Well-Dispersed $\alpha$-Fe$_2$O$_3$ Particles for Lead-Free Red Overglaze Enamels through Hydrothermal Treatment

Hideki Hashimoto,*‡ Kazuki Higuchi,† Hiroyumi Inada,‡ Yuki Okazaki,‡ Taigo Takaishi,‡ and Hidetaka Asoh‡

‡Department of Applied Chemistry, School of Advanced Engineering, Kogakuin University, 2665-1 Nakano, Hachioji, Tokyo 192-0015, Japan

Kyoto Municipal Institute of Industrial Technology and Culture, 91 Chudojiawatacho Kyoto Shimogyo-ku, Kyoto 600-8815, Japan

ABSTRACT: The traditional Japanese overglaze ceramic, akae porcelain, typically known for Kakiemon-style wares, has been prized around the world for over 400 years. The red color of akae porcelain provides an attractive contrast to white porcelain. In recent years, because the use of leaded frit in making akae has been restricted by law owing to the effects of lead on human health and the environment, lead-free glass frit mixtures for overglaze ceramic wares have been developed in various porcelain production areas throughout Japan. However, current lead-free frit for red overglaze enamels produces a color that is duller than that of conventional leaded frit. Therefore, the development of red pigments that are suitable for use with lead-free frit is strongly desired. In this study, we used a hydrothermal process to prepare nanosized iron oxide and oxyhydroxide powders, which showed good particle dispersion in molten lead-free frit. The precursor paste was prepared by reacting iron nitrate with ammonium hydrogen carbonate and heated in a sealed vessel at 80–150 °C. The sample powder prepared at 90 °C was almost monophase $\alpha$-Fe$_2$O$_3$ (hematite) and exhibited the brightest red color (highest $L^*$, $a^*$, and $b^*$ values). This powder featured primary particles of ~15 nm in diameter that aggregated to form secondary spherical particles of ~100 nm in diameter. This powder was mixed with lead-free frit and applied as a red paint to a porcelain test piece. The resultant akae showed a bright red color with high $L^*$, $a^*$, and $b^*$ values that exceeded the values of akae prepared using conventional hematite powder. Microscopic analysis revealed that the hematite particles were well dispersed in the resultant glass layer, indicating that the hematite powders have good dispersibility in molten frit.

INTRODUCTION

$\alpha$-Fe$_2$O$_3$ (hematite) is one of the oldest known red pigments used by humans since prehistoric time. Recently, hematite has attracted much attention in the field of nanotechnology because of its potential to be used as catalysts, gas-sensing materials, anode materials for lithium-ion batteries, and photoanode materials for photoelectrochemical water-splitting reactions.1–8 Widespread contemporary research on hematite red pigments has focused on the nanostructure of hematite, yielding novel red pigments with high chemical and/or thermal stabilities.9–20 The color tone of hematite powder strongly depends on its particle size and dispersibility. The color can range from bright yellowish red for small and/or well-dispersed particles to dark gray for large and/or strongly aggregated particles.21 Here, we define “bright”, “good”, or “high-quality” red colors as those having high $L^*$, $a^*$, and $b^*$ values and similar $a^*$ and $b^*$ values in the CIE 1976 color space.22

Traditional Japanese red overglaze ceramic ware, akae, was developed in the early 17th century and is admired by porcelain lovers around the world. Kakiemon-style ware was first exported to Europe in the 17th and 18th centuries. These porcelain wares were highly regarded by royalty and the aristocracy at that time, which significantly influenced the production of porcelain for overseas markets.23,24 Today, porcelain producers around the world use akae techniques for a variety of purposes. Traditionally, Japanese akae porcelain is produced as follows.25,26 First, red paint is prepared by mixing a low-melting-point glass frit powder, 10–25 wt % hematite red pigment, and a solvent in a wet process. The red paint is then applied to a white porcelain body; the painted porcelain is dried and finally heated at 700–900 °C in air. The obtained overglaze enamel is a composite of hematite particles and glass, which has come to be known as akae.

Although leaded glass frit with low melting points is conventionally used in traditional akae porcelain, the use of glass frit containing lead is now regulated owing to concerns for human health and the environment. In addition, the high-quality red pigment Fukiya bengala,27–31 which had the largest market share in Japan, went out of use when antipollution laws came into effect in the 1970s. The porcelain industry has since been seeking new lead-free frit and high-quality hematite pigments. We have previously developed lead-free frit mixtures for Kyo and Kiyomizu wares and provided these frit mixtures to many porcelain producers.26,32
also developed thermostable hematite powders, inspired by the historical pigment, Fukiya bengala. Recently, we studied the optimal preparation process for high-quality red paint using lead-free frit and conventional hematite powder. Our results indicated that high-quality ake requires hematite particles to exist in the interspaces of frit particles with a low degree of aggregation among the hematite particles. However, primary hematite particles tend to aggregate into larger secondary particles in hematite powders prepared through conventional dry heating processes. This makes it difficult to achieve a good dispersion of primary hematite particles in red paint mixtures and the final ake glass layer. Here, we prepared nanosized iron oxide and oxyhydroxide powders through a hydrothermal treatment, which produced well-dispersed hematite particles in red paint and molten lead-free frit. In addition, we made high-quality ake test pieces based on the prepared powders.

## EXPERIMENTAL SECTION

A precursor sample was prepared based on a method modified from that of Smith et al. First, 0.025 mol Fe(NO₃)₃·9H₂O (Wako Pure Chemical Industries, 99.9%) was crushed to a fine powder using an alumina mortar and pestle. Then, 0.3 mol NH₄HCO₃ (Wako Pure Chemical Industries) was added to the powder and mixed using the pestle to form a thick red ocher paste. Then, one-third of this precursor paste was moved to a polytetrafluoroethylene vessel to which 15 mL of deionized water was added. The vessel was sealed, locked in a stainless-steel container, and heated at 70, 80, 85, 90, 120, and 150 °C for 24 h. The process above was repeated for each temperature. Each slurry sample was washed with ~40 mL of deionized water and ~12 mL of ethanol before drying at 80 °C overnight. The crystallographic structures, reflectance spectra and colors, and microstructures of the obtained powder samples were characterized using X-ray diffractometry (XRD, RINT2500VHF, Rigaku), spectrophotometry (CM-S, Konica Minolta Sensing), and scanning electron microscopy (SEM, JSM-6701F, JEOL), respectively. The colors of the powders were determined against the CIE standard illuminant D₆₅. The samples heated at 90, 120, and 150 °C appeared dark and bright brown, respectively. The samples that appeared red showed similar a* and b* values and relatively high L* values, whereas positive and negative values of b* indicate the yellowish and bluish color, respectively.

## RESULTS AND DISCUSSION

Figure 1a shows photographs and color measurement results of our powder samples. The samples heated below 80 and at 85 °C appeared dark and bright brown, respectively. The samples heated above 90 °C appeared red and became darker at higher heating temperatures. The reflectance curves for the samples (Figure 1b) show the distinctive profile of hematite, and the reflectance values above 580 nm increased in the order of 150 < 120 °C = 90 °C < reference sample (PC) < 85 °C. The sample heated at 85 °C exhibited a bright yellowish brown color because of strong reflection of visible light in the range of 500–600 nm. Figure 1c shows the plot of L*, a*, and b* values of the powder samples. For the sample heated at 85 °C, the value of L* was highest and the value of b* was 10 higher than that of a*, giving rise to a color closer to a bright yellowish brown rather than red. The samples that appeared red showed similar a* and b* values and relatively high L*, and these values decreased with increasing heat treatment temperature. The values of the red samples were close to those of a conventional hematite powder (PC) composed of particles of 40–120 nm in diameter.

Figure 2 shows the XRD pattern of the samples. Two broadened peaks centered on 2θ values of 34 and 62° were observed in both the samples heated at 70 and 80 °C, indicating the formation of nanocrystalline iron oxyhydroxide, two-line ferrihydrate. A mixture of hematite and α-FeOOH (goethite) diffraction peaks was observed in the sample heated at 85 °C. The diffraction peaks of hematite dominated the pattern; however, low-intensity peaks attributed to goethite appeared in the sample heated at 90 °C. Monophasic hematite was found in the sample heated above 120 °C. Dissolution and precipitation of iron oxides and oxyhydroxides occurred during heat treatment under pressure. Thus, two-line ferrihydrate precipitation proceeded below 80 °C, appearing as the two
broad peaks in XRD patterns. Above 80 °C, the transformation of two-line ferrihydrite to goethite and goethite to hematite occurred simultaneously. Two-line ferrihydrite, goethite, and hematite powders typically show dark brown, yellow, and red colors, respectively.21 Thus, the sample powder colors reflected varying degrees of mixing of these original colors (Figure 1). The crystallite sizes, estimated from the full width half-maximum of the (104) hematite diffraction peak located at $2\theta = 33.15^\circ$, were 15, 15, 23, and 31 nm for the samples heated at 85, 90, 120, and 150 °C, respectively, and these values increased with increasing heat treatment temperature. Hematite powder pigments composed of small particles are known to have more desirable color properties.21 The higher $L^*$, $a^*$, and $b^*$ values of powders synthesized at lower heating temperatures may be related to the variation in their crystallite sizes.

Figure 3 shows SEM images of the samples. The sample heated at 80 °C composed of 2-line ferrihydrite featured large needle-like particles of 1.3–6.0 μm in width and 4.9–30 μm in length (Figure 3a). Similar needle-like particles of 0.4–2.6 μm in width and 2.7–11 μm in length were observed in the sample heated at 85 °C (Figure 3b), which was composed of a mixture of goethite and hematite phases. This sample also featured small spherical particles of 60–180 nm in diameter (Figure 3c, arrow). Small needle-like particles of 40 nm in width and 200 nm in length (Figure 3c, arrowhead) were also observed on the surface of the large needle-like particles. The spherical particles were composed of smaller primary particles of 10–13 nm in diameter. On the basis of the particle morphologies, abundance ratio of each particle type, and the XRD results, the fine needle-like and spherical particles likely arose from goethite and hematite phases, respectively. The sample heated at 90 °C, which appeared to be almost monophasic hematite by XRD, featured only spherical secondary particles made up to primary particles of 9–19 nm in diameter (Figure 3d). The primary and secondary particles of the sample heated to 120 °C grew to 13–21 and 40–160 nm (Figure 3e), respectively. The sample heated at 150 °C featured only large primary particles of 30–85 nm in diameter (Figure 3f). The primary particle size dependence on temperature observed by SEM agreed well with that determined from the XRD results.

The primary particle size of the sample heated at 90 °C was smaller than that of the sample heated at 120 °C. Although the secondary particle sizes of both samples were comparable, the $L^*$, $a^*$, and $b^*$ values of the sample heated at 90 °C were higher than those of the sample heated at 120 °C. The primary particle size of the sample heated at 150 °C was larger than those of samples heated at 90 and 120 °C. The sample heated at 150 °C also showed the lowest $L^*$, $a^*$, and $b^*$ values among the samples. These results indicate that the hematite powder color depends on the primary particle size rather than the secondary particle size. Hematite with smaller primary particle sizes showed higher $L^*$, $a^*$, and $b^*$ values.

Next, samples prepared at 90, 120, and 150 °C were applied to the white porcelain test pieces to prepare akei overglaze enamels. The akei test pieces prepared based on these samples were compared with an akei test piece prepared using a conventional hematite powder (PC) as a reference. Figure 4 shows color measurements and photographs of the test pieces. The reflectance values of the test pieces based on samples prepared at different temperatures showed similar reflectance values, which were consistently higher than those of the reference sample (Figure 4a). Although the reference sample exhibited a dark dull red color, the test pieces based on the sample heated at 90 °C showed a bright yellowish red color (photographs in Figure 4b). This bright red color resembled that of Kakiemon-style wares, a highly ranked traditional
Japanese akae porcelain. The test piece based on the sample heated at 90°C exhibited significantly higher L*, a*, and b* values than those of the reference sample (Figure 4b). This suggests that the hematite powders prepared in this study are suitable for use as red overglaze enamels. The highest CIE parameter values were obtained from the sample heated at 90°C, which also featured the smallest primary particle size.

We used microscopy to evaluate the dispersion of hematite particles within the glass layer in the test pieces prepared from the sample heated at 90°C and from the reference sample. Figure 5 shows gray-scale dark-field light microscopy images, where white dots and areas of dark contrast represent hematite particles and regions of the glass containing no hematite, respectively. The test piece prepared with the reference sample contained large hematite particle aggregates of ~5 μm and large regions of glass (~10 μm) containing no hematite (Figure 5a). However, well-dispersed hematite particles were observed in the test piece prepared with the sample heated at 90°C (Figure 5b). These particles appeared to be of similar sizes, and the regions of glass containing no particles were around 2–3 μm, which is close to the particle size of the frit starting material. This indicates that our hematite powders have superior dispersibility in molten lead-free glass frit. Thus, the good dispersion of hematite particles in the glass layer allows us to realize the bright red color of the akae test piece.

CONCLUSIONS

To prepare hematite powders suitable for use with lead-free frit, we used a hydrothermal treatment to synthesize hematite powders that showed good dispersion in molten glass. The precursor paste, prepared by mixing iron nitrate and ammonium hydrogen carbonate, was sealed in a container and heated at 70–150°C. Dark brown powders that formed below 80°C showed two broad features in the XRD pattern indicative of the formation of a two-line ferrihydrite phase. A bright brown powder containing a mixture of goethite and hematite phases formed at 85°C. Red powders mainly composed of hematite were obtained above 90°C, and powders of monophasic hematite formed above 120°C. The red samples, heated at higher temperatures, showed higher reflectance values of visible light. The highest CIE parameter values were found in the sample heated at 90°C. The samples prepared at 90 and 120°C featured secondary spherical particles of ~100 nm in diameter, which were composed of smaller primary particles of ~15 nm. The sample heated at 150°C was composed only of primary particles of ~60 nm in diameter. We prepared akae test pieces using these red powders as a pigment and obtained bright red akae. The CIE parameters of these test pieces were significantly higher than those of an akae prepared using a conventional hematite powder. Microscopic observations suggested that excellent dispersion of the hematite particles in the glass layer led to the bright red color of the resultant akae. We expect that the hematite powder prepared in this study not only will be applied to the porcelain industry but may also have wider applications in the field of nanotechnology such as in energy conversion materials.

AUTHOR INFORMATION

Corresponding Author
*E-mail: hideki-h@cc.kogakuin.ac.jp. Phone: +81 426284537. Fax: +81 426284537.

Notes
The authors declare no competing financial interest.

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