

The development and characterisation of zinc crystal glazes used for Amakusa-like soft porcelains

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Abstract

In porcelain production, as well as bodies expected to have white colour, compaction and translucency, suitable glaze compositions have great importance from both a technological and decoration point of view. Supplying the desired firing conditions is generally quite difficult for the porcelains having white colour after being fired in reducing atmospheres. In the present study, firstly it has been tried to make porcelain bodies similar to the Amakusa porcelain, which has been traditionally prepared in the Nagasaki Prefecture of Japan and widely used, by applying domestic raw materials and firing them in an oxidation atmosphere. Secondly, several zinc-containing glazes coloured with different colorants have been developed and applied to those bodies. After biscuit and gloss firing procedures, products have been characterised using dilatometry, X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Porcelain is one of the most outstanding products that ceramists have discovered. They can be used with or without glazes for both technical and artistic purposes. For their applications, beside strength in many cases, translucency may also be required.¹ It is possible to divide porcelains into two main groups such as soft and hard porcelains. Soft ones are fired at relatively lower temperatures due to their high level of fluxing agent contents. However, because of low clay content, their plasticity is lower and their tendency to breaking is higher. Compared with soft porcelains, hard porcelains are fired at relatively higher temperatures of $\approx 1400^\circ\text{C}$ in reducing atmosphere to prevent bubbling and to achieve a white coloured body.

Having been biscuit-fired at approximately $900\text{--}1000^\circ\text{C}$, porcelain bodies possess suitable amount of porosity (above 30% apparent porosity) and consequently can be easily glazed. Depending on the type of porcelain, glaze maturing temperatures range between 1250 and 1480°C .²

Crystalline glazes are widely preferred, especially to improve the attraction of porcelains to be used for ornament productions. These glazes can be either raw or fritted. If the glaze does not contain water-soluble constituents, then such a raw glaze will be more advantageous than a fritted one, due to being matured in a shorter time with lower cost. For their formation, precise firing cycles are required. In such application, in the cycle the glaze should be cooled down slowly from melting temperature to required temperature levels and finally to room temperature. Since the glaze is very fluid, one must be careful enough to ensure that it should not run off the substrate during crystal formation.¹ Consequently, both chemical composition and heat treatment procedure of glazes determine when, how and what kind of crystals would form.

The oxides in glaze compositions such as MgO, CaO and Al_2O_3 should be kept at a certain limit since they increase glaze viscosity and prevent crystal formations. On the other hand, K_2O and Na_2O are preferable due to their ability to decrease viscosity and facilitate crystal formations.³ Similarly, BaO is also used at a certain level although it causes an increase in viscosity when used at higher levels. In glazes, ZnO is employed up to approximately 10%.³ If present above this level, it can cause the glaze to have a matt appearance. By using

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lead, feldspar and boric acid with ZnO, defects like bubbling, boiling, pin holes and discoloration, which appear if ZnO is used on its own, can be eliminated. When a higher level of ZnO is present in glaze composition, willemite crystals easily occur during slow cooling.³ Zinc is a constituent of glazes that gives a very large selection of naturally occurring decorative crystals in which colouring agents like transition metals are absorbed. Combination of zinc with colouring constituents has a capacity of forming very different crystal formation and distribution. Therefore, the intensity and depth of colour that are possible in crystalline glazes along with the variability of crystal size and shape have maintained many ceramists' interest.⁴

If glaze raw materials introduce some amount of iron oxide into a glaze composition, the final appearance of the glaze may be rather patchy, cloudy and darker. In the case of copper presence, bright turquoise green occurs. Ti is also reported to promote zinc silicate crystal formation by forming zinc titanate, which is a good nuclei for willemite.^{3,5}

The best results in crystal glaze studies on biscuit porcelain bodies are achieved with firing under a neutral or oxidising atmosphere in electrically heated furnaces. From the view point of achieving suitable atmospheric conditions in crystal glaze applications, soft porcelains fired in an oxidising atmosphere are more advantageous than hard porcelains usually fired in a reducing atmosphere.

When producing crystal glazes, as well as glaze composition, heat treatment cycles also have a very strong effect on the concentration, shape and size of crystallites expected to form from original glazes. It is a very well known fact that when lower crystal growth temperatures are employed, the final shape of crystallites is spherical, unlike higher growth temperatures which cause single bars or double axe-head shaped crystals.⁶ Therefore, ceramists are producing unique modifications by using different compositions and heat treatment cycles, of course without ignoring matching properties of glaze and bodies.

The aim of this study was to produce Amakusa porcelain⁷ (Table 1), which is originally and traditionally produced by using only one raw material named as Amakusa stone whose deposit in Japan is decreasing, by employing domestic raw materials, to develop suitable

glaze compositions for Amakusa-like porcelains produced and then to investigate the crystallisation behaviour of these glazes.

2. Experimental procedure

2.1. Body preparation

Firstly, eight bodies have been prepared by selecting different raw materials (Table 2) and compositional ratios (Table 3). Each body composition was undertaken for wet milling and mixing in a ball mill with 1.5 kg dry charge capacity for about 4–5 h. After milling, slips were put through 100 mesh (150 μm) sieves and it has been seen that the amount remained over the sieve was negligible.

For preparing body samples (with the dimensions of 40×50×10 mm or alternatively 60×60×15 mm), plastic slips were hand-pressed into plaster of Paris moulds. At the same time, for the measurement of dry strength, bars with the dimensions of 200×15×15 mm have been slip cast. After drying, dry strength values of 8 bars for each body were determined by using a three-point-bending test. Additionally, eight different dried bodies have been heated to 1280°C with a rate of 5°C/min and fired for 1 h in an oxidising atmosphere in order to determine firing and total shrinkage.

2.2. Glaze preparation

Three different base glaze compositions [one is transparent (PS1), the other two zinc containing crystal glazes coloured with 0.3% CoO (PS2 and PS3 with higher ZnO content)], which are still used on traditionally-produced Amakusa body were selected and prepared, as were glazes coloured with Fe₂O₃ (PS4, PS5) and CuO (PS6, PS7). The Seger formulas of the glazes used on the bodies can be seen in Table 4.

After precise weighing of all raw materials to be used for preparation of the glaze, slips mixtures were charged into ball mills and milling carried out for about 1–2 h. During colouring of the slip, desired colouring agents in the form of pure oxide were added into mills in the last 45 min of wet mixing. After milling operations, prepared glaze slips were put through 100 mesh sieves and the sieved material was taken for glaze applications. Glazes were applied onto P3, P4 and P5 bodies prefired at 1000°C for 1 h in oxidising atmosphere by means of dipping and pouring.

For crystal glaze production, different heat treatment cycles (HTC) have been tried (Table 5).

2.3. Characterisation

Thermal expansion coefficient values (α) of P3, P4 and P5 biscuit bodies and PS1, PS3 glazes were determined

Table 1
Some physical properties of Amakusa porcelain body⁷

Physical properties		
Thermal expansion coefficient (700°C)	Body	60–75×10 ⁻⁷ °C ⁻¹
	Glaze	50–65×10 ⁻⁷ °C ⁻¹
Drying shrinkage (%)		4±1
Total shrinkage (%)		13±1

Table 2
The compositions of raw materials used for porcelain body preparations

Raw materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Ignition loss
Sındırgı kaolin	71.15	17.95	0.56	0.98	0.70	1.56	0.32	0.40	–	6.38
Alliören kaolin	71.50	16.06	0.40	0.42	0.30	0.46	0.30	0.35	2.20	8.01
Uşak kaolin	64.56	20.12	1.00	0.20	0.85	1.06	0.75	5.90	–	5.56
A-404 kaolin	55.41	30.93	1.15	0.74	0.78	0.35	0.27	0.12	–	10.25
Kütahya K-felds.	69.95	19.00	0.60	0.15	1.00	0.60	3.37	5.00	–	0.33
Na-felds.	67.60	19.05	0.08	0.20	0.63	0.56	11.00	0.88	–	–
Akas clay	50.76	32.11	1.70	1.10	0.40	0.18	0.40	1.80	–	11.55
Quartz sand	99.83	–	0.10	0.07	–	–	–	–	–	–

Table 3
The compositions of porcelain bodies prepared in this study

Body	Sındırgı kaolin	Alliören kaolin	Uşak kaolin	A-404 kaolin	Kütahya K-feldspar	Na-feldspar	Akas clay	Quartz sand
P1	–	–	–	33	18	3	–	46
P2	–	33	–	–	18	3	–	46
P3	–	–	–	22	20	3	–	55
P4	–	22	–	–	20	3	–	55
P5	–	–	–	50	20	5	–	25
P6	–	50	–	–	20	5	–	25
P7	–	11	–	11	20	3	–	55
P8	9	20	6	20	8	8	14	15

Table 4
The Seger formulas of the glazes used on the P3, P4 and P5 bodies

PS1	0.222 Na ₂ O 0.018 K ₂ O 0.687 CaO 0.073 MgO	0.490 Al ₂ O ₃ 0.007 Fe ₂ O ₃	3.810 SiO ₂ 0.021 TiO ₂
PS2	0.187 Na ₂ O 0.010 K ₂ O 0.097 CaO 0.025 MgO 0.584 ZnO 0.097 BaO	0.240 Al ₂ O ₃ 0.001 Fe ₂ O ₃	1.950 SiO ₂ 0.006 TiO ₂
PS3	0.097 Na ₂ O 0.005 K ₂ O 0.048 CaO 0.039 MgO 0.763 ZnO 0.048 BaO	0.240 Al ₂ O ₃ 0.003 Fe ₂ O ₃	1.910 SiO ₂ 0.011 TiO ₂
PS4 ^a , PS6 ^b	0.185 Na ₂ O 0.010 K ₂ O 0.097 CaO 0.027 MgO 0.633 ZnO 0.048 SrO	0.240 Al ₂ O ₃ 0.002 Fe ₂ O ₃	1.654 SiO ₂ 0.006 TiO ₂
PS5 ^a , PS7 ^b	0.185 Na ₂ O 0.010 K ₂ O 0.097 CaO 0.027 MgO 0.633 ZnO 0.048 SrO	0.240 Al ₂ O ₃ 0.002 Fe ₂ O ₃	2.240 SiO ₂ 0.006 TiO ₂

^a 0.3 and 0.6% Fe₂O₃ added, respectively.

^b 0.3 and 0.6% CuO added, respectively.

by dilatometry measurements. Additionally, α value of PS1 was calculated by using Appen's Method,⁷ which is very valuable to estimate thermal expansion coefficients of transparent glazes before dilatometry measurements.

The crystalline phases in the bulk materials were identified by X-ray diffraction (XRD-Rigaku Rint 2000 Series) using CuK α radiation. Two different kind of samples were investigated using scanning electron microscopy (SEM): (i) as-received samples from the top and (ii) broken samples from the side (edge-on). The samples were coated with a thin film of gold-palladium and examined using a CamScan S4 at 20 kV. An ultra thin window energy dispersive X-ray spectrometer (EDX-LINK ISIS 300) attached to SEM was also used for chemical analysis.

3. Results and discussion

At the beginning of the current study, eight different bodies similar to Amakusa,⁷ which consisting of 75.55% SiO₂, 16.95% Al₂O₃, 0.21% Na₂O, 3% K₂O, 0.08% MgO, 0.13% CaO, 0.1% TiO₂, 0.28% Fe₂O₃ and 3.70% loss of ignition, have been produced by taking Amakusa's rational analysis, which can also be represented as 1.77% Na-feldspar, 17.74% K-feldspar, 33.37% clay substance and 47.12% quartz, and tested for their colour and shrinkage (Table 6). P3, P4 and P5 bodies (Table 3) have given the whitest colour and, out of these three samples, P4 was the whitest and gave the smallest

Table 5
Heat treatment cycles used for maturing and crystallisation processes of PS1, PS2, PS3, PS4, PS5, PS6 and PS7 glazes^a

Glaze	Heat treatment cycles (HTC)				HTC no.
	Gloss firing temperature (°C)	Holding time (h)	Crystal growth temperature (°C)	Holding time (h)	
PS1	1280	1	–	–	1
PS2	1280	1	–	–	2
PS2	1280	3	–	–	3
PS2	1280	6	–	–	4
PS3	1280	1	–	–	5
PS3	1280	2	1180	3	6
PS3, PS4, PS5, PS6 and PS7	1280	3	1180	5	7
PS3, PS4, PS5, PS6 and PS7	1280	3	1080	5	8

^a Heating rate 5°C min⁻¹ and cooling rate 2°C min⁻¹.

Table 6
Some physical properties of P3, P4 and P5 bodies

Body	Drying shrinkage (%)	Firing shrinkage (%)	Total shrinkage (%)	Dry strength (kg cm ⁻¹)
P3	2.73	7.40	10.30	20.84
P4	2.50	4.64	7.14	27.26
P5	1.30	9.20	10.5	18.70

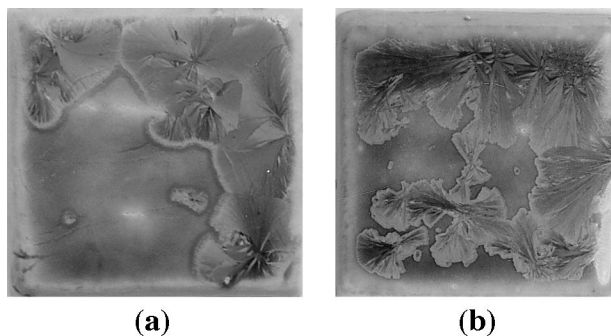


Fig. 1. (a) P4 and (b) P5 bodies which were glazed with PS3 containing 0.3% CoO as colouring agent and treated by HTC 1.

firing shrinkage value because of high silica content in its body receipt (Tables 3 and 6). On the other hand, although the silica content of P4 body is 55% (Table 3) and expected to give smaller dry strength value, the dry strength decreasing effect of silica has been balanced by using high plasticity Allören kaolin for the preparation of P4 body (Table 6). It was observed that P3, P4 and P5 bodies had at least equal whiteness compared to the original Amakusa body. According to the results, it has been decided to continue further studies with P3, P4 and P5 bodies. α values of porcelain biscuit bodies of P3, P4 and P5 were measured by dilatometry and found to be 59×10^{-7} , 68×10^{-7} , and $66 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ accordingly. The studies for improving the properties of these bodies are continuing.

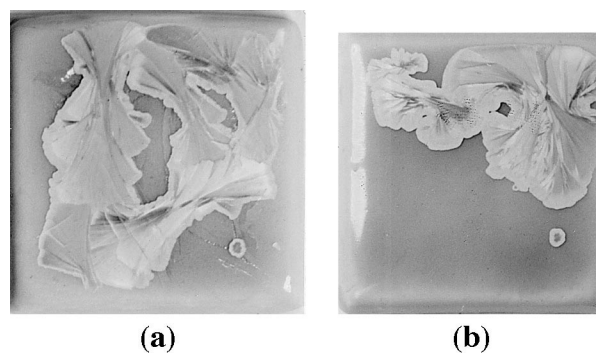


Fig. 2. (a) P3 and (b) P4 bodies which were glazed with PS6 containing 0.3% CuO as colouring agent and treated by HTC 1.

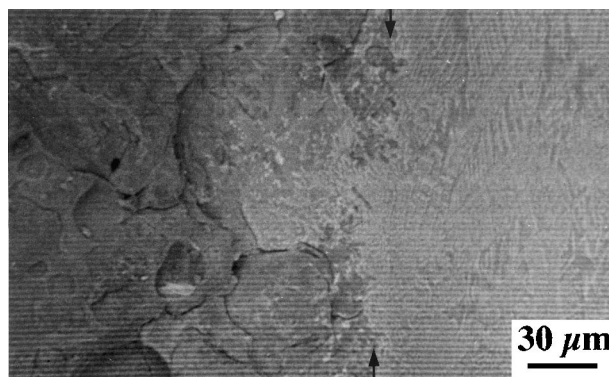


Fig. 3. The interface (arrowed) between porcelain body (on the right) and PS3 glaze treated by HTC 8.

After this stage, the study has been concentrated on the preparation of relevant glaze compositions (Table 4). α values of the developed PS1 glaze were calculated to be $60 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ by using Appen's method as compared to $63 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$, which is determined by dilatometry studies. Since no mismatching problem of glazes and bodies was observed after gloss firing, α values of both bodies and glazes should be close to each other.

In order to produce crystals from the original glazes, several HTC were employed (Table 5). Fig. 1 shows P4

and P5 bodies which were glazed with PS3 containing 0.3% CoO as colouring agent and treated by HTC 1, whereas Fig. 2 represents P3 and P4 bodies which were glazed with PS6 containing 0.3% CuO as colouring agent and treated by HTC 1.

Holding PS2 and PS3 glazes at 1280°C, which seemed to be sufficient for liquid formation, for 1 and 3 h (Table 5), has a positive effect for crystal nucleation. However, staying longer (for 6 h) at this temperature results in

dissolution of nuclei. Additionally, holding the porcelain samples with CoO coloured glazes longer at this temperature caused the colour to be lightened. In HTC 2, 3 and 4, the best glaze-body fit was observed with P5 body.

Since the temperature (1280°C) was not sufficient for maturing iron containing crystal glazes (PS4 and PS5), smooth glaze formation could not be obtained in this case.

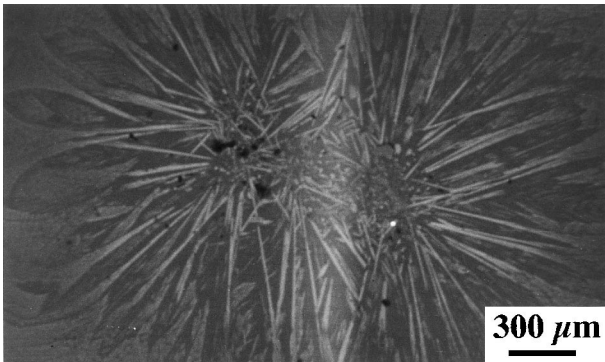


Fig. 4. The spherical crystal growth of PS3 glaze treated by HTC 8.

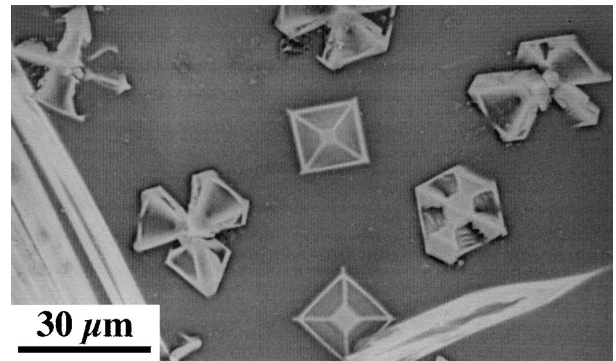


Fig. 6. Willemite rods and gahnite star-like crystals in PS3 glaze treated by HTC 7.

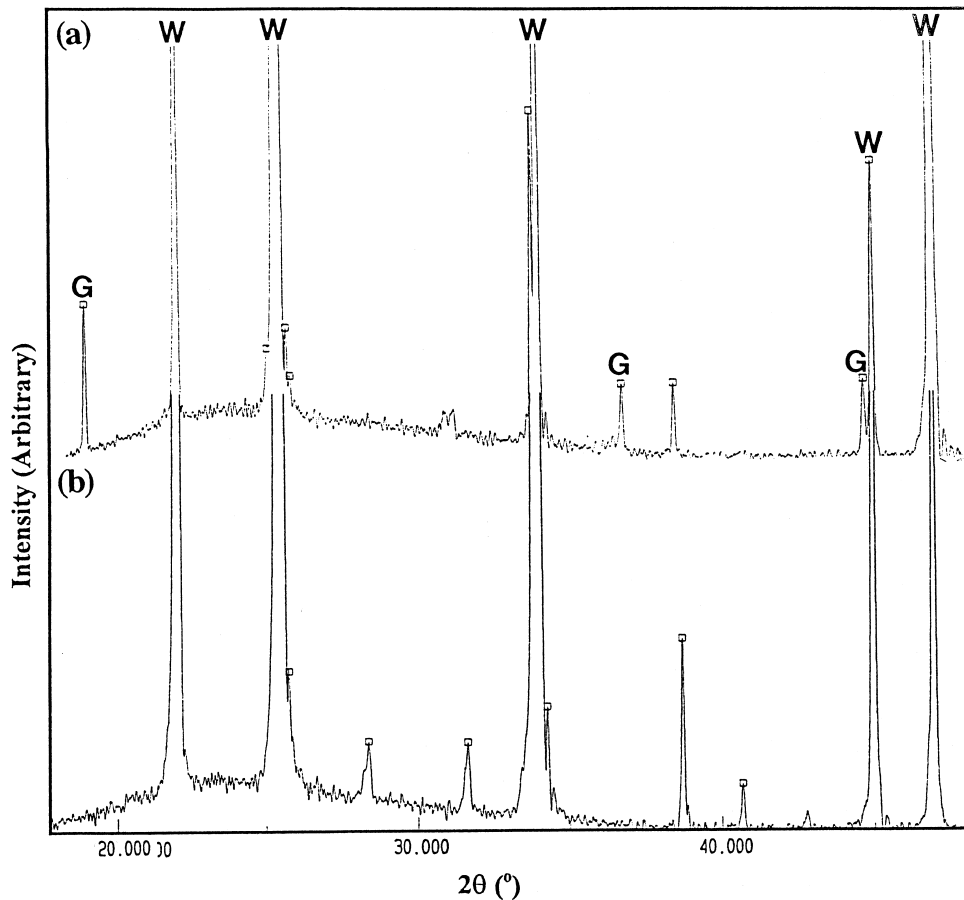


Fig. 5. (a) XRD pattern showing willemite (W) and gahnite (G) formation in PS3 glaze treated by HTC 7; (b) XRD pattern showing willemite formation in PS3 glaze treated by HTC 8.

Once a liquid phase forms, attack on the body begins, leading to the formation of intermediate compositions which could be either vitreous or crystalline. The mechanism of this corrosion is similar to acid-base reactions in aqueous solution.⁸ There is subsequent diffusion of chemical species from the body into the glaze and from the glaze into the body. A well developed reaction zone takes place and influences the ability of the glaze to resist imposed stresses. Once the zone is formed, the reactions slow down.³ As can be seen from

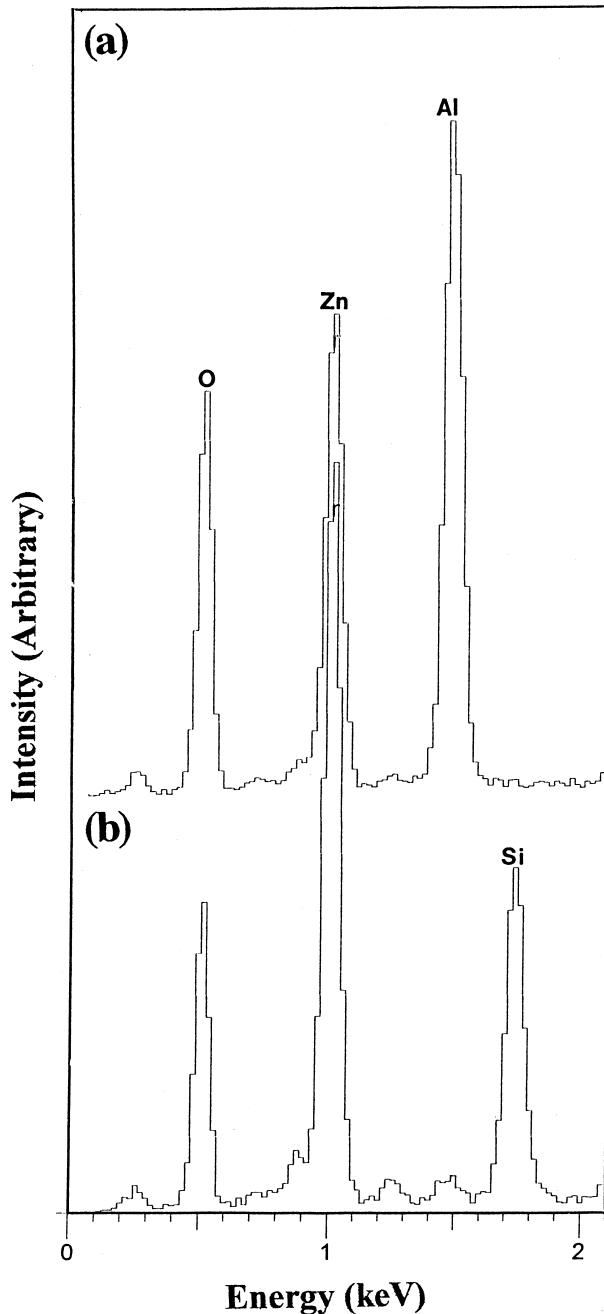


Fig. 7. (a) EDX pattern taken from a star-like crystal showing gahnite formation in PS3 glaze treated by HTC 7; (b) EDX pattern taken from a rod-like crystal showing willemite formation in PS3 glaze treated by HTC 7.

Fig. 3, which shows the edge-on interface between PS3 glaze treated by HTC 8 and the porcelain body, glaze attack on the substrate is quite obvious. The crystals have also grown in a perpendicular direction to the body surface. Crystallisation occurred through the whole thickness of the glaze.

Although it has been reported that in crystal glaze applications a thicker glaze layer than those for other applications has to be used, an optimum thickness of glaze must be determined to prevent cracking during drying and eventually regional glaze shrinkage problems on the double-fired porcelain. In this study, thickness of 100 μm of glaze seems to be sufficient to get rid of such problems.

In HTC 6, holding P3 porcelain glazed with PS3 at crystal growth temperature, 1180°C, for 3 h did not result in homogeneously matured and distributed glaze. On the other hand, the best results for forming plate-like

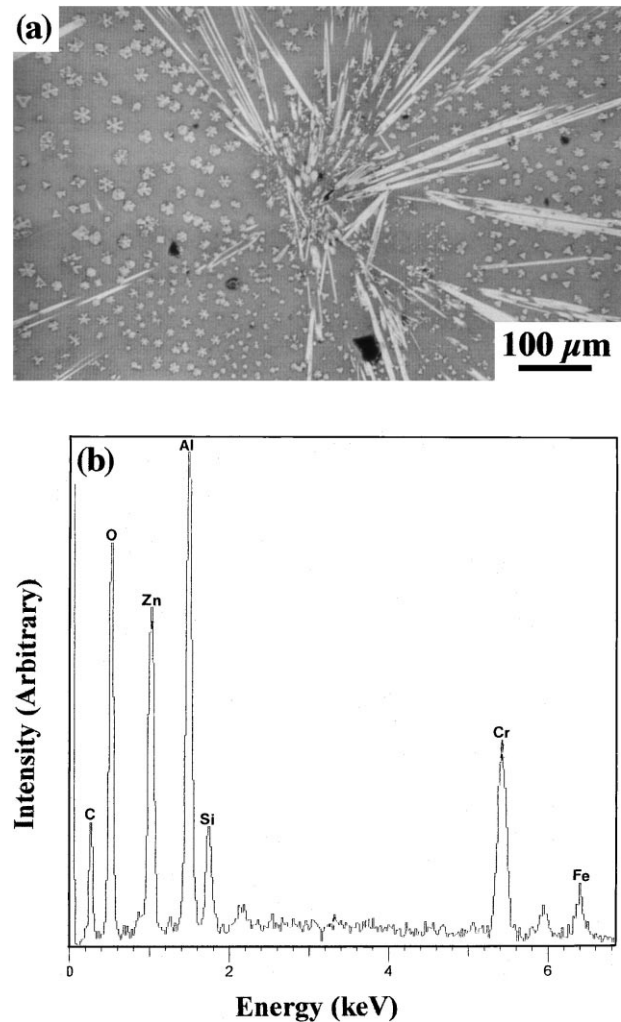


Fig. 8. (a) The centre of a plate-like crystal of PS3 glaze treated by HTC 7 in which iron-based dirt acted as a heterogeneous nucleus. (b) EDX pattern taken from the centre of a plate-like crystal of PS3 glaze treated by HTC 7 in which iron-based dirt acted as a heterogeneous nucleus.

crystals and spherical shape crystals (Fig. 4) were achieved by HTC 7 and 8, respectively (Table 5). Increasing crystal growth temperature from 1080 to 1180 °C causes crystals to adopt themselves from spherical shape into plate-like form.

SEM investigations showed different crystal morphologies in two dimensions; star-like, rod-like and faceted (Figs. 5 and 6). EDX spectra obtained from these crystals showed that star-like crystals have a composition similar to gahnite [zinc aluminate (ZnAl_2O_4)] [Fig. 7 (a)] whereas rod-like and faceted crystals have a composition similar to willemite [zinc silicate (Zn_2SiO_4)] [Fig. 7 (b)]. These results match well with the XRD results that HTC 7 results in the formation of both willemite and gahnite [Fig. 5 (a) and 7 (a)] and HTC 8 gives rise to the formation of willemite crystals only [Fig. 5 (b) and 7 (b)].

With these studies, it has also been shown that mechanically (and accidentally) introduced iron-based dirt may be acting as a heterogeneous nucleus from which willemite crystals might have also grown [Fig. 8 (a) and (b)].

4. Conclusions

1. P3, P4 and P5 bodies which were produced by using domestic raw materials were found to be similar to Amakusa porcelain in many ways, such as ease of forming, whiteness after firing in oxidation atmosphere and suitable fitting with different crystalline glaze.
2. The smallest shrinkage and highest dry strength values are obtained with P4 body.
3. Transparent glaze application without cracking has been successfully achieved by PS1 glaze.
4. Willemite crystals can have either a rod-like shape or be faceted while gahnite crystals only show a star-like shape.
5. Plate-like crystals and spherical-shape crystals were achieved by HTC 7 and 8, respectively. Increasing crystal growth temperature from 1080 to 1180 °C causes spherical crystals to change themselves into plate-like form.
6. HTC 7 results in both willemite and gahnite crystal formation, unlike HTC 8 which only forms willemite crystals.
7. It has also been observed that mechanically introduced iron-based dirt acted as a heterogeneous nucleus from which willemite crystals may have also grown.

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References

1. Rado, P., *An Introduction to The Technology of Pottery*. The Institute of Ceramics. Pergamon Press, 1988.
2. Ryan, W. and Radford, C., *Whitewares: Production, Testing and Quality Control*. Pergamon Press, 1987.
3. Taylor, J. R. and Bull, A. C., *Ceramics Glaze Technology*, Pergamon Press, 1980.
4. Scott, J., Crystalline glazes are studio potter's forte. *Advanced materials and processes*, 1998, **7**, 8.
5. Preda, M. and Rehner, H. H., Crystallised glazes K_2O – ZnO – TiO_2 – SiO_2 quaternary system. *Conference and Exhibition of The European Ceramic Society*, 20–24 June 1999, Brighton, in press.
6. Creber, D., Crystalline glazes on porcelain. *Canadian Ceramics Quarterly*, 1990, **62**, 31.
7. Anon. *Ceramic Development Technology II Course Documents*. JICA (Japan International Corporation Agency), Japan, April–October 1997.
8. Roberts, W. and Marshall, K., *Trans. Brit. Ceram. Soc.*, 1970, **69**, 221–224.