Structural properties of the red-color overglazes on the Kakiemon-style porcelains produced in the later 17th century by means of X-ray diffraction (I)

(Propriedades estruturais, por difração de raios X, de esmaltes vermelhos de porcelanas do estilo Kakiemon produzidos no fim do século 17 (I))

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Abstract

Kakiemon-style porcelains produced at Arita areas (SAGA) in Kyushu Island are famous Japanese porcelains. The porcelain-techniques creating its elegant and bright red-color underglaze and overglaze were found and developed in 1650's (early Edo period) first by Kakiemon kiln. Red-color overglaze and transparent glaze of the Kakiemon-style porcelains have been investigated by means of X-ray diffraction using synchrotron radiation. The results suggest that the red-color brightness is mainly induced by micro-structural correlation between α–Fe_2O_3 fine particles, as red-color emission elements, and other oxides of SiO_2, Al_2O_3, CaO, KNaO, PbO. The stability of the red-overglaze on the porcelain surface is related to interfacial fusion of the glasses existing in the fritted red-overglaze and the transparent glaze on the porcelain body. The ancient porcelain-techniques of the Kakiemon-style porcelains are clearly based on the micro-structural and material properties of the overglazes, the underglazes, and the transparent glazes, though the techniques were experimentally and accidentally found and developed in the Edo period.
Keywords: Kakiemon-style porcelains, red-overglaze enamel, transparent glaze.

Resumo

As porcelanas do estilo Kakiemon produzidas nas áreas de Arita (SAGA) na ilha Kyushu são porcelanas japonesas famosas. As técnicas de produzir porcelanas com os elegantes e brilhantes vidrados de cores vermelho brilhante foram encontradas e desenvolvidas nos anos 1650 (início do período Edo) primeiramente em fornos Kakiemon. Vidrados vermelhos e vidrados transparentes de porcelanas do estilo Kakiemon foram investigadas por meio de difração de raios X com radiação sincrotron. Os resultados sugerem que o brilho de cor vermelha é principalmente induzido pela correlação microestrutural entre finas partículas de α–Fe_2O_3, como elementos emissores de cor vermelha, além de outros óxidos como SiO_2, Al_2O_3, CaO, KNaO, e PbO. A estabilidade dos vidrados na superfície da porcelana com vidrado vermelho está relacionada com a fusão interfacial dos vidros existentes no vidrado vermelho calcinado e o vidrado transparente do corpo da porcelana. As antigas téncias de porcelana do estilo Kakiemon são claramente baseadas nas propriedades microestruturais do material dos vidrados sobrepostos, os sub-postos e os transparentes, embora as técnicas tenham sido encontradas e desenvolvidas experimental e acidentalmente no período Edo.
Palavras-chave: porcelanas do estilo Kakiemon, red-overglaze enamel, transparent glaze.

INTRODUCTION

It is well known that HIZEN porcelains produced in the early Edo period of Japan are classified mainly by four kinds of porcelain styles; Shoki-Iroe (Kokutani-style), Kakiemon-style, Kinran-style, and Nabeshima ware. The Kakiemon-style porcelains had been exported from the later 17th century and were estimated to be very famous for interior decorations and dinner-sets in Europe and America, as Chinese porcelains. The Kakiemon-style porcelains are characterized by spatial elegant patterns with several bright colors in the underglaze and overglaze on the surface of white porcelain body. The Kakiemon-style porcelain-techniques creating its elegance and brightness were developed in 1650's (Edo period) first by Kakiemon kiln and quickly distributed in the localized areas around Arita [1-17]. In the Edo period, the white porcelain body of the Kakiemon-style porcelains was made of the Izumiyama ferromagnetic porcelain ceramics of white color, called by "Hakujikou", which Korean-potters discovered at a small mountain, Izumiyama, sited at a center of Arita in the early 17th century. Hakujikou is a raw porcelain ceramics of high quality. Thus, the Kakiemon-style porcelains had been produced only at the Arita areas localized in SAGA prefecture (called by HIZEN domain in the Edo period) of Kyushu island, Japan. The Izumiyama porcelain ceramics were grouped by content of α–Fe_2O_3 as a raw material; about 0.6 wt.% for Kakiemon-style porcelains and Nabeshima wares, while several wt.% for celadon, called SEIJI, which were made in the Arita areas from the early 17th century. At the beginning, the porcelains, called by "Shoki-Imari", had been produced with a Korea porcelain technique. From 1640~50's, the underglazes and colored overglazes were made by the porcelain technique due to Keitokuchin-kiln (China), while the celadon porcelains due to Ryusen-kiln (China).

In the middle 18th century a large quantity of α-Fe_2O_3 fine powders, called Fukiya-style Bengara, were produced at Fukiya village in Okayama prefecture of Honshu island, Japan, by chemical treatment from $FeSO_4.7H_2O$ to Fe_2O_3 at about 650 °C in atmosphere [18-21]. From the later18th century (1760's), the Fukiya-style Bengara was also used as the red-overglaze enamel of the HIZEN porcelains [18, 19]. However, in the Arita area, the red-color overglazes were already made in the early 17th century [22]. It is known that, in 1661 to 73's, Akae Machi was located at Arita to quickly produce a lot of the export Kakiemon-style porcelains of high quality. At Akae Machi, there were about 11 to 16 Akae Ya, which were porcelain traders having a special kiln and were called "Kin gama", permited by Nabeshima domain. This means that there is another source of the HIZEN red-overglaze enamels, which were imported from China or not. More recently, we found that the Izumiyama porcelain ceramics of white-yellow, called Izumiyama Rouha, show similar red-color brightness to those of the HIZEN porcelains [23]. Since the Izumiyama sites at the center of Arita area and near the Akae Machi, it is assumed that some Kakiemon-style porcelain kilns already used the Izumiyama ceramics of white-yellow color (Izumiyama Rouha), as a red-overglaze enamel even in the early 17th century.

In order to study the creation of the elegance and brightness of the Kakiemon-style porcelains developed in the early Edo period and to find the applications of its porcelain-techniques to modern porcelain-techniques, we carried out researches the structural properties of the red-overglazes of the Kakiemon-style porcelains, in addition to the transparent glazes, by means of X-ray diffraction using synchrotron radiation.

MATERIALS

In the present investigations, we used 6 broken pieces lined under the ground of Hongou campus at the University of Tokyo in Japan. The campus was sited as Edo-premises of Kaga domain in the Edo period. The premises were suffered four times from big fires occurred in 1650, 1682, 1703 and 1730 years. A lot of high quality porcelains have been excavated at the campus. The four fires strongly contribute to establish the produced date of the porcelains lined under the campus ground. Thus, it can be more exactly estimated that the broken porcelains were made mainly from the end 17th to the early 18th century in the Edo period. The specimens were the colored porcelain pieces of a bowl, a dish, and a rice-bowl, as shown in Fig. 1. The bowl porcelain pieces of (a), (b), and (c) in Fig. 1 are Kakiemon-style and were made in 1670-90's. The porcelain piece (d) of bowl is not Kakiemon-style, while (e) of dish and (f) of rice-bowl in Fig. 1 are Kakiemon-style, where (d) was made in 1690-1730's, and (e) and (f) were made in 1670-90's. The porcelain bodies of (a), (b), and (d) are clearly white-color, while those of (c), (e), and (f) are white-color slightly including light-blue. This suggests that the body ceramics of (c), (e), and (f) have a slightly larger content of α–Fe_2O_3 than those of (a), (b), and (d) as a raw material.

It is known that the elegant floral patterns drawn on the Kakiemon-style porcelains are spatially distributed in unsymmetry, and the porcelain parts of white-color are kept widely on the surface, as shown in Figs. 1a, b, and (c).

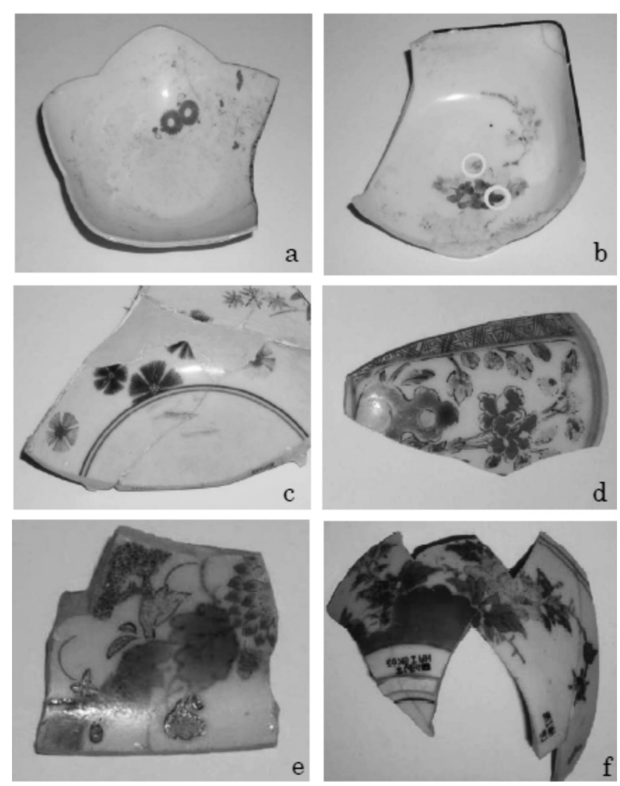

Figure 1: Broken pieces of the porcelains produced at the Arita areas: a, b and c (bowl, Kakiemon-style, 1670-90's), d (bowl, Arita, 1690-1730's), e (dish, Kakiemon-style, 1670-90's), and f (rice-bowl, Kakiemon-style, 1670-90's).

[Figura 1: Peças quebradas de porcelanas produzidas nas áreas Arita: a, b e c (tigela estilo Kakiemon, 1670-1690), d (tigela, Arita, 1690-1730), e (prato, estilo Kakiemon, 1670-1690), e f (tigela para arroz, estilo Kakiemon, 1670-1690).]

Table I - Composition of the raw materials used in the transparent glaze of the Kakiemon-style and Arita porcelains [17, 24].
[Tabela I - Composição das matérias-primas usadas no vidrado transparente do estilo Kakiemon e nas porcelanas Arita [17, 24].]

wt%	SiO	Al_2O_3	K_2O	Na_2O	CaO	MgO	Fe_2O_3
Sirakawa Yamatuti	76.62	12.85	4.56	3.92	0.44	0.16	0.32
Taisyu Tyouseki	78.18	13.25	0.75	5.65	0.34	0.32	0.32
Izumiyama Toseki	79.08	14.00	2.76	0.42	0.12	0.06	0.56
Isubai	28.74	1.43	1.72	0.60	37.8	1.29	0.32
Izumiyama rouha	48.0	11.0	5.5	0.09	14.0	0.04	14.0

To correspond to huge orders of the porcelains from overseas in that time, many kilns supported to produce the export porcelains in the Arita areas. Some kilns developed own drawing patterns of the colored overglazes and underglazes. Although the (c), (e), and (f) in Fig. 1 are also grouped in the Kakiemon-style, the porcelains are different to those of (a) and (b), because the formers have the underglaze patterns of blue-color. Thus, the Kakiemon-style porcelains are often sub-grouped with non-underglaze pattern of blue-color.

However, the red-color overglazes of the porcelain piece (f) in Fig. 1 show a dark-brown color, but not red-color brightness. This means that the red-color overglazes were chemically changed by the big fires occurred in 1703. The blue-color of the underglaze has the similar brightness to the other porcelain pieces in Figs. 1c to 1e. This results from the different thermal treatment between the color-overglaze and underglaze. It is known that the porcelain body painted with the blue-color underglaze was first coated with the transparent glaze, and secondly heated at higher temperature of about 1300 °C with the porcelain body. After that, the color-overglazes were heated at about 900 to 1000 °C, but to about 1200 °C for some porcelain kilns. Thus, the blue-color underglaze was shield by the coated transparent glaze to the fire oxidation in air, while the red-color overglazes was affected by the fire oxidation. As described latter, the fire oxidation of the porcelain piece in Fig. 1f gives important structural information for the overglaze materials of the Kakiemon-style and Arita porcelains produced in the early Edo period from the end 17^{th} to the early 18^{th} century.

The porcelain pieces in Fig. 1 are very important cultural assets in Japan. Thus, we needed to study the structural properties of the present porcelains only by means of nondestructive methods. This means that we cannot use an ordinary X-ray fluorescence analysis with white X-ray beams having higher energy, because X-ray photons of high-energy chemically affect the properties of the present porcelains. We cannot also remove the partial overglaze on the porcelain surface to estimate the component materials of the porcelain glazes. However, the old documents for the ancient porcelain-techniques kept by the related kilns gave important information for the used raw materials. The results are listed in Table I. The data were taken for the used raw materials by the ordinary X-ray fluorescence spectroscopy. In Table I, the Izumiyama Toseki, which was collected at Izumiyama sited at the center of Arita area, was used as a porcelain body of white-color and a flitted material, as shown in Fig. 1. Furthermore, at the Edo periods, the Sirakawa Yamatuti and/or the Taisyu Tyouseki had been also used in the transparent glazes and the fritted color-overglazes, in addition to the Isubai (natural wood ash). More recently, Kajihara [24] succeeded the reproduction of the ancient transparent glaze in the early Kakiemon-style porcelains with components of 0.45 KNaO, 0.53 CaO, 0.02 MgO, 0.56 Al_2O_3, and 4.89 SiO_2 in mol%, by using the raw materials in Table I. It is also known that the ancient porcelains produced at the Arita areas have the following component region for the transparent glazes; (0.35-0.46) KNaO, (0.52-0.65) CaO, (0.02-0.04) MgO, (0.56-0.99) Al_2O_3, and (4.61-7.70) SiO_2 in mol%. On the other hand, in wt.%, the fritted red-color overglaze of the ancient Arita porcelain consists approximately of 6.0 K_2O, 0.34 Na_2O, 0.04 CaO, 0.04 MgO, 3.2 Al_2O_3, 70.0 SiO_2 and 0.08 Fe_2O_3, in addition to 20.5 PbO [24].

EXPERIMENTAL

After doing several preliminary examinations for the nondestructive method using the synchrotron radiation, we confirmed that the X-ray diffraction with the incident X-ray beams of energy closed to Cu-K_α (about 8050 eV) does not affect the overglazes and uderglazes on the porcelain surface and can be used as the nondestructive method in the present investigations. The synchrotron radiation having high-brightness and high-resolution gives the structural and electronic information for small area at the painting floral part in the colored overglazes and other area closed to its part in the transparent glaze on the porcelain surface. The fritted red-color overglazes of the porcelains were usually coated on the thin transparent glaze of about 0.5 to 1 mm in thickness. However, the X-ray photons diffracted from the colored enamels in the underglaze and in the overglaze are not so largely reduced by the coated transparent glaze and by the fritted materials of the overglaze, respectively. The

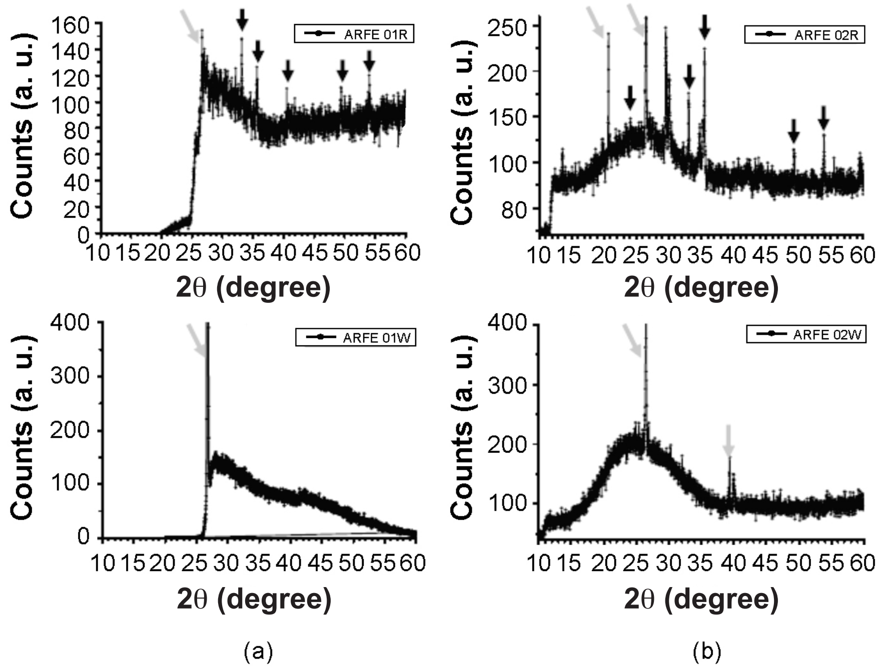

Figure 2: X-ray diffraction patterns of the Kakiemon-style porcelains in the red-color overglaze (upper part, R) and the transparent glaze (lower part, W); (a) ARFE01 and (b) ARFE02 in Fig.1(a) and (b) respectively. The arrows show the reflections diffracted by α–Fe_2O_3.
[Figura 2: Difratogramas de raios X de porcelanas do estilo Kakiemon nos vidrados vermelhos (acima, R) e o vidrado transparente (abaixo, W); (a) ARFE01 e (b) ARFE02 na Fig. 1a e 1b, repectivamente. A seta mostra as reflexões difratadas por α-Fe_2O_3*.]*

reason results mainly from a lower X-ray absorption of basic raw materials used, as SiO_2, Al_2O_3, K_2O, Na_2O so on, when the porcelain are produced.

In the present investigations, we used a high resolution 4-circle X-ray diffractometer at room temperature. The synchrotron radiation was at the Pohang Light Source (2.5 GeV) of the Pohang Accelerator Laboratory (Korea). After setting the porcelain pieces in Fig. 1 on a specimen stage of the 4-circle X-ray diffractometer, we irradiated the red-color floral parts of the overglaze with the incident X-ray beams, of which the size was about 0.1 mm in diameter. The diffraction method was a 2θ scan with each stepping angle of $\Delta 2\theta = 0.02$ degrees in the region of $2\theta = 10.00$ to 70.00 degrees, where the specimen was always fixed at an angle θ of about 5.0 degree during measurements.

RESULTS AND DISCUSSION

Figs. 2a and 2b show the X-ray diffraction patterns of the Kakiemon-style porcelain pieces (1670–90's) in Figs. 1a and 1b, respectively. In the diffraction patterns, the upper parts were taken at the red-color floral parts, while the lower one was taken at the transparent glaze closed to its floral parts. In Fig. 2a the scattered X-rays are abruptly reduced and disappeared below about $2\theta = 27.0$ degrees. This results from absorption of the scattered X-rays at the edge part of the porcelain piece, since the piece has a slightly convex surface. The absorbing effect of the scattered X-rays was often observed for the other porcelain pieces. However, we carried out X-ray diffraction by means of nondestructive methods for the present porcelains to be very important cultural assets, even if we can get only partial diffraction patterns. In Fig. 2 the black-arrows and the gray-arrows represent the reflections diffracted from the α–Fe_2O_3 structure and the SiO_2 structure in the red-color overglaze, respectively.

The diffraction pattern of the upper part in Fig. 2a shows many weak extra peaks, but not the α-Fe_2O_3 reflections, in addition to a weak halo-like background. We deduce that some extra reflections result from new oxygen complexes based on the raw porcelain materials of SiO_2, Al_2O_3, K_2O, Na_2O, and PbO in the fritted red-color overglaze. The lower part in Fig. 2a, that is transparent glaze closed to its red-color floral overglaze, shows the glass state, in addition to a strong peak occurring at about $2\theta = 26.5$ degrees. The strong peak results from the SiO_2 structure. On the other hand, the upper part in Fig. 2b shows the extra peaks, but not the α-Fe_2O_3 reflections, in addition to the weak halo-like background. It is not easy to index the strong and weak extra peaks in the diffraction pattern. As for the synchrotron X-ray diffraction using narrow incident X-ray beams, we must consider a preferred orientation of fine polycrystalline powders in the fritted color-overglaze and a thermal effect to the crystallographic lattice parameters of the glaze oxides because the colored overglazes and the transparent glazes of the Kakiyemon-style and Arita porcelains were usually heated up at about 900-1100 °C and 1300 °C, respectively.

Figs. 3a and 3b show the diffraction patterns of the red-color floral part in the overglaze of the Kakiemon-style porcelain pieces (1670–90's) in Fig. 1c. The black and gray arrows show the reflections of the α-Fe_2O_3 structure and the

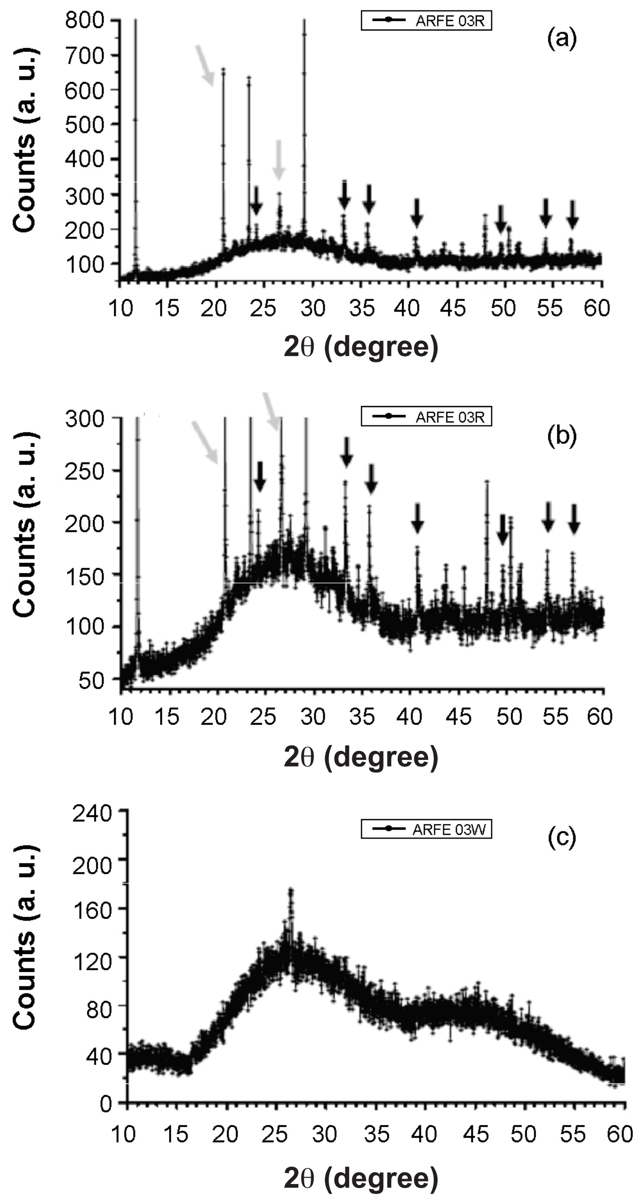

Figure 3: X-ray diffraction patterns of the Kakiemon-style porcelain; (a), (b) the red-color floral pattern of ARFE03 of Fig. 1c, and (c) the transparent glaze closed to its floral patterns, where the black arrows and the gray arrows show the reflections of the α–Fe_2O_3 and SiO_2 structure, respectively.

[Figura 3: Difratogramas de raios X de porcelana do estule Kakiemon; (a), (b) modelo floral vermelho de ARFE03 da Fig. 1c, e (c) vidrado transparente próximo dos modelos florais. Setas preta e cinza mostram as reflexões de α-Fe_2O_3 e SiO_2, respectivamente.]

SiO_2 one, respectively. In Fig. 3c the diffraction pattern was taken at the transparent glaze closed to its floral part, and a weak peak at 2θ = 26.5 degree was indexed by the SiO_2 structure. Thus, it is found that the diffraction pattern of the red-color overglaze also shows many clear extra reflections and the halo-like scatterings, in contrast to the upper patterns in Figs. 2a and 2b. The extra reflections of strong intensity are observed at about 2θ = 11.7, 20.8, 23.4, 26.5, and 29.2 degrees. It is deduced that the extra peak at about 20.8 and 26.5 degrees, denoted by the gray arrows, are the (1,0,0) and (1,0,1) reflections of the SiO_2 structure, respectively. However, the peak is accurately a doublet having maximum counts of 301 at 26.58 degree and 263 at 26.68 degree. The peak at about 20.8 degree is also accurately a doublet having maximum counts of 660 at 20.76 degree and 166 at 20.88 degree. The intensity I_{100} of the (1,0,0) reflection of the SiO_2 structure is usually weak than that I_{101} of the (1,0,1) one because of theoretically $I_{100} < I_{101}$. Thus, the strong intensity of the peak at about 20.8 degree suggests that the other peak slightly overlap on the (1,0,0) reflections. We suspect that there is a possibility to grow some new complexes based on the raw materials of SiO_2, Al_2O_3, CaO, MgO, and KNaO in Table I in the red-color overglaze under higher-temperature treatment of about 900 to 1200 °C. The clear extra peaks in Fig. 3b indicate the oxygen complexes, of which the crystallographic unit cell is larger than the other raw oxides because of the appearance of the strongly extra peak at a low angle of 11.66 degree. It is usually expected that the structure of the oxygen complex has a lower symmetry as triclinic one of mineral compounds. For simplicity, its lattice constant is about 12.8 Å, if the complex has a cubic symmetry structure. It is usually considered that the complexes based on the Al_2O_3-SiO_2 system having a large crystallographic

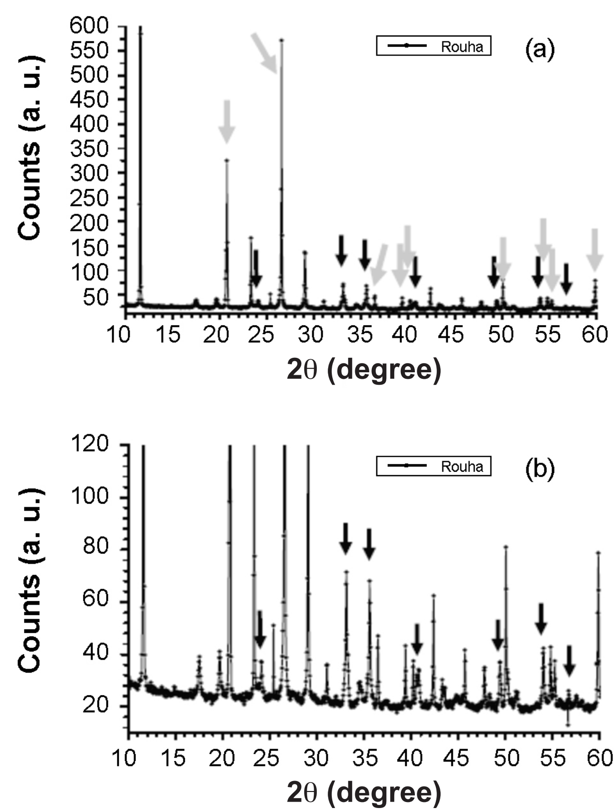

Figure 4: X–ray diffraction patterns of the Izimiyama rough made of the raw ceramics of white-yellow, which were taken at the small mountain, Izumiyama. The porcelain body was produced with the Izumiyama Toseki of white-color in Table I.

[Figura 4: Difratogramas de raios X de artefato Izimiyama feito de matéria-prima cerâmica branca-amarela originárias de uma pequena montanha, Izumiyama.]

unit cell make nanoscale cavities containing the α-Fe_2O_3 fine particles.

We are very interested in the raw materials of the red-color enamel for the porcelains produced at the Arita areas in the early Edo period. Historically, after 1760's, the red-color enamels of high-quality α-Fe_2O_3 were mass-produced at Fukiya village, which is in a south region of Honshu island, but not Kyushu island, Japan. The Fukiya-style red-color enamels of α–Fe_2O_3, called "Bengara", were distributed to wide areas in Japan. However, before 1760's, it is still ambiguity whether the α-Fe_2O_3 powders were Chinese ones or domestic ones. It is known that the Kakiemon-style porcelains were developed in 1650's (Edo period) and completed in 1670-80's first by Kakiemon family. The most elegant and bright Kakiemon-style ones were mass-produced in 1710-40's under systematical organization and specialization of the porcelain procedure and the potters, who were migrated at Akae Machi (Arita) for the mass-production of the Kakiemon-style and Koimari–style porcelains.

From the middle 17th to the early 18th century, the high-quality porcelain ceramics of white-color had been mined at Arita, as a raw material of the porcelain body. In the early Edo period, many porcelain kilns were sited around the Izumiyama at Arita. Thus, we expected that the Izumiyama ceramics of white-yellow color were used as red-overglaze enamel, when theKakiemon-style and Koimari-style porcelains were produced in the early Edo period, The amount of α-Fe_2O_3 in the white-yellow Izumiyama ceramics is larger than that in the white-color one. Recently, we found that the Izumiyama rough of elegant and bright red-color was obtained from the white-yellow Izumiyama ceramics by water-washing and thermal treatment [23]. The material components of the Izumiyama rough are also listed in Table I.

The X-ray diffraction pattern of the Izumiyama rough is shown in Figs. 4a and 4b, where the black and gray arrows represent the reflections of the α-Fe_2O_3 structure and the SiO_2 structure, respectively. The reflections of the SiO_2 structure are observed at 2θ = 20.8, 26.6, 36.4, 39.3,

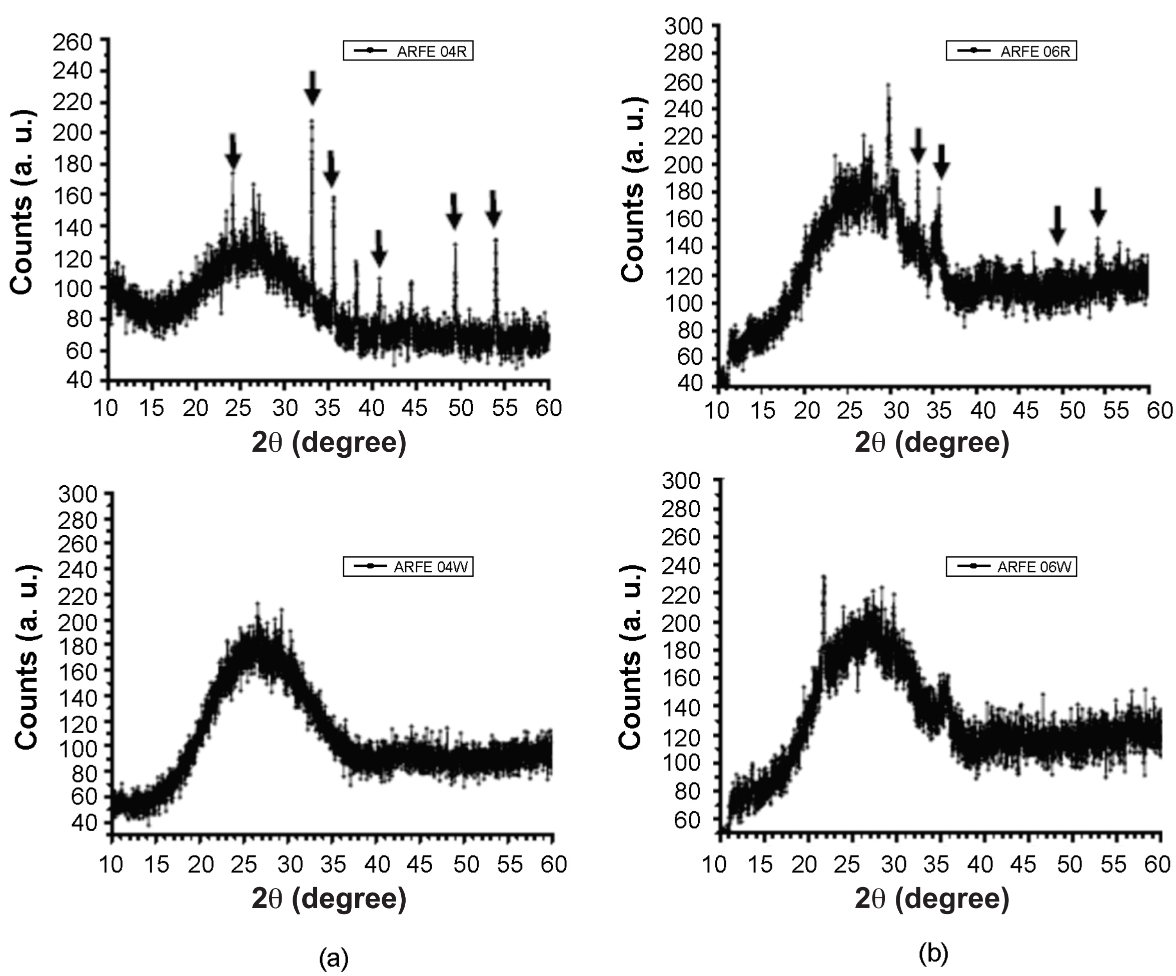

Figure 5: X-ray diffraction patterns of the red-color overglazes; (a) Arita porcelain (ARFE04) and (b) Kakiemon-style one (ARFE06) in Figs. 1d and 1e, respectively. The upper patterns were taken at the red-color floral part, while the lower ones were taken at the transparent glaze closed to its floral patterns.

[Figura 5: Difratogramas de raios X de vidrados vermelhos; (a) porcelana de Arita (ARFE04) e (b) do estilo Kakiemon (ARFE06) nas Figs. 1d e 1e, respectivamente.]

40.2, 50.0, 54.7, 55.2, and 59.8 degrees. This means that the present Izumiyama rough also include the SiO_2 structure. For comparison of Figs. 3a, 3b and Figs. 4a, 4b, it is found that, as for the extra peaks, the diffraction pattern of the Kakiemon-style porcelain piece (1670-90's) of Fig. 1c is approximately similar to that of the Izumiyama rough, except the intensity modulation. This indicates that one of the kilns producing the Kakiemon-style porcelains clearly used the Izumiyama rough, but not Chinese materials, as the red-color overglazing enamel.

Figs. 5a and 5b show the X-ray diffraction patterns of the Arita porcelain (1690 to 1730's) in Fig. 1d and the Kakiemon-style one (1670 to 90's) in Fig. 1e, respectively. The upper patterns were taken at the red-color floral part, while the lower ones were taken at the transparent glaze closed to its floral part. For the upper part, the diffraction patterns show the reflections of the α-Fe_2O_3 structure, denoted by the arrows, in addition to the weak extra reflections and the halo-like one. The halo-like X-ray scatterings suggest that there is a short range order of glass-like in the fritted red-color overglaze, similar to those in the transparent glaze. Thus, from the different diffraction patterns in Figs. 2, 3, and 5, we confirm that the potters did not yet establish the Kakiemon-style porcelain techniques at Arita in 1670-90's, except the Kakiemon family. The Kakiemon family already completed the technique in 1670-80's. However, it is deduced from the clear diffraction pattern ARFE03 in Fig.4 that the kiln producing the porcelain in Fig. 1c almost completed the Kakiemon-style technique. It is also possible to consider that its kiln was a Kakiemon kiln. More recently, we found that the most elegant and bright Kakiemon-style porcelains were produced at Akae Machi of Arita in 1710-50's by means of the similar X-ray diffraction using synchrotron radiation [25].

Fig. 6 shows the X-ray diffraction patterns of the Kakiemon-style porcelain pieces ARFE08 (1670–90's) in Fig. 1f. The upper part was taken at the dark-brown floral part in the overglaze, while the lower part at the transparent glaze closed to its floral part. The dark-brown color of the overglaze was chemically changed from the red-color by the big fires occurred in 1703. The strong peaks are observed at 2θ = 30.7, 31.3, 36.4, 43.4, 50.4, and 52.4 degrees. Although two peaks at about 26.6 and 36.4 degrees, as denoted by gray arrows in Fig. 5, are indexed by the SiO_2 reflections, the intensity ratio of both peaks is not theoretically, as in Fig. 4. This implies that the extra peak overlap the SiO_2 reflection at 36.4 degree. Furhermore, we could not observe any reflection of the α-Fe_2O_3 structure. This suggests that the α–Fe_2O_3 fine powders in the fritted red-color overgalze were changed to other oxides by the big fires. It is known that α-Fe_2O_3 is changed above about 1350 ºC to a mixed phase of Fe_3O_4 + O_2. However, it is not found any reflections of the Fe_3O_4 structure in the diffraction pattern of the overeglaze. Thus, it is consider that the α-Fe_2O_3 was melted above about 1400 ºC in the red-color overglaze. As we will describe in other paper [26], we confirmed Fe ions in the red-color overgalze by means of the X-ray absorption spectra. Thus, the strong extra peaks suggest that the oxygen complexes based on the Al_2O_3-SiO_2 system, not to be feldspar and quartz, were grown by the high-temperature of the big fires based to the raw oxides of SiO_2, Al_2O_3, CaO, MgO, K_2O, Na_2O et al. Thus, it is considered that the high-temperature treatment of the red-color overglazes induces the crystallization of the new oxygen complexes due to the α–Fe_2O_3 fine red-color enamel and the other fritted oxides. Furthermore, the lead oxide (PbO, melting point of about 880 °C) is usually included in the fritted overglaze as a supporting material of the red-color emission. In the present investigations, we also found that there is no reflection of PbO and other complex of PbO-SiO_2 in the X-ray diffraction patterns of the porcelains in Fig. 1. However, we confirmed that Pb elements are included in the red-color overglaze by means of the X-ray absorption spectrum. This also suggests that Pb ions contribute to make the oxygen complexes, in addition to decreasing a transition temperature to the glass-state of the fritted overglazes.

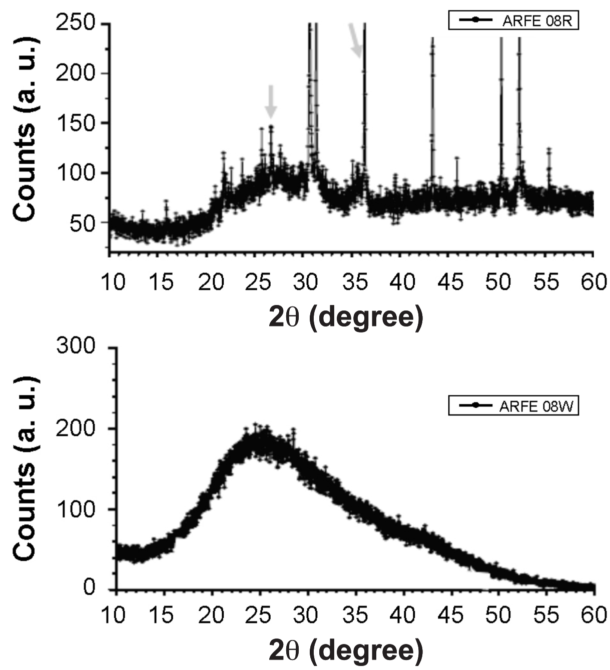

Figure 6: X-ray diffraction patterns of the Kakiemon-style porcelains (ARFE08) in Fig.1f. The upper patterns were taken at the red-color floral part, while the lower ones were taken at the transparent glaze closed to its floral patterns.
[Figura 6: Difratogramas de raios X de porcelanas do estilo Kakiemon (ARFE08 na Fig. 1f).]

CONCLUSIONS

In order to study the ancient porcelain-techniques of the famous Kakiemon-style porcelains developed in the early Edo period of Japan, we carried out the X-ray diffractions (XRD) using the synchrotron radiation for the red-color overglazes and the transparent glazes. The XRD results showed that the elegant brightness of the red-color overglazes results mainly from the micro-structural correlation between the α-Fe_2O_3 crystalline fine powders, as a red-color emission source, and the surrounding raw oxides of SiO_2, Al_2O_3, CaO, MgO, K_2O, Na_2O, PbO. Especially, the weak extra peaks observed in the diffraction patterns of the red-color overglazes suggested that the oxygen complexes based on the Al_2O_3-SiO_2 system having a lager crystallographic unit cell are grown in the fritted overglazes. We are interested that some extra peaks in the diffraction patterns can be indexed by the complex structure of (K,Na)$AlSi_3O_8$ and/or $CaAl_2Si_2O_8$ grown in the red-color overglazes. The complexes are usually observed in natural alumina silicates of Al_2O_3-SiO_2 system including the other oxides of CaO, MgO, K_2O, Na_2O, PbO so on, as referred in Table I. It is well known that the complexes have a lot of nano-scale cavities. Thus, we consider that the cavities can keep the α-Fe_2O_3 fine particles, as the red-color enamels, in the glazes and contributes to the elegance and brightness of the red-color overglazes for the Kakiemon-style porcelains.

In Figs. 2, 3, 5, and 6 the diffraction patterns of the red-color overglazes and the transparent glazes also show the hallo-like diffuse scatterings, which indicate the glass-state of short-range order in both glazes. Thus, we also consider that the glass-state play an important part for the structural stability of the red-overglaze on the porcelain surface, as a porcelain adhesive. The adhesive function is related to an interfacial fusion of the glasses on the porcelain body.

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