Microstructure and formation conditions of the reddish *hi-iro* marking on traditional Japanese ceramics

Yoshihiro KUSANO,[†] Teruaki DANN,^{*} Keiko TOKUNAGA,^{**} Nobuaki KAMOCHI,^{***}
Hideki HASHIMOTO,^{*} Makoto NAKANISHI,^{*} Tatsuo FUJII,^{*}
Minoru FUKUHARA^{****} and Jun TAKADA^{*}

Department of Fine and Applied Arts, College of the Arts, Kurashiki University of Science and the Arts,
2640 Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505

^{*}Graduate School of Natural Science and Technology, Okayama University,
3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530

^{**}Department of Applied Chemistry, Faculty of Engineering, Okayama University,
3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530

^{***}Saga Ceramics Research Laboratory, 3037-7 Kuromuta, Arita-cho, Nishimatsuura-gun, Saga 844-0022

^{****}Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Okayama University of Science,
1-1 Ridai-cho, Kita-ku, Okayama 700-0005

The microstructure and conditions for the formation of the reddish color referred to as *hi-iro* on Japanese ceramics were investigated through model experiments. The *hi-iro* marking was found to be formed by the reaction between clay and alkali ions supplied from the glaze. When a mixture of porcelain clay and 20 wt % KCl was heated in air at 1250°C and then cooled slowly to 800°C, *hi-iro* clearly appeared on the sample surface. In *hi-iro*, corundum [α -(Al,Fe) $_2$ O $_3$], hematite (α -Fe $_2$ O $_3$) and a liquid phase are formed. Upon heating until 1250°C, corundum is firstly precipitated as hexagonal plate-like crystals. During the cooling process, hematite precipitates on the edges of the corundum crystals to form specific composite particles. When rapidly cooled from 1250°C to room temperature, a brownish red color appeared on the sample surface, which was found to be caused by the formation of approximately 50 μ m Al-substituted hematite (Fe $_{1.9}$ Al $_{0.1}$ O $_3$) particles. The relationship between the microstructure of the phases formed and the color is discussed.

©2011 The Ceramic Society of Japan. All rights reserved.

Key-words : Traditional ceramics, Reddish color, Microstructure, Hematite, Corundum, *Hi-iro*

[Received May 30, 2011; Accepted September 29, 2011]

1. Introduction

There have been many studies regarding starting materials used in the production of pottery and porcelain, such as clay, glaze, and pigments;¹⁾⁻⁴⁾ however, there have been very few studies of the patterns formed on the products. This is most likely because there are many parameters, such as the chemical composition of the clay, firing temperature, heating and cooling rates, and effective oxygen partial pressure involved in the firing process. However, we believe that much interesting chemistry remains hidden in the traditional technologies and arts.

We have previously reported a mechanism for the formation of the reddish *hidasuki* pattern on Bizen stoneware.⁵⁾⁻¹¹⁾ Firstly, corundum (α -Al $_2$ O $_3$) is precipitated as hexagonal plate-like crystals above 1100°C in a liquid phase formed by the reaction between potassium in rice straw and Bizen clay containing approximately 2–3 wt % Fe $_2$ O $_3$.¹²⁾ Secondly, hematite (α -Fe $_2$ O $_3$) is grown epitaxially on the edges of these crystals during cooling after heating at 1250°C. Hematite covers the corundum crystals to form a specific composite of α -Fe $_2$ O $_3$ / α -Al $_2$ O $_3$ / α -Fe $_2$ O $_3$ sandwich-like particles. In addition, the artificial reproduction of *hidasuki* was demonstrated using potassium chloride instead of rice straw.

Occasionally, a reddish marking known as *hi-iro* appears on pottery and porcelain, even when the starting clay has a low iron content and is heated without rice straw. This pattern seems to be produced by the same mechanism as that for *hidasuki*,⁸⁾ although the details of *hi-iro* formation have yet to be clarified. Here the microstructural features and mechanism for the formation of *hi-iro* are reported from the results of model experiments.

2. Experimental procedure

The dried porcelain clay starting material, of which the chemical composition is given in **Table 1**, was ground and pelletized to form a green body 20 mm in diameter and approximately 2 mm thick. Ground potassium chloride (KCl, reagent grade, 0.1 g) was also formed into a pellet 15 mm in diameter and approximately 0.4 mm thick, and placed on the clay pellet. Clay pellets, with and without KCl pellets were heated to 1250°C at a rate of 5°C/min in air and held for 15 min. This temperature is close to that utilized in actual kilns. The samples were quenched or cooled to 800°C at different rates (1–37°C/min) and then rapidly cooled to room temperature. Mixtures of

Table 1. Chemical composition of porcelain clay (wt %)

SiO $_2$	Al $_2$ O $_3$	TiO $_2$	Fe $_2$ O $_3$	CaO	MgO	K $_2$ O	Na $_2$ O
73.2	20.7	0.19	0.52	0.37	0.14	4.03	0.65

[†] Corresponding author: Y. Kusano; E-mail: yoshi-k@arts.kusa.ac.jp

Fig. 1. Typical reddish *hi-iro* marking on the foot of a celadon bowl.

clay and KCl (10–40 wt % KCl in the mixture) were also formed into pellets 15 mm in diameter and approximately 1.6 mm thick, and then heated using the same heating process. The chemical composition of the clay was analyzed using X-ray fluorescence spectroscopy (XFS; Rigaku RIX2100). The crystalline phases formed on the as-prepared pellet surfaces were identified using powder X-ray diffraction (XRD; Rigaku Rint2100, Cu K α radiation). Microstructural observations were conducted using transmission electron microscopy [TEM; Topcon EM-002B, Jeol JEM-4000EX and JEM-2100F with a Cs-corrector (CEOS) and energy-dispersive X-ray analysis (EDS)] and scanning electron microscopy (SEM; Jeol JSM-6490). As reported in a previous paper, crystals are embedded in the glassy phase;⁸⁾ therefore, the samples for TEM and SEM were prepared by treating the surface of a pellet with 47% hydrofluoric acid for 15 s to 2 min to remove the glassy phase. For TEM, the crystals were then dispersed in carbon tetrachloride by ultrasonication and collected on a microgrid. The colors of the sample surface were measured using a colorimeter with a standard illuminant of D₆₅ (CM-2600d, Konica Minolta Sensing, Inc.). Mössbauer spectra of the as-prepared sample surfaces or fragments scraped from the sample surface were obtained at room temperature.

3. Results and discussion

The typical reddish marking known as *hi-iro* on the foot of a commercial celadon bowl is shown in **Fig. 1**. This reddish marking is frequently observed on unglazed bodies close to the glazed part, as shown in the figure. It is thought that the turquoise blue of celadon is generally caused by ferrous ions in a glassy phase. On the other hand, it is obvious that the reddish color of *hi-iro* results from ferric ions.¹³⁾

To clarify the microstructure of *hi-iro* formation, SEM and TEM observations of *hi-iro* on celadon were performed, and representative images are shown in **Fig. 2**. The sample for the TEM observations was obtained from light reddish part of *hi-iro*. The stick-like particles are mullite crystals (Al₆Si₂O₁₃), which is formed by the heat treatments in traditional ceramics, that function as a framework. The large hexagonal plate-like particles approximately $\sim 3.0\mu\text{m}$ in width (**Fig. 2**) were identified as corundum by EDS and electron diffraction (ED; inset in **Fig. 2**). This phase is usually assumed to have hexagonal rod-like crystals, but can form hexagonal plate-like crystals when synthesized in the presence of additional elements such as Si, Ca, Mg, and Na,^{14)–17)} which are all present in commonly

Fig. 2. Typical (a) SEM image of the surface of *hi-iro* on celadon and (b) TEM image of crystals obtained from *hi-iro*. The schematic illustration indicates the relationship between hematite and corundum. The [0001] ED pattern (inset) of the phases indicates the epitaxial growth of hematite on corundum (c: corundum and h: hematite).

Fig. 3. (a) HAADF-STEM image of a crystal formed in *hi-iro*, and (b) Al and (c) Fe map images.

used clay. Fine particles of approximately $0.1\mu\text{m}$ in size were precipitated on the edges of the corundum particles, as schematically illustrated in **Fig. 2**. These fine particles were identified as hematite by EDS and ED measurements. The ED pattern in the inset indicates hexagonal symmetry with growth that proceeded preferentially in the basal planes. Moreover, both crystal directions are the same, which indicates an epitaxial relationship between the two phases. It seems that *hi-iro* is colored by the precipitation of hematite on corundum crystals, as reported for reddish *hidasuki* on Bizen stoneware.^{5)–8), 11)}

It is well known that corundum forms a solid solution of Al_{2–x}Fe_xO₃ ($x \leq 0.18$) at 1250°C¹⁸⁾ and that this solid solution has an ochreous appearance. This phase is also probably involved in the *hi-iro* coloring. Analytical TEM observations were conducted to confirm this. **Figure 3** shows a high-angle annular dark-field scanning-TEM (HAADF-STEM) image (a) of a crystal formed in *hi-iro* with mapping images for (b) Al and (c) Fe. **Figure 3(b)** confirms that aluminum is not incorporated into the

Fig. 4. Typical colors of sample surfaces covered by KCl pellets, heated at 1250°C for 15 min and then (a) quenched (K/Q) or cooled to 800°C at a rate of (b) 37 (K/37), (c) 10 (K/10) and (d) 1°C/min (K/1) in air.

outer fine hematite particles. However, the corundum was found to contain approximately 4 mol % Fe, which indicates that the chemical composition of this corundum is $\text{Al}_{1.92}\text{Fe}_{0.08}\text{O}_3$. The solid solution with a nominal composition of $\text{Al}_{1.92}\text{Fe}_{0.08}\text{O}_3$ prepared in this study from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ had a lightly ochreous appearance with $L^* = 84.9$, $a^* = 0.8$ and $b^* = 25.8$. Therefore, it was concluded that the reddish color of *hi-iro* was caused by the precipitation of hematite and Fe-substituted corundum. Hereafter, we refer to this solid solution as corundum for simplicity.

The slow cooling from 1250 to 800°C and the supply of potassium from rice straw are important for the formation of the *hidasuki* pattern;^{5)–8),11)} however, in the case of porcelain, no rice straw is used during the heat treatment. Therefore, it is supposed that alkali ions are supplied from the glaze because *hi-iro* appears on an unglazed part close to glazed part (Fig. 1). Potassium feldspar [for example, orthoclase: KAlSi_3O_8 and/or sanidine: $(\text{K},\text{Na})\text{AlSi}_3\text{O}_8$] is commonly used as a raw material for glaze and was thought to be the source of the alkali ions. Preliminary experiment showed that sodium addition lowered the melting point of the clay, and the sample shape was deformed after heat treatment at 1250°C. In this study, we examined the effect of potassium addition to the porcelain clay on the formation of *hi-iro*.

Model experiments were conducted to determine the importance of the cooling rates and the presence of alkali ions in *hi-iro* formation. When the porcelain clay was heated without KCl at 1250°C and then cooled to 800°C at a rate of 1°C/min in air, the sample surface had a whitish porcelain color (sample NK/1, not shown). The color of this sample was not dependent on the cooling rate. On the other hand, the surfaces of samples covered with KCl pellets exhibited a reddish color. **Figure 4** shows typical colors of the sample surfaces after heat treatment at 1250°C for 15 min and then quenched (K/Q) or cooled to 800°C at a rate of 37 (K/37), 10 (K/10), and 1°C/min (K/1) in air. The $L^*a^*b^*$ values of the sample surfaces are summarized in **Table 2**. The color of the K/Q surface was similar to that of the sample heated without a KCl pellet, although it had a glassy appearance. The samples shown in Figs. 4(b)–4(d) had surfaces with a reddish glaze-like appearance. The color of the sample

Table 2. Color of sample surfaces heated with and without KCl

Cooling rate/°C/min (Sample name)	Hue [†]		
	L^*	a^*	b^*
1 (NK/1 [‡])	82.7	−0.7	6.1
Quenched (K/Q)	80.7	−1.3	9.5
37 (K/37)	56.5	11.7	28.0
10 (K/10)	54.6	15.4	28.2
1 (K/1)	54.4	18.9	31.2

[†]CIE 1976 $L^*a^*b^*$ color space. L^* indicates lightness, and a^* and b^* indicate chromaticity, i.e. color directions. Positive and negative values of a^* indicate reddish and greenish color, respectively, while positive and negative values of b^* indicate yellowish and bluish color, respectively.

[‡]Sample NK/1 was heated without KCl.

Fig. 5. XRD patterns of the (a) K/Q, (b) K/37, (c) K/10, (d) K/1 and (e) NK/1 sample surfaces.

surfaces changed from a brownish to reddish color with a decrease in the cooling rate. The reason for this will be discussed later.

XRD patterns of the sample surfaces are shown in **Fig. 5**. Sample NK/1 contains mullite and quartz (SiO_2), which are common phases in traditional ceramics. On the other hand, mullite is absent in the sample surfaces covered by KCl pellets [Figs. 5(a)–5(d)], and a small amount of corundum and hematite is evident. The corundum formation in the liquid phase is a key in the formation of hematite. The intensity of the corundum and hematite peaks increased slightly as the cooling rate was decreased, which resulted in the color becoming more reddish.

TEM images of the crystals formed in the glassy phase of the (a) K/37 and (b) K/1 surfaces are shown in **Fig. 6**. The K/37 surface has the same microstructure as that shown in Fig. 2. The ED pattern shown in the inset of Fig. 6(a) indicates that hematite was grown epitaxially on corundum. At the slower cooling rate of 1°C/min, the hematite crystals [dark particles labeled Fe_2O_3 in Fig. 6(b)] grew larger. The color tone of the sample surfaces was found to be affected by the cooling rate, similar to the *hidasuki* pattern on Bizen stoneware.^{5)–8),11)}

The relationship between the amount of KCl in the porcelain clay/KCl mixture and the color of the pellets was considered. The colors of mixtures of clay and 10–30 wt % KCl heated at

Fig. 6. TEM images of crystals formed on the (a) K/37 and (b) K/1 surfaces. The morphology of the corundum and hematite crystals and their crystallographic relationship as shown in (a) is the same as that of celadon shown in Fig. 2. The size of the hematite crystals increased as the cooling rate was decreased.

Fig. 7. Typical colors of mixtures of clay and KCl at (a) 10 (10.9), (b) 15 (14.2), (c) 20 (17.7), and (d) 30 wt % (25.0 wt %), heated at 1250°C for 15 min and then cooled to 800°C at a rate of 1°C/min in air. The values in parentheses denote the total amount of alkali oxides (K_2O and Na_2O) in the mixture of clay and KCl.

1250°C for 15 min are shown in Fig. 7. The samples were cooled to 800°C at a rate of 1°C/min and then rapidly cooled to room temperature. The samples with 10 and 15 wt % KCl had a slightly yellowish color, whereas those with 20 and 30 wt % KCl had

Table 3. Color of the sample surfaces in Fig. 7

KCl content/wt %	Hue		
	L^*	a^*	b^*
10	79.8	−1.5	8.8
15	80.3	−0.9	10.9
20	71.1	13.0	34.2
30	47.6	17.5	14.6

Fig. 8. XRD patterns of the sample surfaces shown in Fig. 7; mixtures of clay and KCl at (a) 10 (10.9), (b) 15 (14.2), (c) 20 (17.7), and (d) 30 wt % (25.0 wt %), heated at 1250°C for 15 min and then cooled to 800°C at a rate of 1°C/min in air.

a distinct reddish color. The $L^*a^*b^*$ values of these sample surfaces are summarized in Table 3. The total alkali oxide (K_2O and Na_2O) content in the mixtures with 10, 15, 20, and 30 wt % KCl were 10.9, 14.2, 17.7, and 25.0 wt %, considering the amount of alkali components in the clay of which the chemical composition is shown in Table 1. Summarizing the results, *hi-iro* appears when the KCl content exceeds 20 wt % (17.7 wt % alkali oxides) in the mixture, which is equivalent to 13.3 mol % of the total alkali oxides (K_2O and Na_2O) in the mixture.

XRD patterns of the sample surfaces shown in Fig. 7 are presented in Fig. 8. The XRD pattern of the 0 wt % KCl (NK/1) sample shown in Fig. 5(e) indicates that mullite is present, although it is absent in all the other sample surfaces; however, leucite ($KAlSi_2O_6$), corundum and hematite are present in all samples. The formation of hematite was prominent for the sample prepared with 30 wt % KCl.

The relationship between the color and microstructure of the K/37 sample is discussed here. It is well known that the color of hematite changes from yellowish red to black as the particle size is increased.^{1)–3)} Assuming that the coloring crystal is hematite grown on corundum, then the surface of K/37 should have a yellowish red color when cooled rapidly, due to the smaller hematite particle size (approximately 0.1 μm). However, K/37 has a brownish color, as shown in Fig. 4, which suggests the formation of another phase. The inset in Fig. 9(a) shows an optical micrograph of the as-prepared K/37 surface. Large plate-like particles approximately 50 μm in diameter were found on the glassy phase. The EDS spectrum of the black plate-like particles

Fig. 9. (a) EDS spectrum of a particle formed on the K/37 surface and (b) Mössbauer spectrum of powder scraped from the K/37 surface after etching with 47% hydrofluoric acid for 15 s. The inset in (a) shows an optical micrograph of the as-prepared K/37 surface. The magnetic component is assigned to hematite.

shown in the inset indicates that this phase consists of mainly Fe, Al and O with an Fe/Al atomic ratio of 0.95/0.05. Considering the XRD result in Fig. 5(b), these particles are Al-substituted iron oxide. A small amount of Mg and Si appears to originate from the glassy phase. A Mössbauer spectrum of the powder scraped from the K/37 surface after etching is shown in Fig. 9(b). A magnetic component assigned to hematite is clearly evident. The paramagnetic component corresponds to Fe^{3+} in the glassy phase and in corundum; therefore, the plate-like particles in Fig. 9(a) can be identified as Al-substituted hematite, represented as $\text{Fe}_{1.9}\text{Al}_{0.1}\text{O}_3$. In summary, the brownish color of the K/37 surface is a mixed color of the blackish hematite ($\text{Fe}_{1.9}\text{Al}_{0.1}\text{O}_3$) crystals on the sample surface and the reddish composite particles of hematite on corundum in the glassy phase. Further studies of the formation mechanism of single crystalline hematite are expected to be of significant interest because this phase seems to be related to other crystalline glazes, such as oilspot glaze.

4. Conclusions

The microstructure and conditions for the formation of the reddish marking known as *hi-iro* were investigated using model experiments. The formation mechanism of *hi-iro* was the same as that for *hidasuki* formation on Bizen stoneware despite the fact

that the iron content in the porcelain clay was 1/4–1/6 that of Bizen clay. Namely, the Fe-substituted corundum formation in the liquid phase and the Fe^{3+} diffusion in the liquid during the cooling process were essential to *hi-iro* formation. *Hi-iro* was formed as follows: (1) a liquid phase is formed on the surface by reaction between the clay and mainly potassium supplied by the glaze, (2) Fe-substituted corundum ($\alpha\text{-Al}_{1.92}\text{Fe}_{0.08}\text{O}_3$) precipitates as hexagonal plate-like crystals in the liquid phase, and then (3) the Fe^{3+} diffused in the liquid phase and precipitated as hematite ($\alpha\text{-Fe}_2\text{O}_3$) epitaxially on the edges of the Fe-substituted corundum during the cooling process. An effective amount of potassium chloride (KCl) for *hi-iro* formation was found to be over 20 wt % in the mixture of porcelain clay and KCl. This value corresponds to a total amount of alkali oxides (K_2O and Na_2O) in the mixture of 17.7 wt %, which is equivalent to 13.3 mol % as the total mole fraction of K_2O and Na_2O in the mixture. The rapidly cooled sample ($37^\circ\text{C}/\text{min}$) exhibited a brownish-red color, due to the formation of Al-substituted hematite ($\alpha\text{-Fe}_{1.9}\text{Al}_{0.1}\text{O}_3$) particles of approximately $50\ \mu\text{m}$ in diameter on the sample surface.

Acknowledgements We would like to thank Yoshiyasu Kato and Shingo Aoi (Kurashiki University of Science and the Arts) for preparation of the *hi-iro* samples. This study was supported by Grant-in-Aids for Scientific Research (KAKENHI) numbered 21550194.

References

- 1) T. Takada, *J. Jpn. Soc. Powder Powder Metall.*, **4**, 169–186 (1958).
- 2) T. Takada and M. Kiyama, *J. Jpn. Soc. Powder Powder Metall.*, **4**, 187–192 (1958).
- 3) H. Katsuki and S. Komarneni, *J. Am. Ceram. Soc.*, **86**, 183–185 (2003).
- 4) H. Asaoka, Y. Kusano, M. Nakanishi, T. Fujii and J. Takada, *J. Jpn. Soc. Powder Powder Metall.*, **50**, 1062–1067 (2003).
- 5) K. Yamaguchi, Y. Kusano, M. Fukuhara, A. Doi and T. Takada, *J. Jpn. Soc. Powder Powder Metall.*, **39**, 79–85 (1992).
- 6) K. Yamaguchi, Y. Kusano, M. Fukuhara and A. Doi, *J. Jpn. Soc. Powder Powder Metall.*, **39**, 179–183 (1992).
- 7) M. Fukuhara, M. Fujiwara, K. Yamaguchi and A. Doi, *J. Ceram. Soc. Japan*, **97**, 1420–1423 (1989).
- 8) Y. Kusano, M. Fukuhara, T. Fujii, J. Takada, R. Murakami, A. Doi, L. Anthony, Y. Ikeda and M. Takano, *Chem. Mater.*, **16**, 3641–3646 (2004).
- 9) Y. Kusano, T. Fujii, J. Takada, M. Fukuhara, A. Doi, Y. Ikeda and M. Takano, *Chem. Mater.*, **20**, 151–156 (2008).
- 10) Y. Kusano, A. Doi, M. Fukuhara, M. Nakanishi, T. Fujii, J. Takada, Y. Ikeda, M. Takano, C. Henrist, R. Cloots, A. Rulmont and M. Ausloos, *J. Am. Ceram. Soc.*, **92**, 1840–1844 (2009).
- 11) Y. Kusano, M. Fukuhara, J. Takada, A. Doi, Y. Ikeda and M. Takano, *Acc. Chem. Res.*, **43**, 906–915 (2010).
- 12) A. Doi, T. Sakamoto, S. Tsutsumi, R. Otsuka and C. Kato, *J. Chem. Soc. Jpn. Chem. Ind. Chem.*, **1**, 71–75 (1979).
- 13) I. Miyagawa, “Glaze”, Kyoritsu Shuppan Co., Ltd., Tokyo (1965) pp. 112.
- 14) H. Song and R. L. Coble, *J. Am. Ceram. Soc.*, **73**, 2077–2085 (1990).
- 15) H. Song and R. L. Coble, *J. Am. Ceram. Soc.*, **73**, 2086–2090 (1990).
- 16) A. P. Goswami, S. Roy, M. K. Mitra and G. C. Das, *J. Am. Ceram. Soc.*, **84**, 1620–1626 (2001).
- 17) X. Jin and L. Gao, *J. Am. Ceram. Soc.*, **87**, 533–540 (2004).
- 18) A. Muan and C. L. Gee, *J. Am. Ceram. Soc.*, **39**, 207–214 (1956).