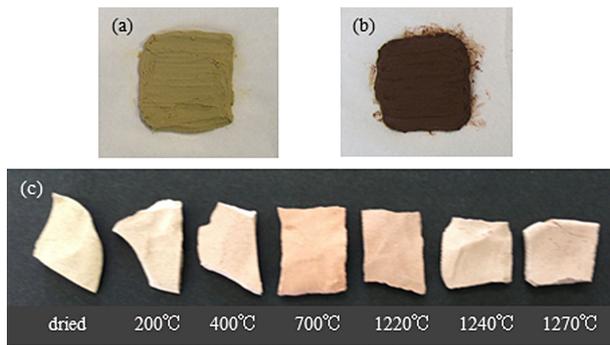
Fig. 1. Photographs of the Daido clay (a) and Mishima clay (b). (c) The change in color of the Hagi ware during the firing process (up to 1270°C).
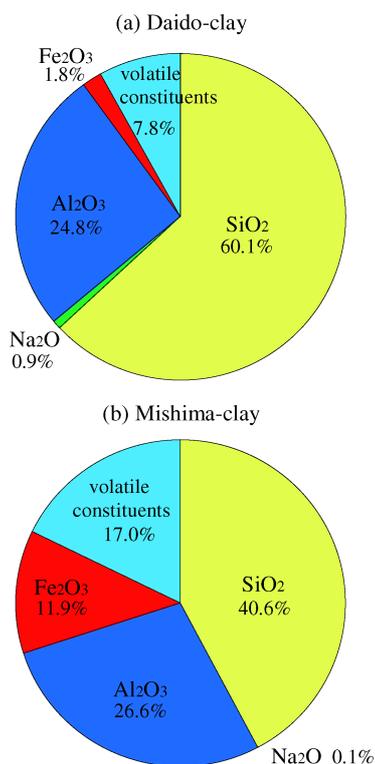
Fig. 2. Chemical components of the dried Daido clay (a) and dried Mishima clay (b), presented as mass ratios.[13] Both clays contain SiO_2, Na_2O, Al_2O_3, and Fe_2O_3 in addition to volatile constituents (mainly water). The ratio of components depends on the firing temperature, and the percentage of the volatile constituents becomes zero during glost-firing.[13]

clay plays an important role in achieving the reddish-brown color of the ware.[14] Both clays are produced in the Yamaguchi prefecture of Japan. In particular, Mishima clay is produced on Mishima island, located in the Sea of Japan; the island was formed by the eruption of Mt. Kasa twelve million years ago.[14] From an industrial standpoint, it appears that it will be difficult to continue mining Mishima clay for a long time in the future. Given these circumstances, we think that it is important to physically study the Fe_2O_3 phase change within Hagi ware during the firing process. Scientific information regarding the production of new Hagi ware without the use of Mishima clay could then be supplied to the earthenware industry. The Fe_2O_3 components of Hagi ware can be classified into three phases, namely, the α-phase, the γ-phase, and poorly crystallized Fe_2O_3.

The magnetic properties of Daido clay can be attributed primarily to the poorly crystallized Fe_2O_3 and slightly to the γ-phase. However, the magnetic properties of Mishima clay can be almost entirely attributed to the γ-phase. Hagi ware is produced by performing biscuit-firing at approximately 700°C, followed by glost-firing on a mixture of Daido and Mishima clays at temperatures above 1200°C for more than one day. Following the biscuit firing, the pottery is glazed and this determines the color of the final pottery. However, we are interested in the change in the intrinsic color of the mixed clays without glazing. Interestingly, the color of the sample becomes darker during the firing process between the temperatures of 35 and 700°C. Subsequently, by increasing the firing temperature to above 1200°C, the color prominently changes to white. As observed in Fig. 1(c), the sample fired at 700°C had the darkest brown color among all the samples that were fired (up to 1270°C). This was accompanied with a significant reduction in volatile constituents. It is well known that the origin of the brown color of Hagi ware (with glazing) can be attributed to Fe_2O_3. Given this background, it is interesting to note form a scientific perspective the correlation between the color of Hagi ware and its magnetic properties. However, the change in the magnetic properties of the Fe_2O_3 within the Hagi ware during the firing process has not been investigated at all. Both raw clays include a significant amount of Fe_2O_3, as shown in Fig. 2. Thus, we investigated the magnetic properties of Daido clay, Mishima clay, and their mixture (termed the Hagi ware), and confirmed via XRD analyses that the Fe_2O_3 phase changes within the two clays. Furthermore, we discuss the change in color that occurs during the Fe_2O_3 phase change.

2. Experimental procedures

We prepared the Daido and Mishima clays that are used in the pottery factories of Hagi ware. X-ray fluorescence analysis was conducted to characterize the chemical components of both clays; the results are presented in Fig. 2.[13] Prior to firing, both clays were desiccated in a thermostat chamber at a temperature of 35°C for one week. Subsequently, both clays were fired at several temperatures using an electric furnace (referring to the actual firing conditions of the Hagi ware). The firing process depends on the maximum temperature, T_{max}. The time required to increase the temperature up to T_{max} depends on T_{max}. The time required to fire up to T_{max} of 700°C is 8 h, 8.75 h for 900°C, and 10 h for 1240°C. A series of firing procedures requires a period of approximately two days in total. Hereafter, T_{max} will be described as the firing temperature, T_f.

We observed changes in the colors of both clays during the firing process: The Daido clay originally had a light-gray color, whereas during the firing process (up to $T_f = 600$°C) it tended to include a brown color. The clay had the darkest brown color at $T_f = 600$°C, subsequently returning to its initial color. However, the color of the Mishima clay during the firing process (up to $T_f = 1270$°C), which was originally reddish-brown, hardly changed. These results suggest that the color change of Hagi ware [Fig. 1(c)] is mainly due to the change in the color of the Daido clay.

We conducted magnetic measurements of Daido and Mishima clays fired at several temperatures using a commercial superconducting quantum interference device (SQUID) magnetometer. The magnetization (M) was measured at room temperature (set as 27°C) as a function of the magnetic field (H) in the range of 20 to -20 kOe. The total mass of the measurement sample was approximately 150 mg. The value of M for the dried and fired clays was evaluated as the value per unit mass for each clay. The evaluation

of M per unit mass for Fe_2O_3 is only meaningful for the dried and glost-fired states, because the ratio of the volatile constituents has been determined there.

In order to scientifically analyze the Fe_2O_3 phase change during the firing procedure, X-ray diffraction patterns of the representative compounds during a series of firing procedures were measured at room temperature. This was conducted using a synchrotron radiation XRD system with a cylindrical imaging plate at the Photon Factory (PF) at the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK).[15] The wavelength of the incident X-rays was 0.68841 Å.

3. Experimental results

3.1 Magnetization curves

Figures 3(a) and 3(b) show the magnetization curves of the dried Daido and Mishima clays, respectively, at room temperature. Both magnetization-curves suggest that there are both ferromagnetic and paramagnetic components. The paramagnetic component exhibits a linear relationship between M and H; this is owed to the poorly crystallized Fe_2O_3. By subtracting this paramagnetic component (χH) (as shown by green lines in Fig. 3) from the total M, we can obtain the former ferromagnetic contribution. Subsequently, when we compare these ferromagnetic properties for all the compounds, a similar analysis will be conducted.

The saturation magnetization (M_s) of the dried Daido clay was 1.6×10^{-3} emu/g, corresponding to 8.9×10^{-2} emu/g (Fe_2O_3). Moreover, the M_s value of the dried Mishima clay was 3.7×10^{-1} emu/g, corresponding to 3.1 emu/g (Fe_2O_3). In the Mishima clay, the linear contribution is small, and the magnetic properties can be mostly attributed to the crystalline Fe_2O_3. When considering the crystallinity of the Fe_2O_3, the Mishima clay is much
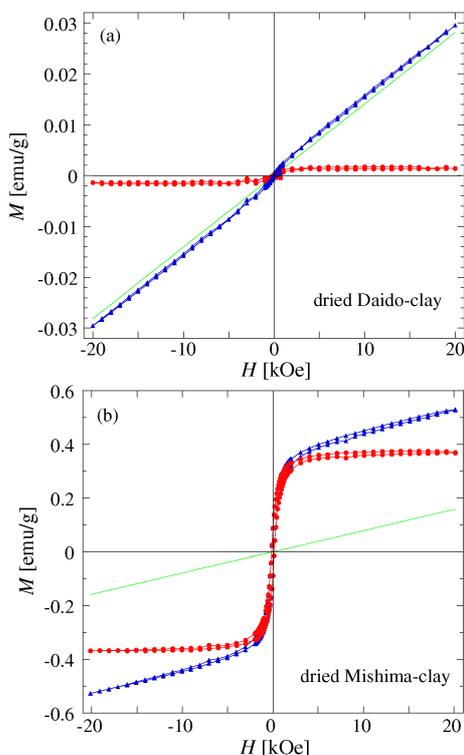
superior to the Daido-clay. A calculation based on the above facts suggests that 98% of the ferromagnetic components of the dried Hagi ware are owed to the Mishima clay. The coercive field (H_c) of the ferromagnetic components in the dried Mishima clay is on the order of 0.1 kOe, and it is determined to consist of the γ-phase of Fe_2O_3 (abbreviated as γ-Fe_2O_3). One unit cell of γ-Fe_2O_3 consists of eight Fe_2O_3 molecules, and the ideal M_s of γ-Fe_2O_3 is 75.9 emu/g. Thus, only 4.1% of the Fe_2O_3 in the Mishima clay consists of the good-crystalline γ-phase. As for the Daido clay, the percentage of the good crystalline γ-phase of Fe_2O_3 is approximately 0.12%.

Figure 4 shows the magnetization curves for the ferromagnetic components of the Daido clays that were prepared at each T_f. As shown in Fig. 4(a), M_s hardly changes during the firing process up to $T_f = 300°C$. However, during the firing up to $T_f = 700°C$, M_s changes remarkably, and it achieves its maximum value at approximately $T_f = 600°C$. The hysteresis loop of the magnetization curve for $T_f = 500-700°C$ is still small, and H_c is on the order 0.1 kOe. The above phenomena suggest that the γ-phase is synthesized from the Daido clay during the biscuit firing process. However, during the firing process from $T_f = 700$ to 1270°C, M_s of the Daido clay continues to decrease, and its magnitude is finally reduced to the level of the initial dried state. Indeed, H_c hardly changes during the whole firing process, suggesting that the good-crystalline Fe_2O_3 within the Daido clay exists as γ-Fe_2O_3 and that it is formed during the series of firing processes. Thus, the Daido clay retains the characteristics of a soft magnet even during the firing process.

Figure 5 shows the magnetization curves for the ferromagnetic components in the Mishima clay prepared at each T_f. Contrary to the results of the Daido clay, the M_s value of the Mishima clay systematically decreases as T_f increases up to 1000°C, remaining

Fig. 3. Magnetization curves of the dried Daido (a) and dried Mishima clays (b) at room temperature. The observed magnetization (blue triangle), paramagnetic component (green line), and ferromagnetic component (red closed-circle) are displayed.
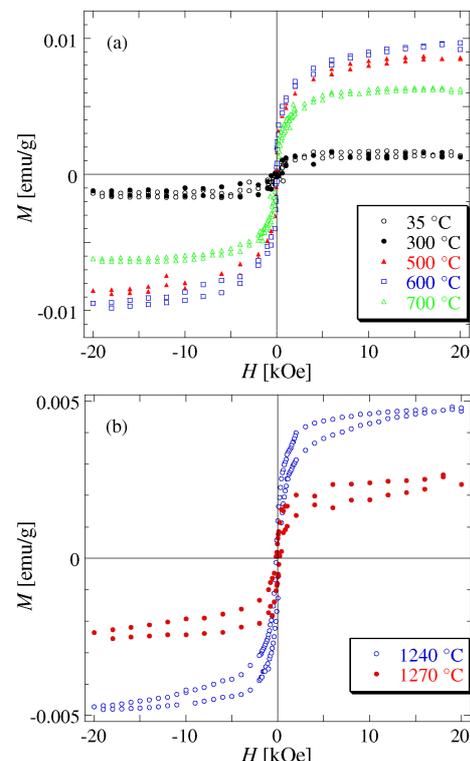
Fig. 4. Magnetization curves of the ferromagnetic components of the Daido clay prepared at each firing temperature (T_f).
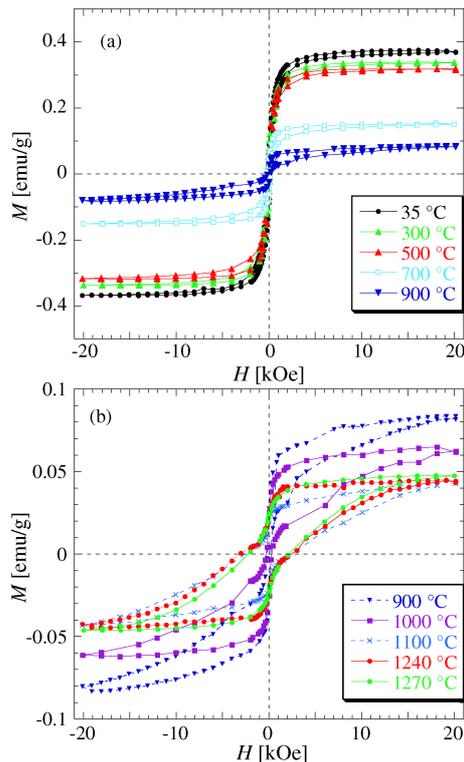
Fig. 5. Magnetization curves of the ferromagnetic components of the Mishima clay prepared at each firing temperature.

Fig. 6. Magnetization curves of the Hagi ware prepared at each firing temperature (a) and the ferromagnetic components (b).

fairly constant at temperatures higher than 1000°C. In particular, the reduction of M_s during $T_f = 700$–900°C is remarkable. The values of M_s for the biscuit firing ($T_f = 700$°C) and the glost firing ($T_f \geq 1200$°C) correspond to 40 and 12%, respectively, of that for $T_f = 35$°C. The Mishima clay fired at $T_f = 1240$°C has an M_s value of 4.3×10^{-2} emu/g, corresponding to 3.0×10^{-1} emu/g (Fe_2O_3). Moreover, the Daido clay fired at $T_f = 1240$°C has an M_s value of 4.7×10^{-3} emu/g, corresponding to 2.4×10^{-1} emu/g (Fe_2O_3). The ferromagnetic components per unit mass of Fe_2O_3 for both clays fired at $T_f = 1240$°C show similar values. Furthermore, the H_c value of the Mishima clay hardly changes during the firing process up to $T_f = 1000$°C. However, it exhibits a considerable increase for $T_f > 1000$°C, and it exhibits an almost constant value for $T_f = 1100$–1270°C.

As mentioned above, the majority of the Fe_2O_3 in the dried Mishima clay is considered to consist of the γ-phase because of its ferromagnetic behavior (with $H_c \sim 0.1$ kOe). The decrease in the M_s value suggests that as T_f increases, the γ-phase changes to another phase. For $T_f > 1000$°C, the H_c value exhibits an increase up to a few kOe. The results indicate that the majority of the γ-phase of the Mishima clay tends to transform into the α-phase during the glost firing. In fact, the hysteresis loop for $T_f = 900$–1270°C is characteristic of a two-component system consisting of soft and hard magnets,[16] and in the present case there is a mixture of the soft γ-Fe_2O_3 and the hard α-Fe_2O_3.

Figures 6(a) and 6(b) exhibit the magnetization curves of the Hagi ware prepared at each firing temperature and those of the ferromagnetic components, respectively. As the T_f value increases, the paramagnetic contribution increases, whereas the ferromagnetic contribution decreases. The ferromagnetic components for $T_f = 1220$°C is characteristic of a two-component system consisting of soft and hard magnets,[16] whereas those
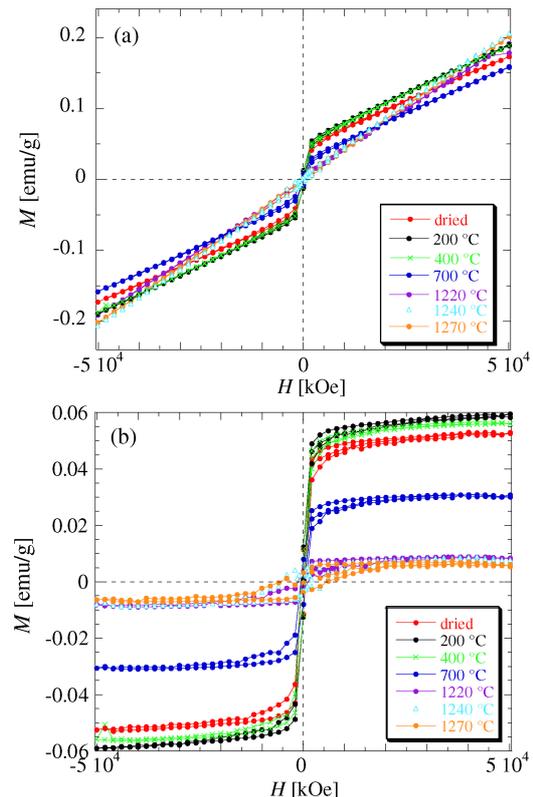
for $T_f = 1240$ and 1270°C are characterized as a single phase. The H_c value for $T_f = 1240$ and 1270°C is over 5 kOe, which is attributed to the α-Fe_2O_3 phase with good crystallinity.

Figures 7(a)–7(c) show the firing temperature (T_f) dependence of the saturation moment (M_s) and the coercive field (H_c) and the gradient of the line (χH) in the magnetization curves for the Daido clay, Mishima clay, and Hagi ware, respectively. First, for the M_s value, it is interesting to note that the characteristic temperature for the maximum M_s value for the Daido clay is close to the characteristic temperature for the decrease in the M_s value for the Mishima clay and the Hagi ware. Secondly, as observed in Fig. 7(b) (for H_c), the prominent change in the Hagi ware is due to the change in the Mishima clay. The prominent magnetic phase of the Hagi ware following the glost firing consists of the α-Fe_2O_3 phase of the Mishima clay. Finally, the paramagnetic component, owing to the poorly crystallized Fe_2O_3, tends to increase as the T_f increases. Over the whole firing temperature range, the Mishima clay has a greater amount of paramagnetic components than the Daido clay. Looking at the data at approximately 600°C in Fig. 7(c), the χ of the Daido clay slightly decreases, and an amount of the poorly crystallized Fe_2O_3 surely transforms into the γ-phase, suggesting a correlation with the increase in the M_s value for the Daido clay, as shown in Fig. 7(a). We cannot determine whether or not the γ-phase formed in the Daido clay transforms into the α-phase during glost firing because of the small magnetic moment of the α-phase.

Figure 8 shows the T_f dependence of the ferromagnetic moment of the Hagi ware, in addition to the ratios of the Daido and Mishima clays. The ferromagnetic moment of the Hagi ware exhibits a small jump at approximately $T_f = 500$°C as a result of the increase in the ferromagnetic moment of the Daido clay. This characteristic temperature is consistent with the temperature at
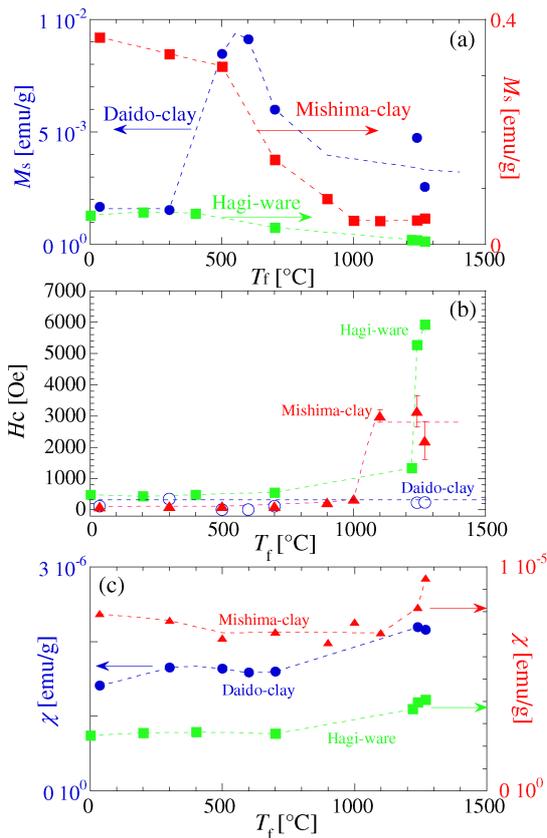
Fig. 7. T_f dependence of the M_s, H_c, and χ values for the Daido clay, Mishima clay, and Hagi ware. The broken lines and curves are for visual guides.
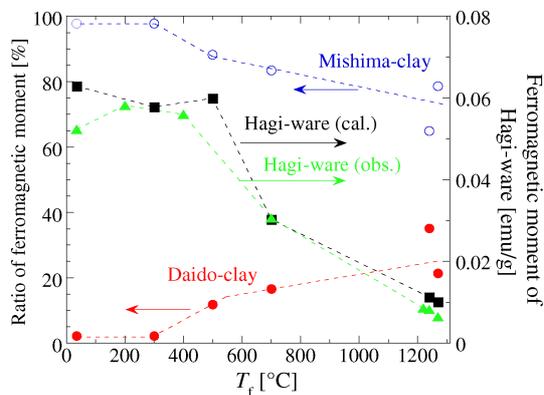
Fig. 8. T_f dependence of the observed and calculated ferromagnetic moment of the Hagi ware in addition to each ratio of the Daido and Mishima clays (in the case of the mixing ratio of the Daido clay and the Mishima clay = 5:1). The broken lines and curves are for visual guides.

which the color of the Hagi ware exhibits the darkest brown color. Indeed, the original material of Hagi ware is a mixture of Daido and Mishima clays (with a ratio of 5:1). According to a calculation, the magnetic moment of the Mishima clay at $T_f = 35$, 700, and 1240°C corresponds to approximately 98, 83, and 65%, respectively, of the M_s value for the ferromagnetic component of the Hagi ware.
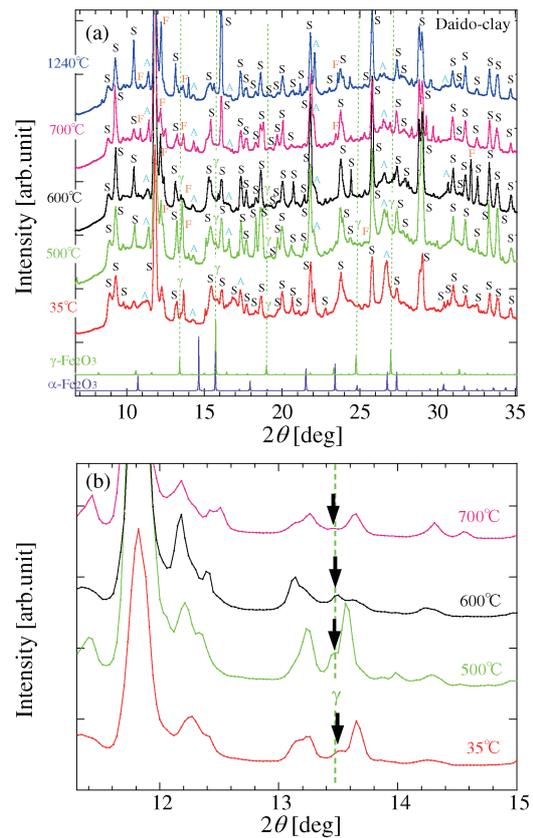
Fig. 9. XRD patterns for the Daido (a) and the data enlarged at approximately $2\theta = 13$ deg (b), together with the simulation patterns for α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$. The labeling is as follows: S: SiO$_2$; A: oxides of Al and Si such as Al$_2$(SiO$_4$)O and Al$_{2.3}$Si$_{0.7}$O$_{4.85}$; F: oxides of Al and Fe such as Fe$_{1.5}$Al$_{0.5}$O$_3$, FeAl$_2$O$_4$, and FeAlO$_3$; α: α-Fe$_2$O$_3$; γ: γ-Fe$_2$O$_3$. In (a), the peak-positions characteristic of γ-Fe$_2$O$_3$ are marked with green dotted lines. In (b), the peaks characteristic of the plane index (220) of γ-Fe$_2$O$_3$ are marked with arrows.

3.2 XRD analyses

Figures 9(a), 9(b) and **10** show the XRD patterns for the Daido and Mishima clays, respectively. There are many diffraction peaks as a result of the inclusion of SiO$_2$, the oxides of Al and Si, the oxides of Al and Fe, the α-phase of Fe$_2$O$_3$, and the γ-phase of Fe$_2$O$_3$. First, for the Daido clay, the components (except for Fe$_2$O$_3$) exhibit many diffraction-peaks as seen in Fig. 9(a), the majority of which are for SiO$_2$. As shown in Fig. 2(a), the quantity of Fe$_2$O$_3$ included in the Daido clay is very little, so that it is difficult to recognize the diffraction peaks due to Fe$_2$O$_3$ in Fig. 9(a). With careful observation of the XRD pattern, we can distinguish between the γ-Fe$_2$O$_3$ peaks and the α-Fe$_2$O$_3$ peaks. As seen in Fig. 9(b), the peaks labeled as the (220) plane index of γ-Fe$_2$O$_3$ at approximately $2\theta = 13.5$ deg become more prominent at $T_f = 500$ and 600°C, suggesting an increase in the amount of γ-Fe$_2$O$_3$. However, at $T_f = 700$°C, it is difficult to recognize the corresponding peaks. This behavior is consistent with the temporary increase in γ-Fe$_2$O$_3$ at approximately $T_f = 600$°C, as observed in the magnetic measurements.

Next, for the Mishima clay, many diffraction peaks due to α-Fe$_2$O$_3$ are observed along with some small peaks that are due to γ-Fe$_2$O$_3$ in the dried state (see Fig. 10). The Mishima clay has a larger amount of Fe$_2$O$_3$ than the Daido clay, suggesting a correlation with the results shown in Fig. 2. In the dried material, the characteristic peaks of γ-Fe$_2$O$_3$ with the plane indices (220),
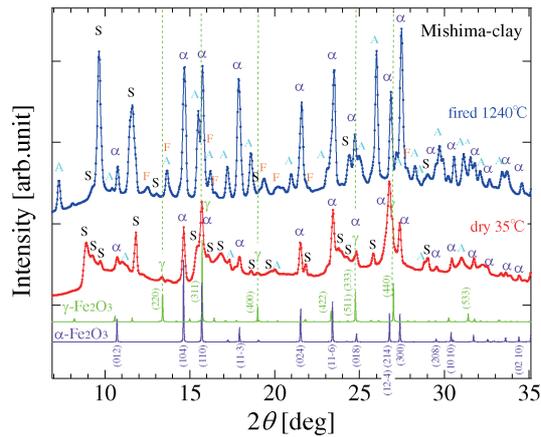
Fig. 10. XRD patterns for the Mishima clays, together with the simulation patterns for α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$. Some plane indices are presented for the corresponding peaks in each simulation pattern. The labeling is similar to that in Fig. 9. The peak positions characteristic of γ-Fe$_2$O$_3$ are marked with green dotted lines.

(311), and (440) appear at approximately $2\theta = 13.4$, 15.8, and 27.0 deg, respectively. The procedure for estimating the volume ratio of α-Fe$_2$O$_3$/γ-Fe$_2$O$_3$ is explained as follows. First, we normalized the observed peak intensity of both α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ with the calculated intensity of each Bragg peak. Indeed, the obtained normalization factor depends on the plane indices, because the present Debye ring includes many spots, and furthermore it is difficult to distinguish the peaks due to α-Fe$_2$O$_3$ and/or γ-Fe$_2$O$_3$ from those due to the other components. Thus, we have to consider averaging in the analysis process. Next, we focused on a plane index of γ-Fe$_2$O$_3$ among the five indices [in the present analysis, (220), (422), (533), etc.]. By comparing the corresponding peak intensity with those of nine plane indices for α-Fe$_2$O$_3$ [(012), (104), (110), etc.], we obtained the distribution of the ratio of α-Fe$_2$O$_3$/γ-Fe$_2$O$_3$ in the unit cell, resulting in obtaining the average ratio. In a similar manner, we then focused on another plane index of γ-Fe$_2$O$_3$ and obtained the average ratio of α-Fe$_2$O$_3$/γ-Fe$_2$O$_3$ in the unit cell. Finally, we transformed the distribution in the ratio of α-Fe$_2$O$_3$/γ-Fe$_2$O$_3$ in the unit cell level into that in the volume ratio of α-Fe$_2$O$_3$/γ-Fe$_2$O$_3$, in order to obtain the mean value of the volume ratio of α-Fe$_2$O$_3$/γ-Fe$_2$O$_3$, which was approximately 10. The α-Fe$_2$O$_3$ survives at $T_f = 1240°C$, whereas any evidence of γ-Fe$_2$O$_3$ disappears at that temperature. This behavior is consistent with the disappearance of the soft ferromagnetic feature, observed in the magnetic measurements.

Thus, in the Daido clay, the soft-magnetism feature owing to the existence of the γ-Fe$_2$O$_3$ becomes prominent at approximately $T_f = 600°C$. However, over the series of firing processes, neither the M-H measurements nor the XRD experiments have exhibit α-Fe$_2$O$_3$. Furthermore, in the Mishima clay, the soft-magnetism feature is gradually suppressed above $T_f = 500°C$. At temperatures above 1000°C, only the hard-magnetism feature due to α-Fe$_2$O$_3$ can be observed.

4. Discussion

The XRD study indicates that the dry Daido clay contains a small amount of γ-Fe$_2$O$_3$ with good crystallinity, whereas the dry Mishima clay contains a high level of iron oxide (including both α- and γ-phases with good crystallinity). The magnetic measurements for the dried clays mainly detected the magnetic properties of γ-Fe$_2$O$_3$. The α-Fe$_2$O$_3$ in the dry Mishima clay seems to be

masked by the large magnetic contribution of the γ-Fe$_2$O$_3$. Thus, we focused on the change in the soft-ferromagnetic feature of the Mishima clay due to the magnetically dominant presence of γ-Fe$_2$O$_3$. Here, let us consider the history of Mishima island:[14] It was formed following a volcanic eruption twelve million years ago. This island mainly consists of basalt lava and volcanic deposits. Indeed, Mishima clay has a dark-red color, which indicates that it includes a high level of iron-related components. Thus, Mishima clay has been heated by volcanic activity. In the dry Mishima clay, the majority of the iron oxide consists of α-Fe$_2$O$_3$ (according to the XRD study), and the color originates from the red α-phase rather than the brown γ-phase. However, the ratio of the iron oxide for the dry Daido clay is small, and thus the color of the Daido clay is surely due to SiO$_2$ and Al$_2$O$_3$.

The magnetic properties of the Hagi ware in both the dry and the glost-fired forms are attributed to the Mishima clay, which accounts for one-sixth of the Hagi ware. However, the magnetic properties of the Hagi ware during biscuit firing are complex. Daido clay in the dry form does not contain much γ-Fe$_2$O$_3$, whereas at temperatures of approximately 500–600°C, the amount of γ-Fe$_2$O$_3$ with good crystallinity temporarily increases. Furthermore, the amount of γ-Fe$_2$O$_3$ with good crystallinity within the Mishima clay continues to decrease. Consequently, the magnetic properties of the Hagi ware in biscuit-fired form originate from both clay components, as shown in Fig. 8. In fact, the Hagi ware becomes dark brown. We can conclude that the change in the color of the Hagi ware is owed to the increase in the γ-Fe$_2$O$_3$ within the Daido clay, which accounts for the majority of the volume in the Hagi ware, as well as to the prominent reduction of the volatile components. Finally, the Daido clay in the glost-fired form has hardly any ferromagnetic components. The ferromagnetic moment of the Mishima clay is quietly suppressed in the glost-fired form, resulting in a transformation into α-Fe$_2$O$_3$. As a result, the magnetic properties of the Hagi ware in the glost-fired form originate from the α-Fe$_2$O$_3$ of the Mishima clay. Indeed, the H_c of the Hagi ware in the glost-fired form is over 6 kOe, which exceeds the highest H_c of all the fired Mishima clays. Furthermore, the M-H curve of the glost-fired Mishima clay is characteristic of α-Fe$_2$O$_3$. These results suggest that cooperative effects (as a result of solid-phase reactions) may occur during the firing process of the Hagi ware. The magnetism of the glost-fired Hagi ware is the same as that of Ayers Rock in Australia. Thus, during the firing process, Hagi ware varies from a soft magnet to hard magnet.

Mishima clay (with α-Fe$_2$O$_3$:γ-Fe$_2$O$_3$ = 10:1) is a necessary raw material in the production of Hagi ware and yields the brown color. The Daido clay originally contains no α-Fe$_2$O, even with firing. Herein, we propose a tentative approach to manufacturing Hagi ware without using Mishima clay. An artificially synthesized Fe$_2$O$_3$ mixture of α-Fe$_2$O$_3$:γ-Fe$_2$O$_3$ = 10:1 (at maximum, 20 g of the artificially synthesized Fe$_2$O$_3$ mixture per 1 kg of Daido clay) could be included in the Daido clay instead of mixing in the Mishima clay. Indeed, in order to evaluate the feasibility of this process, investigations with the use of glazes are required.

5. Conclusion

We investigated the changes in the magnetic properties of Hagi ware. The observed changes can be intrinsically explained by changes in the Fe$_2$O$_3$ phase. During firing at approximately 500–600°C, the Daido clay (which accounts for five-sixths of Hagi ware) exhibits a temporary increase in the amount of γ-Fe$_2$O$_3$ phase with good crystallinity. However, at temperatures above

1200°C, the ferromagnetic behavior is negligible. Furthermore, the magnetic moment of the Mishima clay (which accounts for one-sixth of Hagi ware) begins to rapidly decrease at approximately 500°C, which is close to the temperature of biscuit firing. Most of the γ-phase transforms into the α-phase at temperatures above 1200°C, which corresponds to the temperature of glost firing. This is exhibited as a type of transformation from a soft magnet to a hard magnet. This behavior is related to the change in the Fe_2O_3 phase, which was confirmed in the XRD experiments. The remarkable change in the color of the Hagi ware (without glaze) at approximately 700°C is related to the increase in the amount of the γ-phase of Fe_2O_3 in the Daido clay, as well as to the rapid reduction of the volatile constituents.

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