Effects of cobalt, copper, manganese and titanium oxide additions on the microstructures of zinc containing soft porcelain glazes

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Abstract

Different types of glazes, which are nearly all based upon silicate compositions, are used to meet a wide range of requirements in service. Many artistic effects are achieved by departing from a clear, smooth, transparent system. Coloured glazes are produced by several means such as the inclusion of colouring oxides, addition of stains, dispersing finely divided particles and the use of precious metals, applied in the form of lines or bands, or even screen-printed patterns. Colouring oxides commonly used include iron, copper, cobalt, chromium, manganese, nickel, vanadium, cadmium and selenium. Zinc oxide has a beneficial effect in many coloured glazes amongst which crystalline ones are more noteworthy. With this paper the effects of CoO, CuO, MnO_2 and TiO_2 additions into zinc oxide containing crystal glazes differentially heat-treated are described on micro-scale appearances. Experimental techniques used were X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX). © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Most of important elements used as a source of colour in glazes and enamel stains are to be found in a particular section of the Periodic Table known as the transition elements. They can readily form complexes in solution. This means that they can associate with two or more surrounding ions of opposite sign, sometimes known as ligands, to form a complex group, the properties of which may be very different from those of the original ion. The surrounding field can change the characteristic energy levels in such a way as to bring about a complete change of colour. There are a number of colouring media used in ceramics and they may differ from each other in fundamental ways.[1] The absorption of characteristic wavelengths by elements dissolved in the glaze or by inert pigment particles suspended in the glaze produces colour.

Some elements, such as Pb and Zn, do not themselves contribute any colour, but have a considerable influence on the colour produced by other ions. Zinc oxide is a valuable auxiliary flux in glazes firing up to about 1050 °C. At higher temperatures, it is effective in viscosity reduction and the amount added to a glaze recipe should be adjusted to needs. By its use the firing range of high temperature glazes is extended. While some glazes mature, zinc oxide will dissolve readily even if present in excessive amounts. On cooling, crystals appear as those formed from a saturated solution. The fine crystals collect any pigment or colouring ion present in the glaze to give highly decorative effects.[2]

Although cobalt was isolated only in the eighteenth century, its use as a glass colorant has been known for about 4500 years. Nearly all glasses develop a blue colour with cobalt (as Co^{2+}), although in some compositions a pink one will develop. The solubility of cobalt salts in glass is high. Cobalt is a powerful colorant and as little as 0.02% CoO produces a noticeable tint in a transparent glaze.[2]

As one of the strongest colouring elements, copper was one of the earliest colorants of glaze in early Egyptian faience. It gives a wide range of colours from blue to green and in special circumstances red depending upon composition and the firing atmosphere. Copper compounds are

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very soluble in all type of glaze and frit. On the other hand, copper is an active flux in glaze and it will reduce the firing range of any composition to which it is added. However, it should never be used in glazes for any food contact surfaces.[2]

Manganese exists in various oxidation numbers and gives several derived colours. The tone of these weak colours in either glaze or frit can be modified by kiln atmosphere. In oxidised glazes the colour of manganese is pink, but in a glaze fired in a reducing atmosphere, deep greenish-brown colours predominate. Up to 4% manganese oxide, expressed as MnO_2, can readily dissolve in most glazes, but thereafter precipitation as crystals increasingly occurs on the glaze surface. If present from 5 to 10%, it produces shades of purplish brown and, at 20%, the surface (though dark brown) is metallic. In crystalline glazes manganese produces clusters of coloured crystals. Overfiring causes its colours to fade.[2,3]

Combinations of colouring oxides in a glaze composition result in different colour variations. From the decoration point of view, when a pastel colour is required, one adds an opacifier plus a pigment to the ceramic coating. For example, zircon opacifier should be used with zircon or zirconia-based pigments. Chrome-tin pinks are stronger if some tin oxide opacifier is used. Titania-based pigments used in enamels require titania opacifiers.[4]

In porcelain enamels and in glazes, firing at less than 1000 °C titania in the anatase crystal form is the opacifying agent of choice. However, at a temperature about 850 °C, anatase inverts to rutile in silicates. Once inverted to rutile, titania crystals can grow rapidly to sizes that are no longer effective for opacification. The solubility of titania in molten silicates is around 8–10%. At room temperature, this solubility is reduced to around 5%. Thus, when using titania as an opacifier, substantial amounts, about 15% or more, must be used. In many titania-opacified porcelain enamels, all the titania dissolves in the frit and is recrystallized during firing of the ceramic coating.[4]

The purpose of the present study is to investigate the effect of different colouring agent additions on the microstructure of zinc containing soft porcelain glazes.

2. Experimental procedure

2.1. Glaze preparation

Eight zinc containing soft porcelain glaze (PG) compositions [0.3% CoO (PG1[a]), 0.6% CoO (PG1[b]), 0.3% CuO (PG2[c]), 0.6% CuO (PG2[d]), 0.3% MnO_2 (PG3[e]), 0.6% MnO_2 (PG3[f]), 0.3% TiO_2 (PG4[g]) and 0.6% TiO_2 (PG4[h])] were selected and prepared (Table 1). In order to produce glaze slips laboratory grade $CaCO_3$, $SrCO_3$, ZnO, CoO, CuO, MnO_2, TiO_2 and domestically available

Table 1
The Seger formula of the glazes studied

PG1,[a] PG1,[b] PG2,[c] PG2,[d] PG3,[e] PG3,[f] PG4[g] and PG4,[h]	0.185 Na_2O 0.010 K_2O 0.097 CaO 0.027 MgO 0.633 ZnO 0.048 SrO	0.240 Al_2O_3 0.002 Fe_2O_3	1.654 SiO_2 0.006 TiO_2

[a]0.3 and [b]0.6% CoO, [c]0.3 and [d]0.6% CuO, [e]0.3 and [f]0.6% MnO_2, [g]0.3 and [h]0.6% TiO_2 added, respectively.

Na-feldspar, Sındırgı kaolin and quartz sand were used (Table 2).

After accurate weighing of all raw materials to be used for preparation of 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 wet sieved, taking for glaze applications the fraction passing through a 100 mesh sieve. Glazes were applied onto porcelain 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's) have been tried (Table 3).

2.2. Characterisation

The crystalline phases in heat treated glazes were identified by X-ray diffraction (XRD-Rigaku Rint 2000 Series) using CuK_α radiation. The samples were coated with a thin film of gold-palladium and examined using a scanning electron microscopy (SEM-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

In the current study, to see the effect of CoO, CuO, MnO_2 and TiO_2 additions individually, as 0.3 or 0.6%, into crystalline glaze composition containing of zinc oxide, one major glaze recipe was chosen (Table 1).

3.1. Effect of CoO addition

0.3 and 0.6% CoO were separately added to PG1 glaze during glaze slip preparation. After glaze application, heat treatments at 1180 (HTC 1) and 1080 °C (HTC 2) were applied to the glaze. Fig. 1 shows XRD patterns taken from heat treated PG1 glaze. It is obviously seen that both heat treatments result in willemite and gahnite crystal formations simultaneously. Fig. 2 indicates willemite [zinc silicate (Zn_2SiO_4)] rods and star-

Table 2
The compositions of domestically available raw materials used for glaze preparations

Raw materials	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	I.L.[a]
Sındırgı kaolin	71.15	17.95	0.56	0.98	0.70	1.56	0.32	0.40	–	6.38
Na-feldspar	67.60	19.05	0.08	0.20	0.63	0.56	11.00	0.88	–	–
Quartz sand	99.83	–	0.10	0.07	–	–	–	–	–	–

[a] IL, ignition loss.

Table 3
Heat treatment cycles used for maturing and crystallization processes PG1, PG2, PG3 and PG4 glazes[a]

Glaze	Heat treatment cycles (HTC)				HTC no.
	Gloss firing temperature (°C)	Holding time (h)	Crystal growth temperature (°C)	Holding time (h)	
PG1, PG2, PG3 and PG4	1280	3	1180	5	1
PG1, PG2, PG3 and PG4	1280	3	1080	5	2

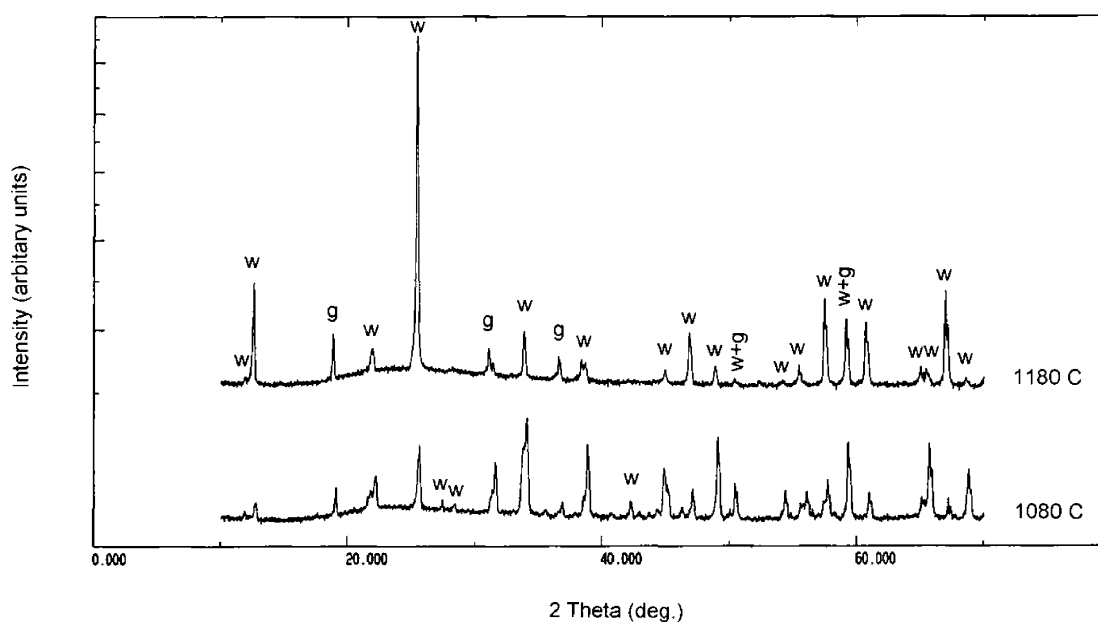[a] Heating rate is 5 °C/min and cooling rate is 2 °C/min.

Fig. 1. XRD results showing willemite and gahnite formations in CoO added PG1 glaze treated by HTC 1 at 1180 °C and HTC 2 at 1080 °C (w, willemite; g, gahnite).

like shaped gahnite [zinc aluminate ($ZnAl_2O_4$)] crystals distributions in PG1[a] glaze with the effect of different glaze maturing temperatures. The main difference between two different heat treatment cycles is that willemite crystals are in the form of well developed rod-like shape at the 1180 °C whereas they are finely distributed throughout the matrix surrounding gahnite crystals at 1080 °C.

3.2. Effect of CuO addition

0.3 and 0.6% CuO were individually incorporated into PG2 glaze during glaze slip preparation followed

by HTC 1 and HTC 2. XRD patterns of PG2 glaze confirm that while higher glaze maturing temperature (1180 °C) leads willemite and gahnite formations, lower temperature (1080 °C) gives only willemite occurrence (Fig. 3). Microstructural studies confirmed these results [Fig. 4(a)–(d)].

3.3. Effect of MnO_2 addition

0.3 or 0.6% MnO_2 additions into PG3 glaze were also made and after glaze applications onto soft porcelain bodies similar HTC were applied. Both XRD and
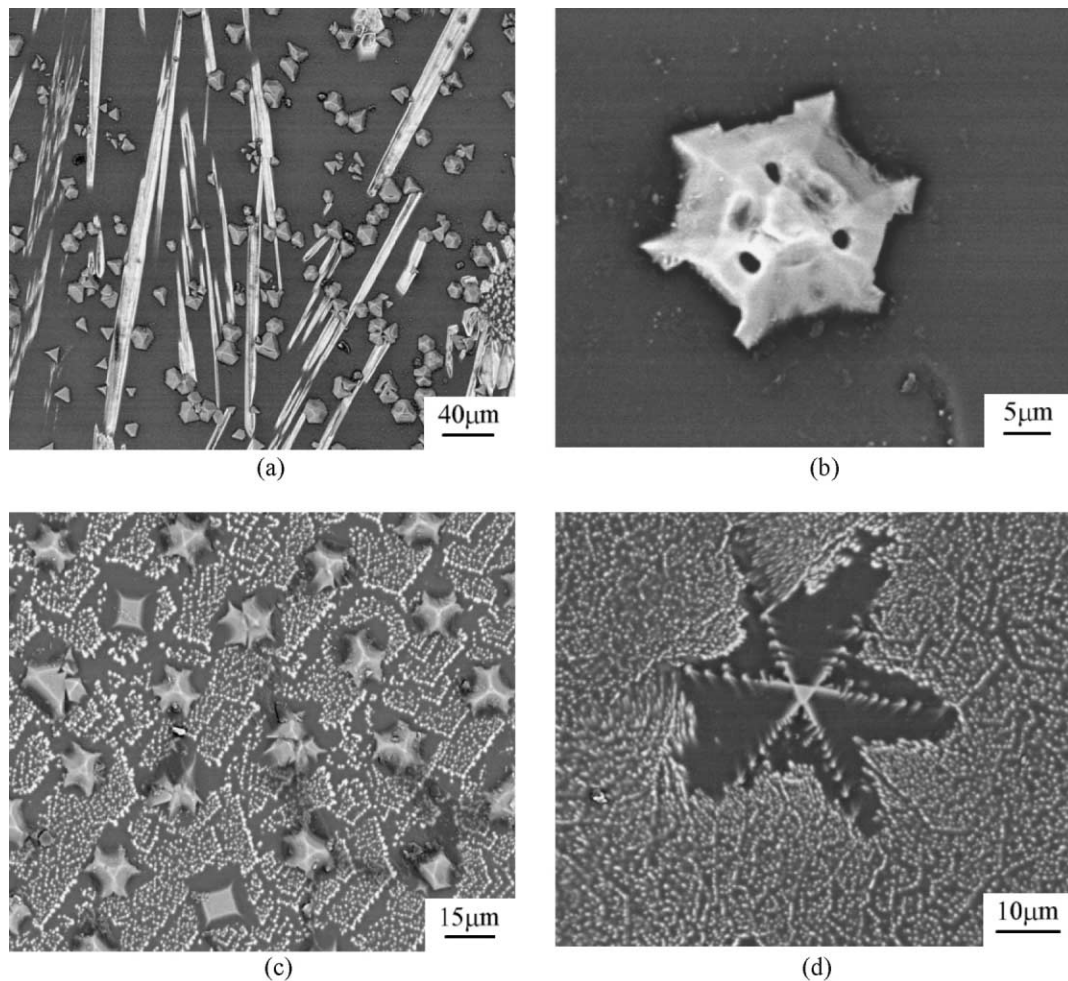
Fig. 2. The microstructures of 0.3% CoO added glaze (PG1[a]) treated by HTC 1 at 1180 °C (a) and (b) showing the formation of rods (willemite) and star-like shaped crystals (gahnite), and HTC 2 at 1080 °C (c) and (d) with star-like gahnite crystals in willemite matrix.

microstructural investigations (Figs. 5 and 6) showed that 1180 and 1080 °C heat treatments caused only willemite crystal formation in MnO_2 additions.

3.4. Effect of TiO₂ addition

TiO_2 was added into PG4 glaze as 0.3 and 0.6%. Its crystallisation promoting effects in zinc containing crystal glazes have been strengthened with XRD patterns taken from PG4 glaze which was undergone different heat treatments showing both willemite and gahnite crystal occurrence (Fig. 7). According to SEM studies, the same conclusion was achieved (Fig. 8). At 1080 °C willemite crystals are finely distributed in the matrix and at 1180 °C rod-like willemite crystals grew (Fig. 8).

4. Discussion

The addition of CoO into glaze composition, even at the level of 0.2%, results in an intense blue colour. With the CuO addition, oxidising firing atmosphere produces

green in zinc containing soft porcelain crystal glazes. When the level of CuO content is increased up to 0.6% then the shade of green colour is strengthened. MnO_2 turns the colour of glaze to white unlike TiO_2 supplying yellow.[5,6]

The effects of composition and HTC on the zinc containing soft porcelain glaze systems have recently been investigated in detail.[5–13] With these studies it was reported that zinc oxide produces willemite and gahnite crystals in soft porcelain crystalline glazes even in the absence of titania, which is known to produce nuclei for the development of zinc-based crystals.[5–13]

According to the XRD results, with CoO, CuO and TiO_2 incorporations into glaze, HTC 1 at 1180 °C produced willemite and gahnite, whereas MnO_2 addition gave only willemite formation in final crystallised glaze in the current study (Figs. 1–8). As to HTC 2 at 1080 °C, it was seen that lower crystal growth temperature produced willemite and gahnite with CoO and TiO_2 incorporations, whereas CuO and MnO_2 gave willemite formation only (Figs. 1–8). However, in the previous studies[7–9] it was reported that the glaze composition containing BaO
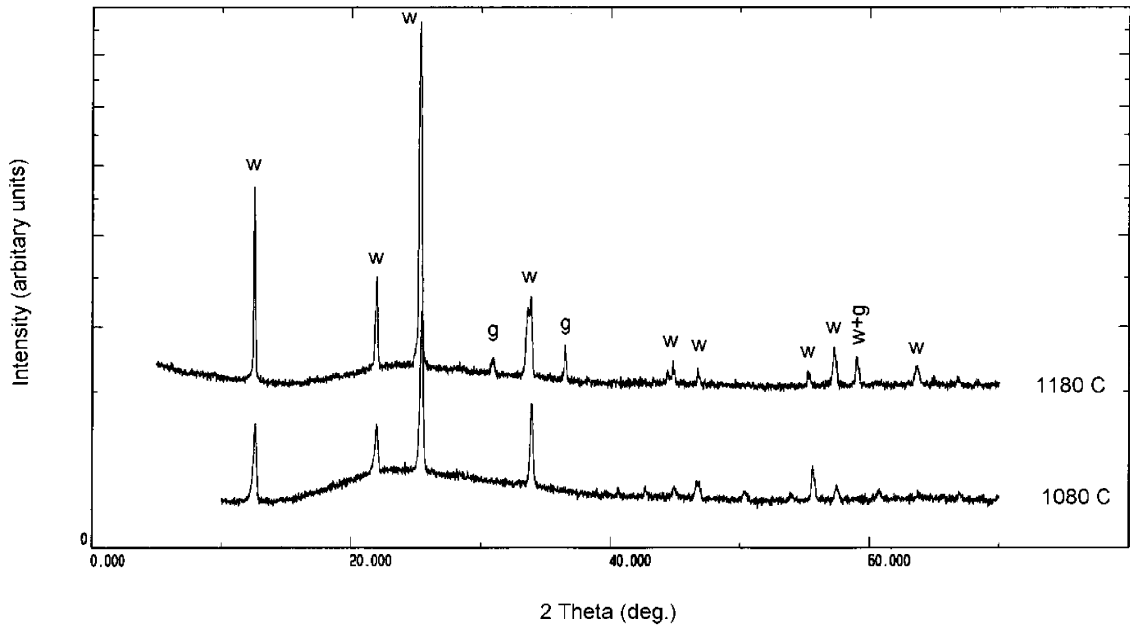
Fig. 3. XRD results showing willemite and gahnite formations in CuO added PG2 glaze treated by HTC 1 at 1180 °C and only willemite formation by HTC 2 at 1080 °C (w, willemite; g, gahnite).
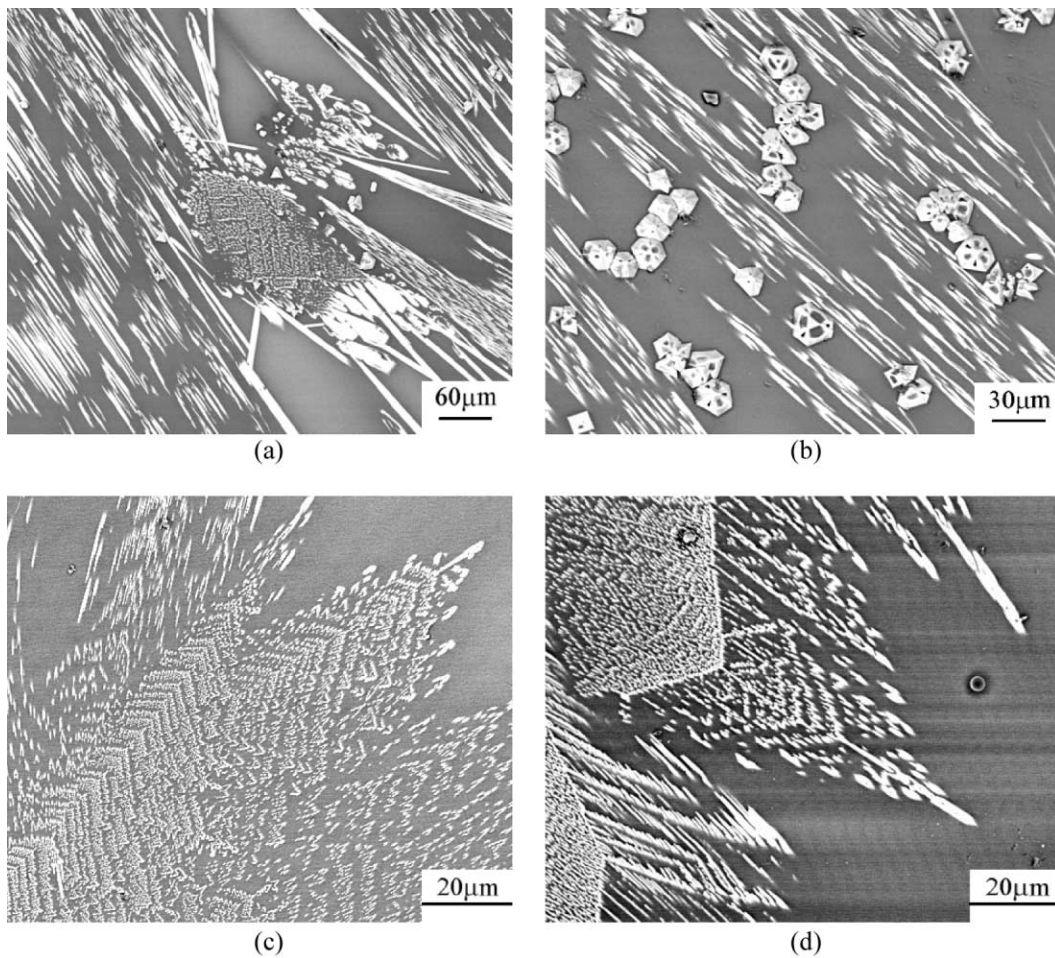

Fig. 4. The microstructures of 0.3% CuO added glaze (PG2^c) treated by HTC 1 at 1180 °C (a) and (b) showing different shapes of willemite and gahnite stars, and HTC 2 at 1080 °C (c) and (d) confirming XRD results that only willemite crystals formed.
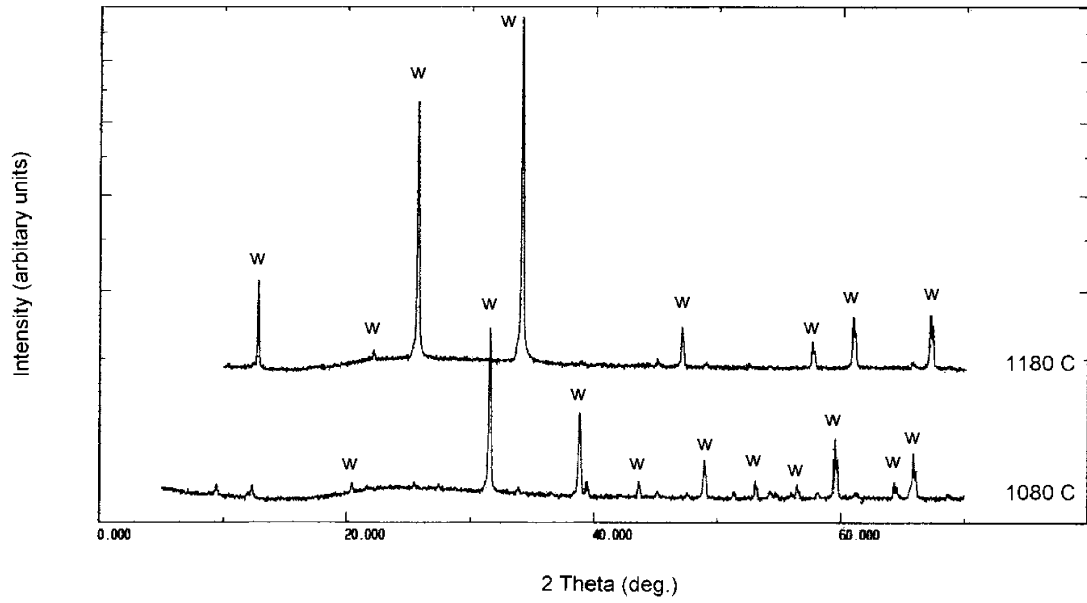
Fig. 5. XRD results showing willemite formation only in MnO_2 added PG3 glaze treated by HTC 1 at 1180 °C and HTC 2 at 1080 °C (w, willemite; g, gahnite).
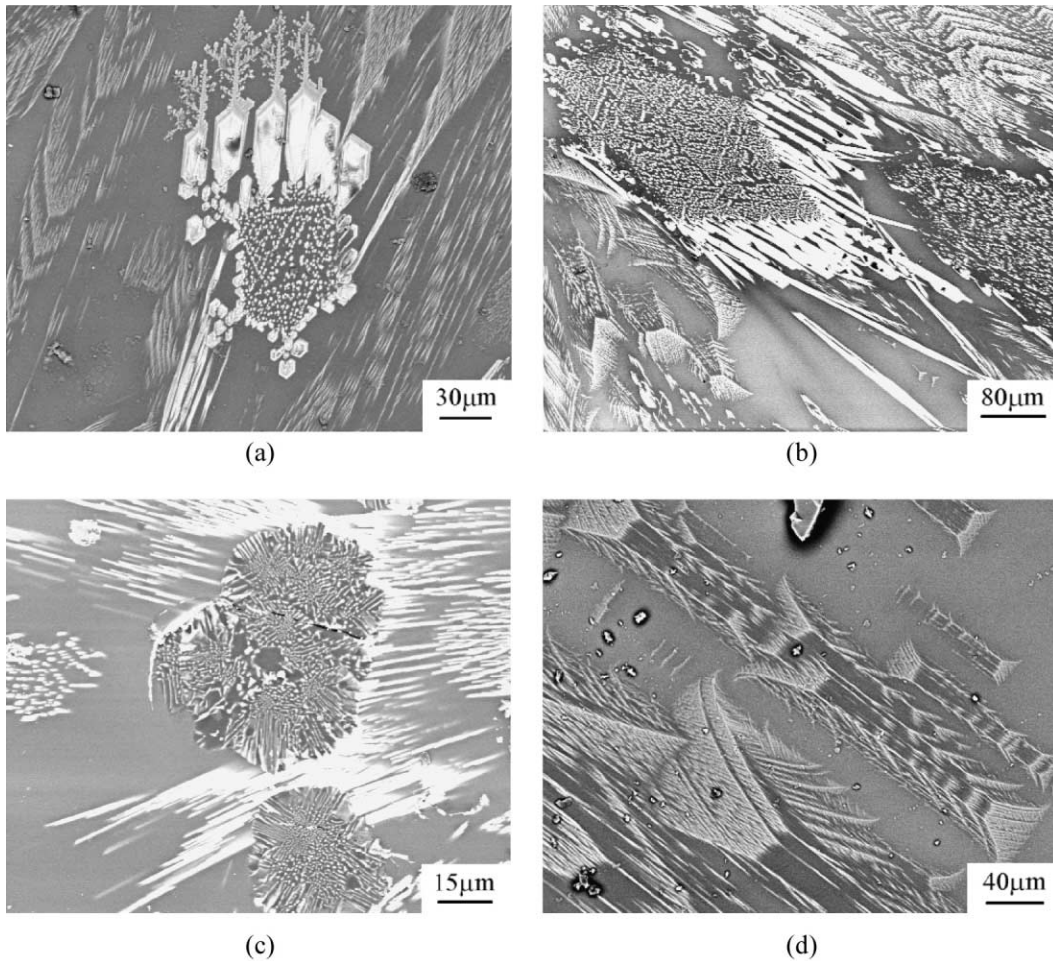

Fig. 6. The microstructures of 0.3% MnO_2 added glaze (PG3^e) treated by HTC 1 at 1180 °C (a) and (b) and HTC 2 at 1080 °C (c) and (d) showing different size and shaped willemite crystals in the absence of gahnite.
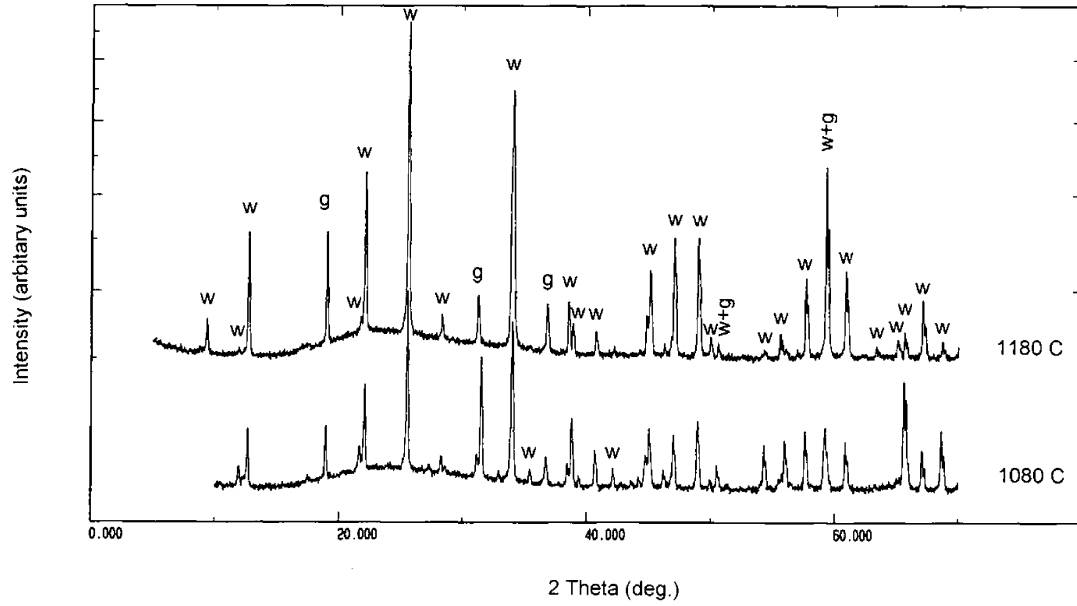
Fig. 7. XRD results showing willemite and gahnite formations in TiO$_2$ added PG4 glaze treated by HTC 1 at 1180 °C and HTC 2 at 1080 °C (w, willemite; g, gahnite).
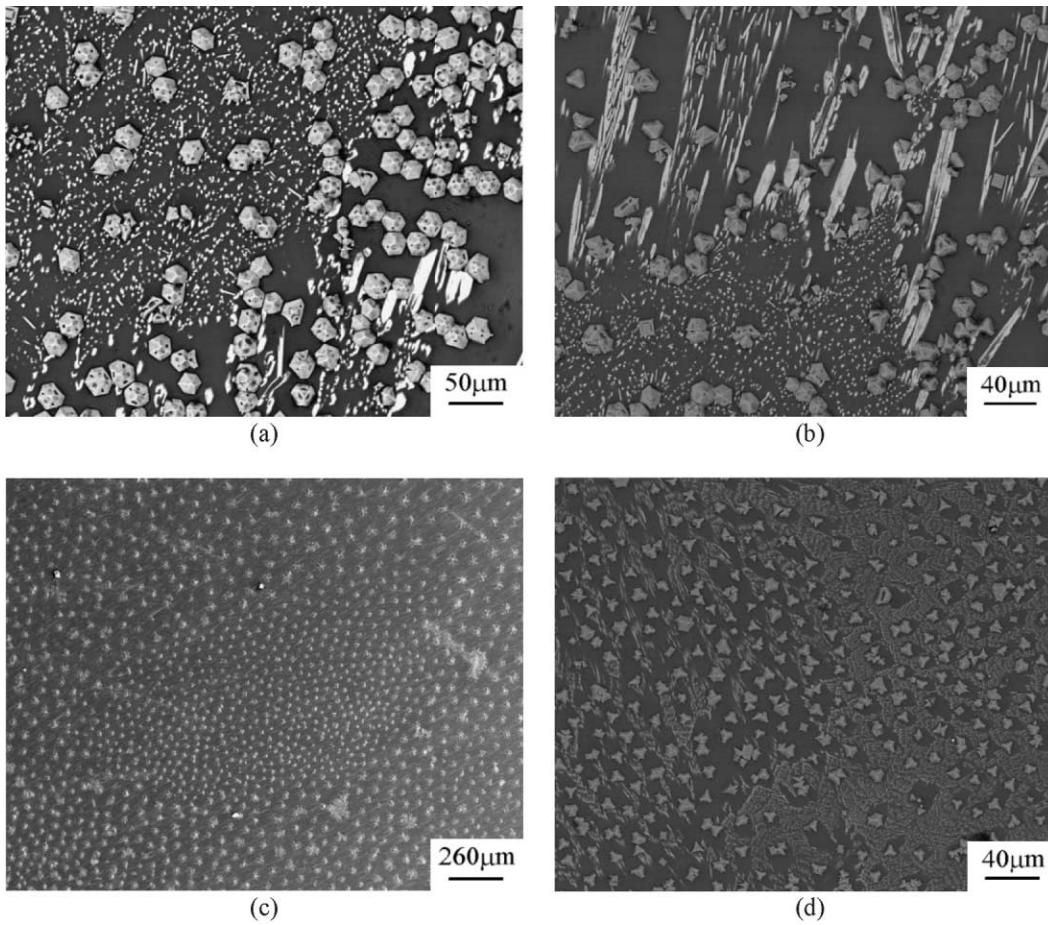

Fig. 8. The microstructures of 0.3% TiO$_2$ added glaze (PG4^g) treated by HTC 1 at 1180 °C (a) and (b) and HTC 2 at 1080 °C (c) and (d) confirming strong effect of titania on formation of both gahnite and willemite crystals.

instead of SrO, and 0.3% CoO as a colouring agent with a different Seger formula[7–9] produced only willemite by HTC 2 at 1080 °C. This seems to indicate that as well as higher ZnO and SiO_2 contents, SrO may accelerate gahnite formation with the addition of CoO. However, confirmation of this result needs further studies.

Figs. 7 and 8 emphasise the fact that titania is acting as a strong nucleating agent in zinc containing soft porcelain crystalline glazes for the formation of both willemite and gahnite crystals no matter what crystal growth temperature (1180 or 1080 °C) is used.

In order to see the overall effects of adding different colouring agents into the glaze on the general texture, the size and shape of crystals at micro scale, SEM studies were employed. Figs. 2, 4, 6 and 8 show that CoO, CuO, MnO_2 and TiO_2 produce different texture depending on heat treatment cycle. Although they all result in plate-like formation with higher crystal growth temperature (1180 °C) and spherical shape formation with lower crystal growth temperature (1080 °C) at macro-scale, at micro-scale both size and shapes of zinc crystals differ with different colouring agent content of the glaze (Figs. 2, 4, 6 and 8).

No matter what sort of colouring agent is used in the glaze, crystal growth temperature of 1180 °C caused either faceted or rod shaped willemite crystal occurrence [Figs. 2(a), 4(a) and (b), 6(a) and (b) and 8(a) and (b)]. When gahnite formation took place, independent of crystal growth temperature, the crystals were star-like shaped [Figs. 2(a)–(d), 4(a) and (b) and 8(a)–(d)].

The crystal growth temperature of 1080 °C results in different shapes of willemite crystals. Instead of rod-like shape, regularly growing, smaller sized willemite crystals formed surrounding star-like shaped gahnite crystals (except in the case of MnO_2 addition) [Figs. 2(c) and (d), 4(c) and (d), 6(c) and (d) and 8(c) and (d)] and producing spherical formation at macro scale.[6] The most interesting shape of willemite crystal is produced with the glaze composition containing MnO_2 [Fig. 6(c) and (d)].

In two similar studies frits based on the $ZnO–TiO_2–Al_2O_3–SiO_2$ system[14] and $ZnO–CaO–Al_2O_3–SiO_2$ system[15] have been previously developed and investigated to determine their crystallisation behaviour. It was reported that in the $ZnO–TiO_2–Al_2O_3–SiO_2$ system gahnite was formed through the progressive β-quartz solid solution, containing Al_2O_3 and ZnO, into gahnite and β-quartz on raising maximum heat treatment temperature.[14] Similarly, in the $ZnO–CaO–Al_2O_3–SiO_2$ system gahnite formation took place through the conversion of a solid solution containing a little zinc, with an anorthite crystalline structure.[15] Unlike the 17.5 ZnO–17.5 Al_2O_3–65 SiO_2 system with 4.5 wt.% TiO_2 addition,[14] the glazes of the present study contain 8.3% Al_2O_3, 57% SiO_2 and no TiO_2 as crystallisation agent and their gahnite formation was not based on the progressive

β-quartz solid solution conversion. Moreover, when compared to the 1.1 Na_2O–0.7 K_2O–7.7 CaO–0.7 MgO–14.6 ZnO–2.4 B_2O_3–15.3 Al_2O_3–57.5 SiO_2 system,[15] in this study CaO content (3.343 mol%) is well below 7.7 mol% although silica content is nearly the same. Consequently, it was thought that oxide composition of the glazes of this study is not suitable for anorthite formation. XRD, SEM and EDX analysis confirmed these results. It is assumed that direct crystallisation of gahnite and willemite occurred on cooling of glazes.

5. Conclusions

1. With CoO, CuO and TiO_2 incorporations into glaze, HTC 1 at 1180 °C produced willemite and gahnite, unlike MnO_2 addition resulting in only willemite formation in final crystallised glaze.
2. HTC 2 at 1080 °C produced willemite and gahnite with CoO and TiO_2 incorporations, whereas CuO and MnO_2 gave willemite formation only.
3. No matter what crystal growth temperature is used titania acts as a strong nucleating agent in zinc containing soft porcelain crystalline glazes for forming both willemite and gahnite crystals.
4. CoO, CuO, MnO_2 and TiO_2 produce different texture depending on HTC.
5. The most interesting shape of willemite crystal is produced with the glaze composition containing MnO_2.

References

1. Dinsdale, A., *Pottery Science*. John Wiley and Sons, Chichester, England, 1986 pp. 188–192.
2. Taylor, J. R. and Bull, A. C. *Ceramic Glaze Technology*, Pergamon Press, 1980, pp. 35, 41–44.
3. Rado, P., *An Introduction to the Technology of Pottery*. The Institute of Ceramics, Pergamon Press, 1988, p. 155.
4. Eppler, R. A. and Eppler, D. R., *Glazes and Glass Coatings*. The American Ceramic Society, Westerville, OH, 2000 p. 142.
5. Karasu, B. and Turan, S., Effect of cobalt oxide and copper oxide additions to zinc-containing soft porcelain glazes. *American Ceramic Society Bulletin*, 2001, **80**(9), 41–45.
6. Karasu, B., Macro-structural harmony of several colouring oxides in zinc containing soft porcelain crystal glazes. *The Journal of Ceramic Art, Science and Technology, Turkish Ceramic Society*, 2001, **14**, 33–35 (in Turkish).
7. Karasu, B., Çakı, M. and Turan, S., The development and characterisation of zinc crystal glazes used for amakusa-like soft porcelains. *The Journal of European Ceramic Society*, 2000, **20**(12), 2225–2231.

8. Karasu, B., Turan, S. and Çakı, M., The effect of heat treatment on the crystal development of zinc in the soft porcelain glazes. *10th International Metallurgy and Material Congress*, Istanbul, 24–28 May 2000, pp. 1457–1464.

9. Karasu, B. and Çakı, M., The application of zinc crystal glazes onto soft porcelains produced under oxidising atmosphere. *4th National Ceramic Congress*, 22–25 September 1998, Eskisehir, Turkey, pp. 287–293 (in Turkish).

10. Karasu, B., Turan, S. and Çakı, M., Scanning electron microscopy studies on the crystallisation effects of zinc in the soft porcelain glazes. *14th National Congress on Electron Microscopy with International Participation*, Bursa, Turkey, 1–4 September 1999, p. 77.

11. Karasu, B., Çakı, M. and Kiliç, A., The use of limonite in soft porcelain transparent and zinc crystalline glazes. *8th Material Symposium*, 26–28 April 2000, Denizli, Turkey, pp. 459–464 (in Turkish).

12. Karasu, B., Çakı, M. and Yesilbas, Y. G., The effect of albite wastes on glaze properties and microstructure of soft porcelain zinc crystal glazes. *Journal of the European Ceramic Society*, 2001, **21**(8), 1131–1138.

13. Karasu, B., Çakı, M. and Yesilbas, Y. G., The utilisation of albite triage waste in soft porcelain crystalline glazes. *10th International Metallurgy and Material Congress*, Istanbul, 24–28 May 2000, pp. 1465–1472 (in Turkish).

14. Escardino, A., Amoros, J. L., Gozalbo, A. and Orts, M. J., Crystallisation in $ZnO–TiO_2–Al_2O_3–SiO_2$ glass: process mechanism. *British Ceramic Transaction*, 1999, **98**(4), 196–199.

15. Escardino, A., Amoros, J. L., Gozalbo, A., Orts, M. J. and Moreno, A., Gahnite devitrification in ceramic frits: mechanism and process kinetics. *The Journal of American Ceramic Society*, 2000, **83**(12), 2938–2944.