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Journal of the European Ceramic Society 27 (2007) 1665–1670

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The influence of incorporation of ZnO-containing glazes on the properties of hard porcelains

D.U. Tulyaganov[a,b], S. Agathopoulos[a], H.R. Fernandes[a], J.M.F. Ferreira[a,*]

[a] *Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *Scientific Research Institute of Space Engineering, 700128 Tashkent, Uzbekistan*

Abstract

New ZnO-containing glazes were developed, characterized and incorporated (5–8 wt.%) in conventional hard porcelain formulation for producing tableware porcelains. The experimental results showed that glaze additives enhancement the densification of porcelains. Maturing temperature range was widened due to the dissolution of quartz crystals. The modified porcelains featured better mechanical properties and whiteness and lower shrinkage than conventional hard porcelains. Good matching of thermal properties between porcelain body and glaze resulted in successful glazing.

Keywords: Firing; Microstructure-final; Mechanical properties; Thermal shock resistance; Porcelain

1. Introduction

In the frame of increasing global commercial competition in the field of whitewares, the main efforts in the processing are currently directed towards the reduction of production costs without risking the productivity rates or product quality. Therefore, advanced technologies with better energy management or reduced pollution problems are welcome.

Porcelains are actually the fired product of ternary mixture of fine-grained clay (commonly kaolin), flux (usually feldspar) and filler (commonly quartz) raw materials.[1] Porcelains are usually classified according to the firing temperature. “Hard porcelains” have been usually fired at 1380–1460 °C, while “soft porcelains” at lower temperatures ∼1200 °C. Obviously, the production cost of soft porcelains is lower due to the lower energy consumption during firing. Moreover, the lower firing temperature allows their decoration with a wider spectrum of colours.

Beyond firing temperature, porcelains are also classified according to their use. Therefore, there are tableware, sanitary, chemical–technical and electrical porcelains, all made of quartz, feldspar and kaolin. Moreover, there are special types of porcelains, such as “frit porcelains” (made of kaolin, quartz and alkali rich frit), or “bone china” (made of kaolin, pegmatite and bone ash).[2,3] Partial or complete substitution of alumina for silica results in porcelains with remarkable mechanical durability, used primarily for technical aims.[4]

In the particular case of tableware porcelains, composition and processing parameters broadly affect their properties, such as densification, firing temperature range, mechanical strength, whiteness, and thermal shock resistance. This work investigated the influence of incorporation of brand-new ZnO-containing glazes in conventional hard porcelain formulation on porcelain properties, such as those referred to above. The study consisted of two sequential stages. The first one comprised the production and the characterization of several ZnO-containing glazes. In the second stage, these glazes were incorporated in batch of conventional hard porcelain. The resulting materials were characterized before and after sintering.

2. Experimental procedure

Table 1 presents the chemical composition of the raw materials used for the production of glazes and porcelains.

Fig. 1 outlines the production line. The production of the glazes comprised ball milling of coarse quartz, dolomite, scrap of glost-fired articles and bentonite until the residue on 56 μm sieve was 3.5–4.0%. Then, pegmatite, alumina and zinc oxide were loaded into the ball mill. Milling lasted until the residue on

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* Corresponding author. Tel.: +351 234 370242; fax: +351 234 425300.
E-mail address: jmf@cv.ua.pt (J.M.F. Ferreira).

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doi:10.1016/j.jeurceramsoc.2006.05.011

Table 1
Chemical compositions of the raw materials (wt.%)

Oxides	Ball clay	Kaolin	Bentonite	Pegmatite	Silica sand	Dolomite	Alumina	Zinc oxide
SiO_2	60.96	46.36	61.97	74.34	96.18	–	–	0.34
Al_2O_3	23.98	36.47	14.83	13.99	1.25	0.33	96.17	0.20
Fe_2O_3	0.67	0.60	0.12	0.21	0.16	0.16	–	0.06
TiO_2	1.18	–	0.24	0.15	–	0.10	0.10	–
CaO	0.84	1.26	4.29	1.54	0.70	30.87	0.84	0.60
MgO	0.58	0.44	2.99	0.28	–	21.00	0.14	0.40
SO_3	0.20	0.26	0.11	0.16	0.12	0.45	0.19	–
Na_2O	0.36	0.13	0.90	3.23	0.13	0.10	0.49	–
K_2O	2.25	0.40	1.80	5.85	1.08	0.10	0.10	–
ZnO	–	–	–	–	–	–	–	98.50
L.o.I.	10.67	14.18	12.73	0.60	0.67	46.68	2.12	–

56 μm sieve was 0.03–0.04%. Porcelains of the basic composition, denoted in this article as P-B, whose composition was 39% kaolin, 11% ball clay, 27% quartz, 17% feldspar from pegmatite, 1% alumina, and 5% scrap of biscuit-fired articles (wt.%), were similarly produced. Quartz, pegmatite, alumina and scrap of biscuit-fired articles were ball milled. Kaolin and ball clay were separately pre-washed (i.e. they were let to swelled in the water), and then combined with non-plastic ingredients until the residue on 63 μm sieve was 0.7–1.0%. Then, porcelain slurry was mixed and homogenized with the glazes in a blunger. During fabrication, the weight ratio between raw materials and water in the slurries of both glaze and porcelain was maintained as 55.5/44.5.

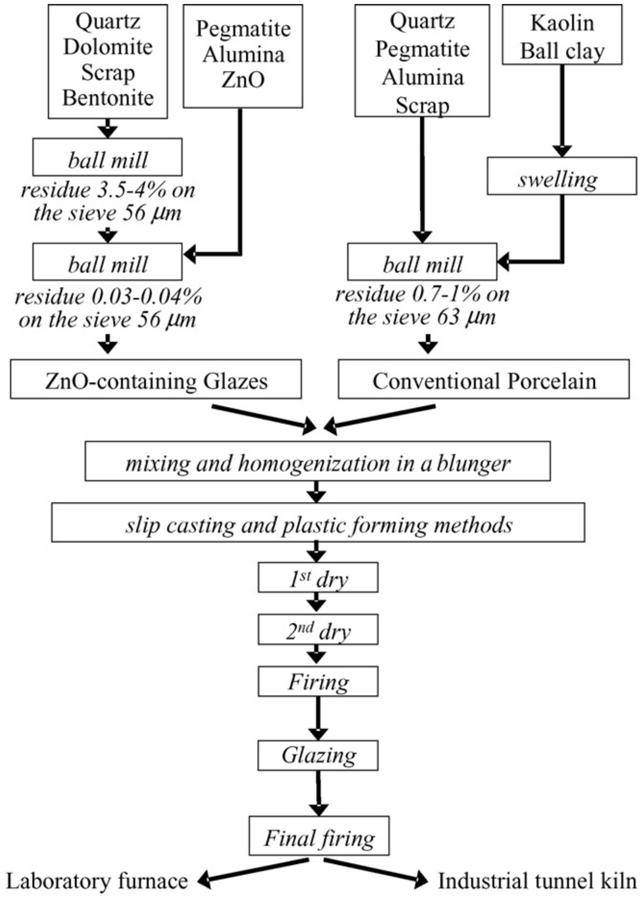

Fig. 1. Flow diagram of the production line.

Porcelain specimens were obtained by slip casting and plastic forming methods. Drying at 60 and 110 °C followed by first firing at 850–900 °C took place in a continuous industrial line of driers and a gas kiln furnace.

Waterfall technique was employed for glazing. Note that the same glaze was used for both coating (i.e. glazing) and incorporation in the porcelain bulk. For glazing, the density of the glaze suspensions varied between 1.35 and 1.44 g/cm^3. Glost firing was carried out either in an electric laboratory furnace at 1250, 1280, 1300 and 1320 °C (heating rate 3–5 K/min), or in an industrial tunnel kiln at 1320, 1350 and 1380 °C (total firing cycle 18–24 h; soaking time at the highest temperature ∼1 h).

Flexural strength (three-point bending) was measured in samples before and after firing (sample dimensions 5 mm × 5 mm × 50 mm). Water absorption was determined by the weight gain of fired samples after immersion in boiling water for 2 h. Whiteness of glazed and non-glazed samples was measured by a photometric method using a plate of $BaSO_4$ as reference. The fired glazed porcelains were subjected to tests of thermal shock resistance (i.e. determination of the maximum temperature difference which causes no cracks at the glaze after quenching into water of room temperature). Dilatometric studies were carried out with green porcelain bodies using a Netzsch (Germany) dilatometer at a heating rate of 5 K/min. The linear coefficient of thermal expansion (CTE) of porcelain and glaze bars, with dimensions 50 mm × 5 mm × 5 mm, was determined using a vertical quartz dilatometer DKV-4, (Russia) at a heating rate of 5 K/min. The linear shrinkage during sintering was calculated from the dimensions of the green and the resulting sintered samples. Density and refractive index of the glaze coatings were determined by the Appen's method.[5] X-ray diffraction analysis was used to determine and identify the crystalline phases formed (XRD, Philips X'PERT, PW 3040, Cu Kα radiation, the Netherlands). The microstructure of polished and etched samples (immersion in 5 vol.% HF solution for 2 min) was observed using a scanning electron microscope equipped with elemental analysis system (SEM/EDS, Jeol 5800 LV, Japan).

Table 2
Compositions of glaze batches tested (wt.%)

Oxides	G-1	G-2	G-3	G-4	G-5	G-B
Feldspar from pegmatite	35	33	33	35	33	36
Dolomite	20	–	21	19	21	14
Quartz	30	32	32	30	32	27
Bentonite	3	3	3	4	3	–
Zinc oxide	2	4	4	6	8	–
Glost scrap	10	7	7	5	–	16
Kaolin	–	–	–	–	–	7
Alumina	–	–	–	1	3	–
Lime	–	21	–	–	–	–

Table 3
Chemical compositions of the glazes (mol%)

Oxides	G-1	G-2	G-3	G-4	G-5	G-B	Bristol glazes
SiO_2	69.86	70.04	68.54	67.47	64.00	73.22	68.93–71.43
Al_2O_3	6.66	6.10	5.99	6.69	6.90	9.53	8.16–11.65
Fe_2O_3	0.07	0.06	0.07	0.07	0.05	0.11	–
TiO_2	0.08	0.08	0.08	0.08	0.08	0.12	–
CaO	9.33	15.26	9.42	8.71	9.43	6.63	5.83–8.16
MgO	8.09	0.64	8.23	7.51	8.18	5.48	0–4.08
SO_3	0.12	0.13	0.06	0.07	0.19	0.19	–
Na_2O	1.87	1.84	1.87	1.89	1.89	2.10	2.04–3.88
K_2O	2.18	2.42	2.31	2.40	2.20	2.61	2.04–3.96
ZnO	1.74	3.43	3.43	5.11	6.90	–	4.08–5.94

3. Results and discussion

3.1. Glazes: composition design and properties

In glazes, ZnO generally resembles alkaline earth oxides. However, the dissolution rate of ZnO is somewhat faster and occurs at slightly lower temperatures than alkaline earth oxides.[6] With regards to the most important demanded properties, the new ZnO glazes had to ensure transparency and maturing performance within the 1250–1300 °C range. According to the aforementioned demands, the compositions of the glazes were designed as follows. Starting from the conventional composition (denoted as G-B), which is used for glazing hard porcelains, appropriate amounts of ZnO were added in order to facilitate fusion of other oxides without creating any opacity effect. Five different formulations were prepared and tested, whose compositions in oxide form and raw materials are summarized in Tables 2 and 3.

Table 5
Porcelain batch formulations (wt.%)

Glaze	Porcelain				
	P-1	P-2	P-3	P-4	P-5
Type	G-1	G-2	G-3	G-4	G-5
wt.% with respect to 100% P-B[a]	8	8	7	5	7

[a] P-B: kaolin 39%, ball clay 11%, feldspar from pegmatite 17%, quartz 27%, alumina 1%, 5% biscuit-fired scrap.

Table 3 also allows the comparison between the chemical composition of the new glazes and conventional Bristol glazes, which contain 4–6 mol% ZnO. Hence, the new glazes contain lower amount of alumina and alkali oxides and higher amount of alkaline earth oxides than Bristol glazes. Bristol glazes are classified as soft porcelain glazes[6,7] and recommended for cone numbers 7–10.[5,6]

The properties of the new glazes measured after firing between 1250 and 1350 °C are summarized in Table 4.

3.2. Porcelains

Table 5 shows the batch formulations and Table 6 summarizes the Seger formulae of the porcelain compositions, denoted as P-1, P-2, P-3, P-4 and P-5 (see also Fig. 1). According to Avgustinik,[2] the new compositions can be referred to as soft porcelains because of their specific ratio of alkaline oxides/alumina/silica.

The experimental results showed that the addition of the investigated glazes in P-B formulation resulted in lowering of plasticity of green body. However, no significant alterations were recorded in viscosity and thixotropic properties of slips.

The incorporation of the ZnO containing glazes caused lowering of the temperature of densification onset. The plots of Fig. 2 allow the comparison between the linear dilatation and shrinkage of P-3 porcelains and the basic formulation P-B over firing temperature. Evidently, in the case of P-3 porcelain, shrinkage starts at 970 °C and ends at 1280 °C, whereas the shrinking range of P-B was between 1040 and 1330 °C.[8] Consequently, these curves point out three important features of the modified porcelains: (a) The body starts to shrink at lower temperature (i.e. 970 °C versus 1040 °C), (b) increasing densification occurs at lower temperatures (i.e. P-3 exhibits steeper slope in the shrinking curve than P-B), and (c) the maturating temperature range of the modified porcelain is almost double with respect to that corre-

Table 4
Properties of the ZnO-containing glazes

Property	Glaze				
	G-1	G-2	G-3	G-4	G-5
Maturation range (°C)	1300–1350	1280–1350	1280–1330	1280–1320	1250–1300
CTE, α ($\times 10^6$ K^{-1}) (20–400 °C)	4.18	4.20	4.22	4.32	4.23
Glass transition temperature (°C)	625	–	640	–	630
Dilatometric softening point (°C)	740	–	765	–	750
Density (g/cm^3)	2.545	2.565	2.560	2.582	2.616
Refractive index	1.521	1.529	1.519	1.523	1.530

Table 6
Seger formulae of the investigated porcelain compositions

Oxides	Porcelain					
	P-1	P-2	P-3	P-4	P-5	P-B
Na_2O	0.20	0.19	0.20	0.20	0.19	0.24
K_2O	0.28	0.28	0.27	0.29	0.26	0.35
CaO	0.31	0.38	0.30	0.29	0.30	0.27
MgO	0.19	0.11	0.19	0.17	0.18	0.14
ZnO	0.02	0.04	0.04	0.05	0.07	–
Al_2O_3	2.62	2.62	2.64	2.84	2.56	3.58
Fe_2O_3	0.03	0.03	0.03	0.03	0.03	0.04
SiO_2	12.36	12.39	12.43	13.19	11.95	16.20
TiO_2	0.07	0.07	0.07	0.08	0.07	0.11

sponding to conventional porcelain P-B. With regards to feature (c), maturing range is generally defined as the range of temperature and time within which ceramics can be safely fired and yield specific and demanded properties. According to Fig. 2, maturing range, which is actually the temperature range of constant maximum shrinkage values, is approximately between 1280 and 1380 °C for P-3, whereas for P-B this range is about 40–50 K, approximately between 1330 and 1380 °C. Feature (c) is a very important advantage because the big difference of temperatures along industrial kilns can result in undesirable distortion effect.

Most probably, the fine particles of fluxes incorporated into the glazes (Fig. 1, Tables 2 and 3) lowered the viscosity and increased the dissolution capability of the melt at the early stages of densification. Usually, excess of fluxes enhances densification[9–11] but narrows maturing range. Among the factors, which can affect the maturation range of whitewares, chemical composition is certainly of major importance.[12,13] Careful study of the microstructure and the crystalline state of the fully dense porcelains can provide an insight about the influence of the chemical species on the mechanism and the kinetics during porcelain production and probably interpret the increasing resistance against deformation during firing.

X-ray analysis (not shown) revealed that quartz and mullite were formed during firing. This result agrees fairly well with SEM observations and EDS analyses, which confirmed that the microstructure of the porcelain body comprises secondary mul-

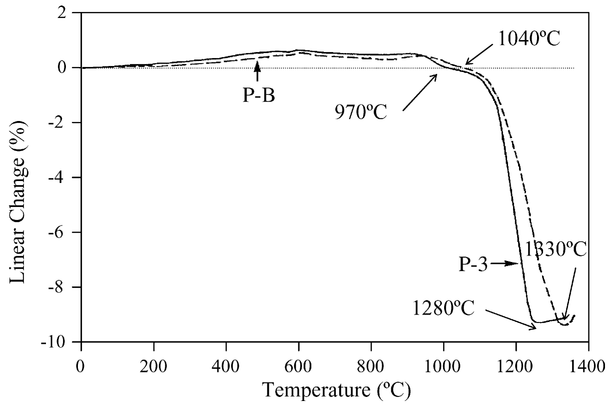

Fig. 2. Comparison of the dilatometric behaviour of porcelain samples made of P-3 and P-B formulations over firing temperature.

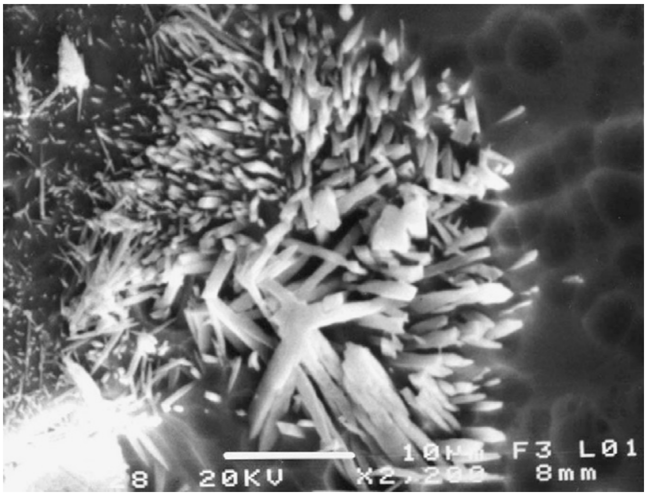

Fig. 3. Secondary mullite needles formed in the P-3 porcelain fired in an industrial kiln furnace at 1300–1320 °C (the bar corresponds to 10 μm).

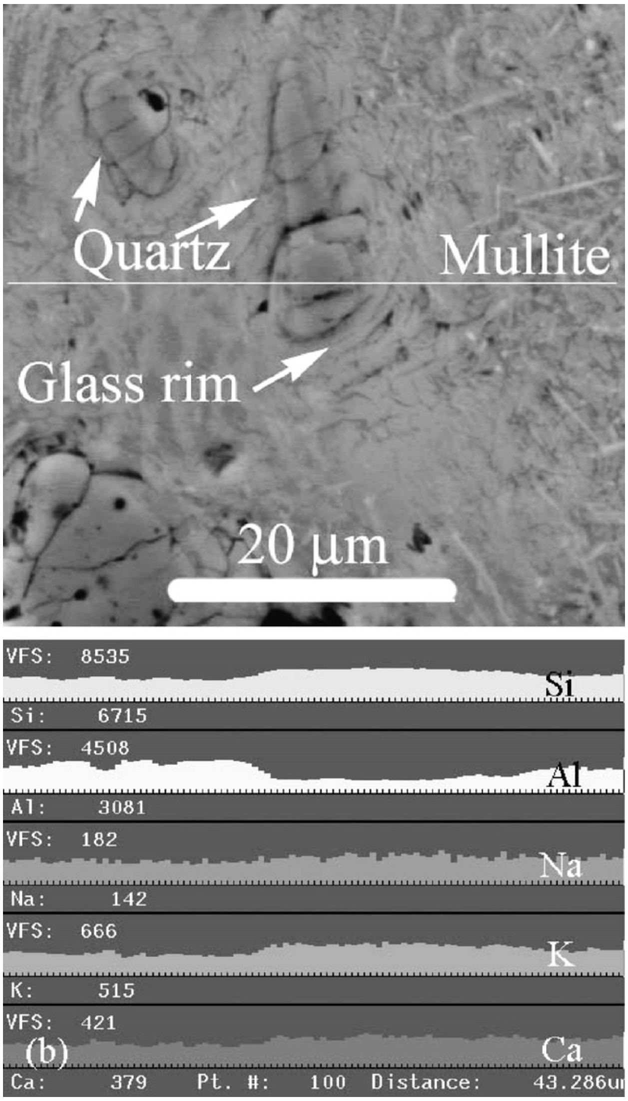

Fig. 4. Typical microstructure of porcelain body in the case of P-3 formulation fired in industrial kiln furnace at 1300–1320 °C (a), and the elemental line scan analysis along the line shown in (a) for Si, Al, Na, K and Ca (b).

Table 7
Properties of porcelains

Property	Porcelain					
	P-1	P-2	P-3	P-4	P-5	P-B
Final firing temperature (°C)	1280	1280	1280	1300	1260	1350
Water absorption (%)	0.03	0.04	0.04	0.05	0.02	0.03
Shrinkage (%)						
Drying shrinkage	3.68	3.70	3.54	3.30	3.45	3.76
Total shrinkage	12.20	12.00	12.14	11.90	12.10	12.62
Bending strength (MPa)						
After drying at 110 °C	3.42	3.40	3.48	3.38	3.54	3.21
After biscuit firing at 900 °C	11.15	11.24	11.30	10.82	11.32	7.68
After final firing	83.8	83.5	84.0	83.6	85.5	80.5
Whiteness (%)						
Non-glazed items	70	70	70	69	70	58
Glazed items	64	64	64	62	65	57
CTE, α ($\times 10^6$ K^{-1}) (20–400 °C)	4.72	–	4.81	–	4.75	–
Thermal shock resistance (°C)	240	240	240	230	230	210

lite, quartz, and liquid phase. Fig. 3 shows characteristic needle shaped crystals of secondary mullite with a length of 10 µm formed in the fired porcelains. Mullite crystals homogeneously formed in the bulk of porcelain (Fig. 4a), evidently resulting in high densification and providing high resistance against distortion during firing. Primary mullite crystals might be also embedded in the liquid phase but their tiny size did not allow their recognition at this magnification.

Quartz crystals were also clearly observed (Fig. 4a). The elemental analysis (measured by EDS, in wt.%) inside quartz crystals was 0.47 Na_2O, 0.15 K_2O, 0.06 CaO, 0.16 Fe_2O_3, 0.50 Al_2O_3, 0.02 TiO_2, and 98.64 SiO_2. A silica rich glassy rim encapsulated quartz crystals, having a composition of 0.84 Na_2O, 3.25 K_2O, 1.02 CaO, 9.66 Al_2O_3, 85.24 SiO_2 (wt.%). Careful observation reveals also cracks in the quartz particles and the glassy rim around them (Fig. 4a), evidencing silica dissolution process. According also to the line scan of elemental analysis shown in Fig. 4b, the observed tiny cracks should result from the diffusion of Na^+, K^+ and Al^{3+} ions into the crystal lattice of quartz.

The glassy phase found at the region of feldspar relicts (i.e. the area of mullite in Fig. 4a) had a composition 1.05 Na_2O, 4.09 K_2O, 1.83 CaO, 0.81 Fe_2O_3, 12.74 Al_2O_3, 0.37 TiO_2, 79.11 SiO_2 (wt.%). Iqbal and Lee[14] and Klykova et al.[15] have reported the presence of heterogeneous glasses with different proportion of oxides in fired porcelains.

Consequently, the early melting of feldspar should result in formation of a low viscous liquid phase. On the other hand, the tested glazes featured sufficient dissolution of silica. The release of silica in the melt resulted in increasing viscosity of the liquid phase. The dissolution of silica and its effect on increasing liquid viscosity are certainly the most important characteristics of the tested glazes because they provide stability against distortion during firing and result in widening of maturation range.

The properties of the modified porcelains are summarized in Table 7. ZnO glazes generally improve the mechanical properties of porcelain and decrease sintering shrinkage. Furthermore, the modified porcelains exhibit significantly higher whiteness comparing to the white ordinary porcelains. The linear coefficient of thermal expansion (CTE) of the porcelain body is slightly higher than the CTE of glazes. This difference ensures the avoidance of tensile stresses on the glaze layer.

Accordingly, the added ZnO-containing glazes should be responsible for the improved firing characteristics of the model porcelain formulations studied in the present work. Evidently, the addition of ZnO-containing glazes favours the early formation and distribution of glassy phase throughout the entire porcelain body, resulting in highly homogeneous and dense structures. Moreover, it is known that improving the macroscopic homogeneity of glass phase during firing process, pyroplastic deformation should decrease. Furthermore, with the diffusion of alkalis from feldspar to clay relicts, faster densification of metakaolinite, and mullite formation will also contribute to good sinterability and development of dense bodies at lower temperatures.[16]

According to the values of the properties shown in Table 7 (also in conjunction with Table 4), P-3 porcelain should be assumed as the best composition among the investigated ones. Therefore, more than 500 pieces of P-3 porcelain were produced at a semi industrial scale and fired in a tunnel kiln furnace at temperatures of 1300–1320 °C. The produced items were of high quality with regards to their mechanical properties, whiteness and thermal shock resistance, in comparison with similar articles fabricated with conventional hard porcelain and fired within the 1350–1380 °C range.

4. Conclusions

This work showed that the appropriate addition of ZnO-containing glaze in porcelain batch formulation can result in faster densification and decreasing of firing temperature, wider maturing range, improved mechanical properties, lower sintering shrinkage values, higher whiteness, and higher thermal shock resistance.

The dissolution of silica and its effect on increasing liquid viscosity are certainly the most important characteristics of the tested glazes because they provide stability against distortion during firing and result in widening of maturation range.

The good properties of the new model compositions are further reflected at the fact that there was no significant influence of firing conditions on the properties whether the porcelains were fired in a laboratory furnace or in an industrial kiln.

Acknowledgements

The financial support of CICECO and the FCT-Portugal are gratefully acknowledged.

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