Microstructural evolution of fast firing soft porcelain

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The present work deals with the study of the microstructural evolution of fast firing soft porcelains. Soft porcelains are those sintered at low temperatures (bellow 1350°C), and the thermal treatment used was similar to that of industrial products, with 10 minutes of sintering time. As raw materials kaolin, sodium feldspar, potash feldspar and talc, all except the former used as melting oxides in order to form eutectics at low temperatures. The compositions were formulated according the mixture design technique, four factors at three levels, with coordinate transformation by independent variables. The minerals were characterized to determine its chemical and mineral compositions and particle size distribution. Nine compositions were formulated, and the analyses were carried out for the thermal behavior (differential scanning calorimetry, DSC) and evolution of the crystalline phases with temperature (X ray diffraction, XRD). The results were interpreted by analysis of variance (ANOVA) and presented as response surfaces. There was glass formation due the effect of both feldspars (orthoclase and albite). Talc has influenced the porcelain densification. The main crystalline phases obtained were cordierite and cristobalite, due the presence of talc, and mullite and quartz, due the initial content of kaolin.

Keywords: soft porcelains; microstructural evolution; fast firing; mixture design

1. Introduction

Temperature, time and atmosphere in the kiln affect chemical reactions and microstructure development in porcelains, being important in their fired properties. Fast firing of porcelain bodies has gained wide recognition and application in the whiteware industry, reducing production costs by efficient use of energy in the firing process. The fast firing of porcelains requires knowledge of chemical reactions occurring during the process and of microstructural development [1,2].

The sequence of chemical reactions during the firing of porcelain bodies depends on the type of raw materials in the body [3-5]. For a typical clay-quartz-feldspar system the basic reaction steps can be outlined as follows: The crystal structure of kaolin contains hydroxyl groups and the dehydroxylation of these groups forming metakaolin occurs at ~550°C [6]. The dehydroxylation process is an endothermic process that is accompanied by a reorganization of octahedrally coordinated aluminum in kaolinite to a most tetrahedrally coordinated aluminum in metakaolin [3,6,7].

The α- to β-quartz inversion occurs at 573°C; because of the relatively great flexibility of the packed particle network, the quartz inversion is of little consequence during the heating cycle, but extremely important at the cooling cycle. High temperature phases of mixed-alkali feldspars form within 700°C to 1000°C; the formation temperature apparently is dependent on the sodium:potassium ratio [6,8]. Metakaolin transforms to a spinel-type structure and amorphous free silica at ~950°C-1000°C; a γ-alumina-type phase and an aluminosilicate spinel are the predicted reaction products. The silica reaction product is amorphous [6]. The exact structure of the spinel

phase continues to be controversial, and the literature presents evidence regarding the existence of either phase [3,6,9].

The amorphous silica liberated during the metakaolin decomposition is highly reactive, assisting eutectic melting formation at ~990°C. A eutectic melt of potash feldspar with silica starts appearing at ~990°C; the eutectic temperature is dependent on the type of feldspar: for potash feldspar the eutectic melt forms at ~990°C; for soda feldspar it forms at ~1050°C according to the specific phase diagram [6,9]. The lower liquid formation temperature in the potash feldspar system reduces the firing temperature. With the increasing temperature porosity is eliminated via viscous-phase sintering. Porcelains generally contain two different mullite evolution paths: primary and secondary [9]; the formation of these two different types is controversial, but the spinel phase, being a nonequilibrium unstable phase certainly forms mullite above 1075°C. On the atomic level mullite formation can start at 980°C, but homogeneity on the nanometer scale can delay mullite formation to temperatures as high as 1300°C [4-6,9,10].

At ~1200°C the melt becomes saturated with silica-quartz dissolution ends, and quartz-to-cristobalite transformation begins. Above 1200°C mullite crystals grow as prismatic crystals into the remains of the feldspar grains (feldspar relicts). As the body starts to cool pyroplastic deformation and relaxation within the glass phase prevent the development of residual stresses until the glass transition temperature is reached. As the body cools below the glass transition temperature residual stresses are developed because of thermal expansion mismatch between the glass and the included crystalline phase: mullite and quartz and alumina and cristobalite [6,8,11-17].

Cooling through the quartz inversion (573°C) results in quartz particle volume decrease of 2%, which can produce sufficient strain to cause cracking of the glassy matrix and the quartz grains. The cracking severity is dictated by the quartz particle size and the cooling rate. The effect of free quartz on the porcelain strength is object of several studies. Finally, the β- to α-cristobalite inversion at 225°C-250°C is similar to the quartz inversion, but it produces a larger volumetric change (~5%) with a higher activation energy barrier, and the transformation is less severe than that of quartz [6].

In this work fast firing soft porcelain was studied using mixture design in order to determine its microstructural evolution. Kaolin, talc, potash and sodium feldspars were used as factors in a modified mixture design transformed in a 2^3 factorial design with a central point using w_i independent factors [1] resulting in a set of nine compositions.

2. Materials and Methods

Kaolin, potash and sodium feldspars and talc were used as raw materials, table 1. The raw materials were mixed (according the mixture design compositions) in a high energy jar mill (10s, 250g batches). The particle size distribution was controlled by laser diffraction (CILAS 1064, 60s reading time). The thermal behavior was determined by differential scanning calorimetry (DSC, NETZSCH 409, air atmosphere, alumina crucibles, 10°C/min heating time, 20°C-1250°C-400°C). In sequence the compositions were granulated with 6% water and pressed into cylindrical samples (34MPa) and dried (100°C, 24h). Finally, the samples were heat treated at 900°C, 1100°C and 1200°C during heating and at 750°C during cooling – the temperatures were chosen after DSC analysis – at 10°C/min heating rate. The soaking time was 10min at each temperature and the samples were quenched in water (20°C). After heat treatment the samples were analyzed by XRD (Philips PW 1830, CuKα, 0.1°/s, 0°-70°).

Table 1. Chemical, phase and particle size characteristics of the raw materials

raw material	chemical composition [w/w%]						phase composition	D_{50} [μm]
	SiO_2	Al_2O_3	K_2O	Na_2O	MgO	LOI		
kaolin	44.2	40.2	0.4	0.4	0.1	14.0	kaolinite, quartz	2.9
K-feldspar	66.6	18.1	11.5	3.0	0.0	0.3	orthoclase, albite, quartz	7.5
Na-feldspar	71.5	18.0	0.6	8.9	0.1	0.5	albite, quartz	5.2

talc	62.0	0.0	0.0	0.0	32.3	5.0	talc, quartz	10.0

3. Results and Discussion

Because lack of space only the 1200°C heat treatment will be shown in this article. Table 2 shows the mixture design and the crystalline phases formed at 1200°C heat treatment in all compositions. Figure 1 shows the XRD patterns for 1200°C heating treatment. The mixture design was modified and transformed in a 2^3 factorial design with a central point using w_i independent factors [1], resulting in a set of nine compositions. The main objective was the optimization of the design. The analysis of variance (ANOVA) was carried out with the independent factors (w_i) and the surface response analysis was carried out with the dependent (x_i). The dependent variables were transformed in independent variables (and vice-versa) by means of a transformation procedure (not shown).

Table 2. Microstructure evolution at 1200°C heat treatment

composition	quartz[1]	K-feldspar	Na-feldspar	talc	w_1	w_2	w_3	1.200°C[2]
F1	34.3	36.8	25.3	3.6	0.8001	-0.9554	-0.9777	Q,Mu,Cr
F2	44.8	26.3	25.3	3.6	-0.9452	-0.9604	-0.9826	Q,Mu
F3	25.4	35.0	36.0	3.6	0.8956	0.9636	-0.9822	Q,Mu,Cr
F4	35.9	24.5	36.0	3.6	-0.8585	0.9604	-0.986	Q,Mu,Cr
F5	28.0	35.6	24.0	12.4	0.8585	-0.9604	0.986	Q,Mu
F6	38.6	25.0	24.0	12.4	-0.8909	-0.9602	0.9843	Q,Mu
F7	19.2	33.7	34.7	12.4	0.9452	0.9604	0.9826	Q
F8	29.7	23.2	34.7	12.4	-0.7954	0.9588	0.9798	Q,Mu,Co
F9	32.0	30.0	30.0	8.0	0	0	0	Q,Mu,Co

[1]composition in w/w %;
[2]Q=quartz; Mu=mullite; Cr=cristobalite; Co=cordierite.

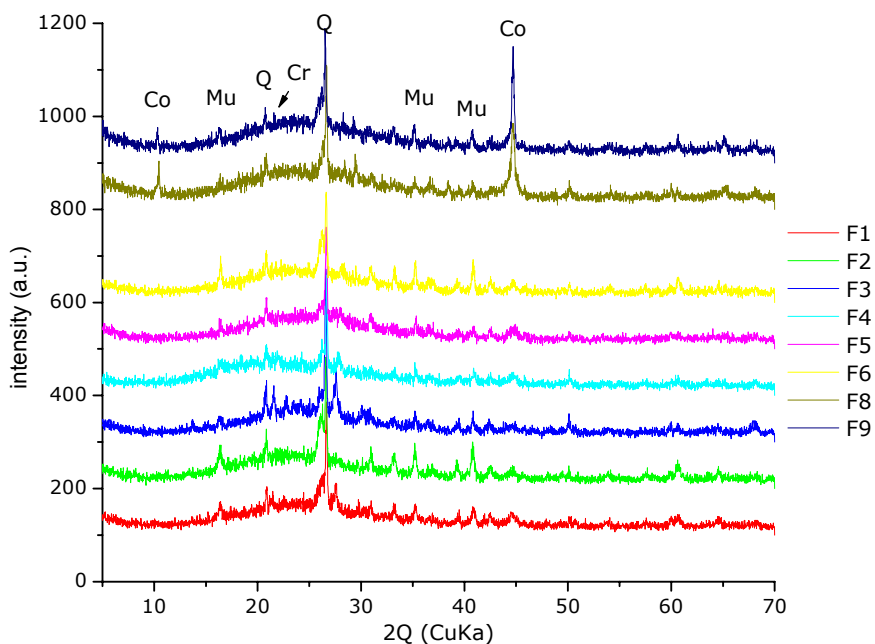At 1200°C there is a better development of mullite, cordierite and cristobalite, figure 1.

Figure 1. XRD patterns of the microstructure evolution at 1200°C heat treatment

Some studies [6,12] show well developed crystallization is hard porcelains, mainly mullite (primary and secondary) and cristobalite; but hard porcelains are fired at ~1400°C during 2h soaking times, and this study was conducted at 1200°C during 10min. Cordierite formation at low temperatures (~1200°C) was studied by Dyatlova et al. [18]. Table 3 shows the ANOVA for the 1200°C heat treatment.

Table 3. ANOVA for the microstructural evolution at 1200°C heat treatment

analysis	SS	dF	MS	F	p	R²
model	5.50	3	1.83	1.51	0.32	0.48
residue	6.06	5	1.21			
total	11.56					

The values correspond to the encoded phases developed at 1200°C. The significant level is low (p~68%) and the model adjustment is not good (R²=0.48), showing the great variance of phase development during heat treatment. The response surface curve are shown in figures 2.
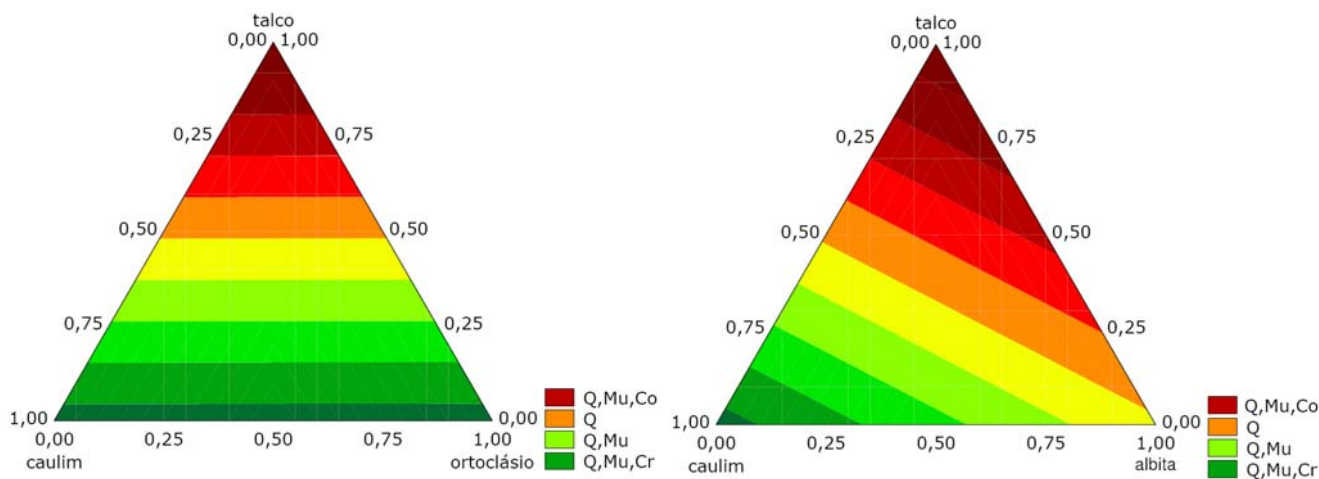

Figure 2. Response surface curve for the microstructure evolution at 1200°C

Analyzing the response surface curves (figures 2 and 3) there is a kaolin influence on quartz, mullite and cristobalite formation due the kaolin chemical composition. The cordierite formation is due the talc presence. There is isolated quartz in intermediary phases, without any other phase formation, an indication of glass phase presence where the other oxides are dissolved (Na_2O and K_2O).

This is a nonequilibrium system and there is no sufficient time to develop all possible thermodynamic stable phases. There are decompositions of the mineral phases present at the raw materials and glass formation with low viscosity; probably there are phase dissolution in the glass matrix and phase precipitation from the glass matrix. Magnesia, potash and soda must form the glass matrix because talc and nepheline additions in porcelain bodies show that a little magnesia content cause mullite dissolution and an increase in the glassy phase [19].

Kaolin dehydroxylates at ~550°C forming metakaolin; the metakaolin forms a nonequilibrium spinel phase liberating amorphous silica beginning at 950°C. At the same time the feldspars react with the amorphous silica forming eutectics according the type of feldspar [8]. Above 1000°C the densification process begins by liquid phase sintering followed by spinel transformation into mullite. Finally, at 1200°C the remaining quartz is transformed into cristobalite and there is glass formation and mullite growth (if the heat treatment is sufficient).

Also, the low viscosity liquid phase catalyses mullite, quartz and cristobalite formation, what apparently is happening in the system studied in this work: the soda, potash and magnesia

probably form a low viscosity liquid glass that increase phase formation. The low viscosity improves mullite formation because there is more alumina dissolution in silica glasses what controls the mullite growth rate [6].

The devitrification of aluminosilicate glasses rich in soda and magnesia is similar to the crystallization of mullite and cordierite ceramics [18,20]. The presence of structural groups in the melted glass similar to the sintered phase (cordierite) activates the sintering process and the liquid phase can form other crystalline phases (secondary mullite). Dyatlova et al. [8] show that cordierite is formed beginning at 1050°C in some cases.

Finally, the potassium and sodium oxides form the glass phase in this study. They are show in the response surface graphs as orthoclase and albite, respectively. At 1200°C apparently there is a low viscosity liquid glass due the well developed crystalline phases formed and due the formation of mullite, cordierite and mainly cristobalite. Secondary mullite and low temperature cordierite form from alkaline glasses. Cristobalite can be formed as a devitrification product from alkaline glasses when the liquid is saturated with silica [6,8,11,12,16].

4. Conclusion

In the kaolin-orthoclase-albite-talc porcelain system at 1200°C mullite and cordierite are consolidated as crystalline phases; quartz remains as an isolated phase and begins the cristobalite precipitation from the glass phase. There is a strong influence of kaolin on mullite and cristobalite formation and of talc on cordierite formation. At intermediate compositions of kaolin, both feldspars ant talc the major phase is quartz, probably dissolved in the glass phase.

The mixture design is a strong and efficient tool to determine the microstructure evolution of ceramic systems, because the design can show the statistically significant effects between the studied variables and their effects on the ceramic system, helping the researcher to avoid misinterpretation of variables and effect correlations.

5. References

[1] Bernardin, A.M. Evolução microestrutural de porcelanas brandas de queima rápia. Florianópolis: Tese de doutorado, Departamento de Engenharia Química, Universidade Federal de Santa Catarina, 2006.
[2] Maity, S.; Sarkar, B.K. Ceramics International 24 (1998) 259-264.
[3] Chaudhuri, S.P.; Sarkar, P. Journal of the European Ceramic Society 15 (1995) 1031-1035.
[4] Lee, W.E.; Iqbal, Y. Journal of the European Ceramic Society 21 (2001) 2583-2586.
[5] Kong, L.B.; Zhang, T.S.; Ma, J.; Boey, F. Journal of Alloys and Compounds 359 (2003) 292-299.
[6] Carty, W.M.; Senapati, U. Journal of the American Ceramic Society 81 (1) (1998) 3-20.
[7] Nosbusch, H; Mitchell, I.V. Clay-based materials for the ceramics industry. London: Elsevier Applied Science, 1988.
[8] Das, S.K.; Dana, K. Thermochimica Acta 406 (1-2) (2003) 199-206.
[9] Chaudhuri, S.P.; Sarkar, P. Journal of the European Ceramic Society 16 (1996) 851-855.
[10] Mizuno, M. Journal of the American Ceramic Society 74 (12) (1991) 3017-3022.
[11] Iqbal, Y.; Lee, W.E. Journal of the American Ceramic Society 82 (12) (1999) 3584-3674.
[12] Iqbal, Y.; Lee, W.E. Journal of the American Ceramic Society 83 (12) (2000) 3121-3127.
[13] Khater, G.A. Ceramics International 27 (2001) 661-668.
[14] Ong, J.L.; Farley, D.W.; Norling, B.K. Dental Materials 16 (2000) 20-25.
[15] Matteucci, F.; Dondi et al., M.; Gaurini, G. Ceramics International 28 (2002) 873-880.
[16] Tucci, A.; Esposito, L.; Rastelli, E.; Palmonari, C.; Rambaldi, E. Journal of the European Ceramic Society 24 (1) (2004) 83-92.
[17] Mustafa, E.; Khalil, N.; Gamal, A. Ceramics International 28 (2002) 663-667.

[18] Dyatlova, E.M.; Minenkova, G.Ya.; Kolontaeva, T.V. Glass and Ceramics 57 (11-12) (2000) 427-430.

[19] Mukhopadhyay, T.K.; Das, M.; Ghosh, S.; Chakrabarti, S.; Ghatak, S. Ceramics International 29 (2003) 587-597.

[20] Pavlov, V.F.; Nemchenok, Z.O.; Mitrokhin, V.S. Glass and Ceramics 35 (1) (1978) 31-36.