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NON-CONTACT DILATOMETRY OF HARD AND SOFT PORCELAIN COMPOSITIONS

Relationship between thermal expansion behaviour and microstructure

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Two different porcelain compositions were studied: a soft and a hard one. DTA, optical non-contact dilatometry and DSC were used to evaluate the thermal behaviour of the porcelain compositions with the aim to master the suitable thermal cycle for each. Results were interpreted on the basis of mineralogy and microstructure: the amorphous phase, abundant in soft porcelain, plays an important role on thermal expansion ($8\cdot10^{-6}$ K^{-1} for soft and $6\cdot10^{-6}$ K^{-1} for hard at 1000°C). Thermal expansion behaviour as function of firing time was also studied. Non-contact dilatometry characterisation of porcelain bodies enable to master the suitable thermal cycle for the sintering.

Keywords: *microstructure, soaking time, soft and hard porcelain, thermal cycle, thermal expansion*

Introduction

Porcelain is a glass-ceramic material with a range of applications including white ware, table ware, electrical porcelain, dental porcelain and porcelain enamel. Some of these applications involve the material in use on deformations, spalling, flaking or weakening due to their exposition at higher temperatures [1]. Thermal behaviour of porcelain materials has been for long subject of particular attention. In conventional bodies, it has been demonstrated that thermal expansion can be reduced by controlling the amount of amorphous phase in the final product [2].

If the expansion of the porcelain is measuring during reheating, the porcelain expands normally until it is close to the glass transition temperature, at which point sufficient thermal energy is available for the molecules to rearrange themselves into more dense structure having smaller volume. This densification process with porcelain thermal expansion, resulting in an overall effective expansion [2–6]. Regarding the composition and the thermal cycle of porcelain, the measure of the thermal expansion can be used to evaluate the quartz dissolution during sintering or the crystallization of new phases. In their study of thermal dimensional behaviour of dental porcelain ceramics [7], the reduction of the amorphous phase, the enhancing of the crystallization and the conversion of the silicate to cristobalite were found to be glass-dependent. The replacement of feldspar by crystallizing glasses has been found to be positive for enhancing crystallization of mullite, cordierite and cristobalite in porcelain processing [2, 6]. This has as effect on eliminating the discontinuity in the thermal expansion curve at around 537°C.

Guiseppe *et al*. [7] showed the influence of crystal phase amount and the nature of the matrix on the thermal expansion and glass-transition of dental porcelain: feldspathic matrix with higher alumina oxide have been found to expand less compared to silicate matrix phase with leucite as crystallizing phase being twice ($13.72\cdot10^{-6}$ K^{-1}) the value of feldspathic matrix phase ($6.7\cdot10^{-6}$ K^{-1}) with respectively 454 and 603°C the temperature of the transition of quartz. Maiti and Kumar [6] showed that the thermal expansion behaviour of porcelain bodies decrease significantly with the replacement of feldspar by crystallizing glasses. Moreover, it is well known that the addition of K_2O in the crystallizing glasses caused an increase in the thermal expansion.

The decrease in thermal expansion bring significant changes in the firing properties namely firing shrinkage, bulk density, and percent water absorption as feldspar was progressively replaced by crystallizing glasses. The reason of the increase of the strength that follow the decrease of thermal expansion on complete replacement of feldspar and irrespective of the content of true porosity in the specimens, evidently lies in changes of microstructure and composition of glass phase. Fairhurst *et al*. [8, 9] showed that the glass transition ranges of dental porcelain shifted to higher temperatures with increasing heating and cooling rates. Final products of porcelain should be well characterized for the better suitability of their applica-

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tion. A suitable study of thermal behaviour should help for the appropriate thermal cycle for each specific application in addition the prediction of their behaviour in thermo-reactive environment.

Conventional dilatometry and thermal gravimetric analysis have been widely used to study the thermal compatibility of porcelains with various materials and to monitor factors that induce changes in their thermal expansion, these analytical method has been also used to monitor conventional, electrical and technical porcelain for industrial applications. Non-contact dilatometry was found to be more convenient for better investigation of thermal expansion behaviour of porcelain products. The possibility to follow-up the sample during characterization, the precision and the reproduction of data collected made this method more attractive for the thermal characterization of ceramic materials.

The work reported here aim to study the sintering behaviour of porcelain compositions and correlated to thermo-gravimetric behaviour for definition of suitable thermal cycle as function of composition. It was expected that the thermal expansion up to higher temperature (>1300°C) correlated to the microstructure in relation to the other ceramic properties enable the prediction of the behaviour of porcelain in service.

Experimental

Porcelain compositions and firing cycles

The porcelain composition used was 7.5(Na_2O+K_2O)–19.9Al_2O_3–72.1SiO_2 (oxide-%) for PS (soft feldspathic porcelain) and GS (soft glass porcelain) and 5(K_2O+Na_2O)–24.2Al_2O_3–70.3SiO_2 for PH (hard feldspathic porcelain) and GH (hard glass porcelain). The source of alkali were a mixture of nepheline syenite with K-feldspar for PS and PH [10] while alkali-silicate glassy matrixes [11] were used for GS and GH. All the compositions present about 0.5% of impurities content as TiO_2 or/and Fe_2O_3. Alumina was introduced in the compositions principally by grey plastic kaolinitic clays while the amount of silica were rise using fine ground grains of quartz.

All the four compositions were prepared by slip casting and fired rapidly (20°C min^{-1}) up to 1225°C for PS and GS, 1325°C for PH and GH. 1, 2, 3 and 4 h soaking time were observed at maximum temperature.

Characterization of porcelain products

Casted and dried PS, GS, PH and GH compositions were used for DTA and to appreciate the sintering reactions that take place during firing.

The sintering behaviour was also studied using an optical microscope (ESS MISURA HSM ODHT model 1600/80) that acquires the sample profile of gently pressed powder of raw batch as function of temperature. The two thermal characterization were performed with a speed of 10°C min^{-1} and considered to appreciate the starting of the densification process.

Contact less dilatometry measurements were performed on shaped fired porcelains (5×5×15 mm) at a heating rate of 10°C min^{-1} up to softening 1325°C for soft porcelain and 1500°C for hard with the same instrument of the sintering behaviour study.

The linear thermal expansion coefficient is also electronically elaborated taking the length modification in the sample (height) with temperature. The error in such measurement is about 0.6 μm which is the minimum variation observable by the telecamera. The dilatation coefficient was directly calculated by the software coupled to the dilatometer.

XRD of fired specimens was evaluated with Ni filtered CuK_{α} radiation. The interpretation of XRD data was carried out using the Rietveld-RIR (1995) method. A software were used to evaluate the phase distribution. The microstructure of the fired specimens was studied by scanning electron microscopy (SEM) (Philips XL40) on freshly fracture surfaces and freshly fracture polished and gold coated sections. Micrographs of samples after dilatometry analysis were also collected.

Results and discussion

Figures 1a and b illustrate the different thermal analysis curves of as-mixed porcelain compositions. These materials are characterized by endothermic reactions around 570 and exothermic at 1000°C which are similar to that from kaolinite. The endothermic peaks indicating clay dehydroxylation, and the exothermic resulting from mullite crystallization [12]. Nepheline syenite and feldspar are known not to develop peaks during thermal treatment apart continuous endothermic drift at >500°C, because of their gradual sintering/melting. The difference in term of intensity of peaks should be ascribed to the total clay content for each compositions for endothermic and difference of mullitisation reactions for exothermic which take in account also the formation of secondary mullite that is not depending only to the clay content but also to the reactivity in the matrix after formation of primary mullite. DTA curves confirmed the glass-ceramics nature of porcelains composition under study and quartz and mullite as principal crystalline phase in the fired specimens. Micrographs from optical microscope were in agreement with the DTA behaviour. Hard porcelains initiated development of liquid phase from 1300°C while soft porcelain

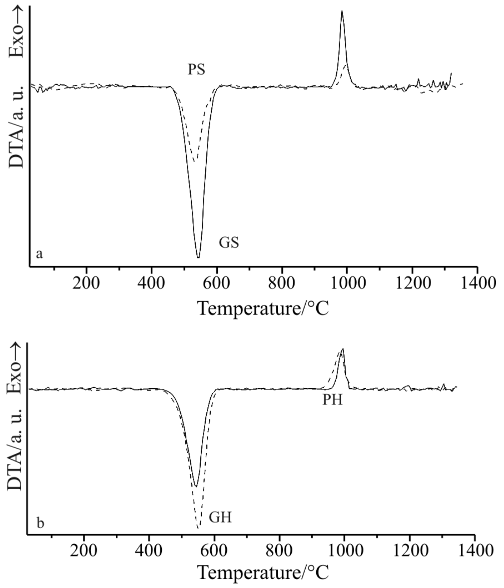

Fig. 1 DTA of a – soft porcelain and b – hard porcelain

developed liquid phase nearest 1190°C. The fusion were after 1520°C for soft porcelain compositions and could not be observed in hard porcelain up to 1600°C, the maximum temperature developing during the study of the sintering behaviour of the porcelain compositions with hot-stage microscope.

As indicated above, a software (Rietveld-RIR, 1995) were used to quantify the different phase present in each fired composition (Table 1). As expected soft porcelain compositions exhibited higher quartz content and low mullite compared to hard. The alumina oxide were present in compositions using alkali-silicate glassy matrixes as replacement of feldspar up to 2 h soaking time.

The thermal expansion behaviour for the four compositions is reported on Figs 2a–d. In each figure, three curves can be seen describing the different behaviour of the corresponding composition of porcelain as function of soaking time observed at the maximum of temperature (1225 for soft and 1325°C for hard) during firing. Generally when the fast firing is

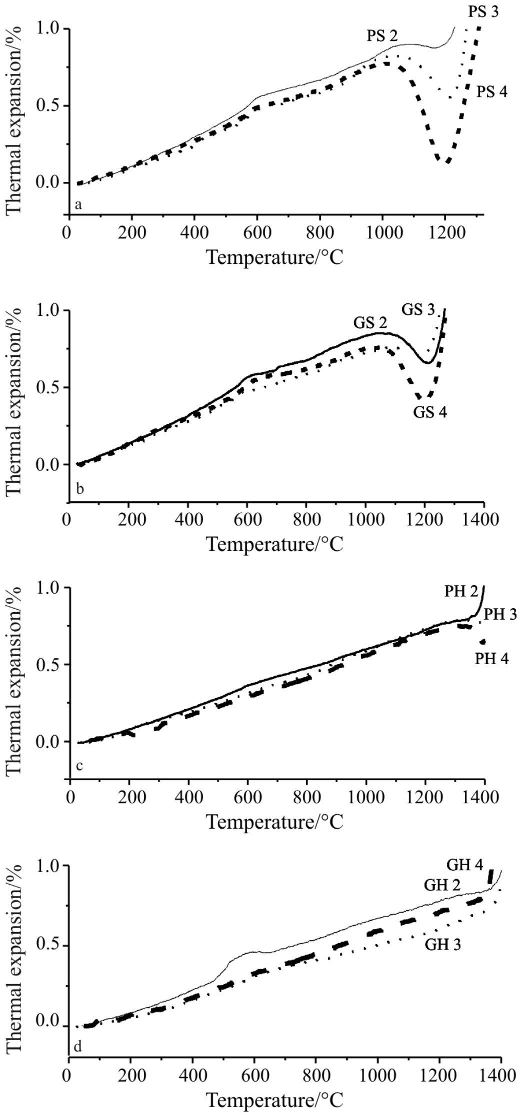

Fig. 2 Variation of thermal expansion of a – PS, b – GS, c – PH and d – GH as function of temperature and soaking time

applied, the soaking time is important for some thermal and physico-chemical reactions to be complete. Very short soaking time leads to incomplete reactions

Table 1 Phase distribution, average dilatation coefficient and bi-axial bending strength of porcelain compositions

Sample	Soaking time/h	cm·10^{-6}/°C	Mullite/%	Quartz/%	Amorphous/%	Strength/MPa
PS	2	8.33	8.76	32.08	59.16	155
	3	8.85	10.92	19.56	69.52	154
	4	7.9	7.01	16.37	76.62	149
GS	2	7.42	6.85	35.07	68.08	155
	3	7.79	9.38	31.18	59.44	157
	4	8.56	11.66	18.16	70.18	152
PH	2	6.21	21.26	17.88	60.86	170
	3	6.06	22.16	16.78	61.06	172
	4	5.99	20.15	16.99	62.86	169
GH	2	5.68	20.95	25.9	53.15	174
	3	5.79	22.21	19.97	57.82	178
	4	6.01	22.99	17.99	59.02	172

within the porcelain bodies with a consequence of the presence of a higher proportion of clay and feldspar relicts in the matrix, insufficient viscous liquid phase formed to embedded quartz and others crystalline phases in the structure. Therefore less dense material is produced with limited mechanical properties. The specimens fired with 1 h soaking time were less translucent specially hard porcelain compositions and were not considered as porcelain in this study.

The thermal expansion were 0.504 and 0.518%, respectively for PS and GS at 573°C, the temperature of allotropic transformation of quartz, for 2 h soaking time. These values were higher regarding those obtained with the same compositions for 3 and 4 h: 0.432 and 0.455% for PS; 0.470 and 0.454% for GS. For hard porcelain, discontinuity of thermal expansion observed with soft porcelain was less visible. Apart from the GH with 2 h soaking time, the effect of discontinuity due to quartz was not significative as far as hard porcelain is concerned. The percentage of free-quartz added to rise the chemical composition were lower in PH and it was assumed that important part of this quartz were dissolved from 3 h soaking time and as consequence dilatometry curves of hard porcelain with 3 and 4 h soaking were almost linear. It has been reported that alumina-containing bodies lead to less discontinuity while higher quartz containing bodies presents considerable discontinuity as function of the degree of dissolution. This dissolution itself is correlated to the grain size of quartz and in this case as in other ceramics bodies to the thermal cycle applied [13–17]. Maiti *et al.* [2] attributed the decrease in discontinuity of thermal expansion to the formation of new crystallizing phases. In fact nucleating agents used for developed more crystallizing phase induce low glass formation and thereby contributed to microstructure and bulk matrix where free-quartz is not more important as phase. The decrease in discontinuity of thermal expansion curves is also leads to quartz dissolution directly affected by soaking time. The high proportion of alkali in soft porcelain should be the reason of high rate of quartz dissolution as function of soaking time.

This study bring out the temperature-time dependence of the sintering of porcelain products and the necessity to design suitable composition compatible with thermal cycle in the aim to achieve desired final product. The control of thermal behaviour through the control of thermal parameters should be determinant for the achievement of the desired properties of porcelain compatible with the purpose application. Additionally, the inversion range of quartz is 550–580°C. The rapid displacive transformation of quartz tends to promote the formation of cracks in bonding bridges. When quartz containing bonds begin to cool from the soaking temperature, it is thought that the liquid phase relieves stresses resulting from thermal expansion mismatch between itself and β-quartz and mullite phases to at least 800°C. At this temperature, stresses will develop in quartz particles and the matrix that cause micro cracking to occur. This fact was not investigated in our study but should be taking in consideration for designing suitable thermal cycle for desired product. This should be done on the basis of the basic composition that play important role on the final characteristic of the product.

Micrographs of fresh fracture of porcelain compositions fired at maximum temperature with 3 h soaking time are showed in Fig. 3. The microstructure shows dense vitrified material with round shaped pores surrounded by the alkali-glassy matrix. These features are different from the narrow and elongated pores present in feldspathic porcelain compositions. The difference in microstructure is clearly observed also with etched samples: Primary mullite grains em-

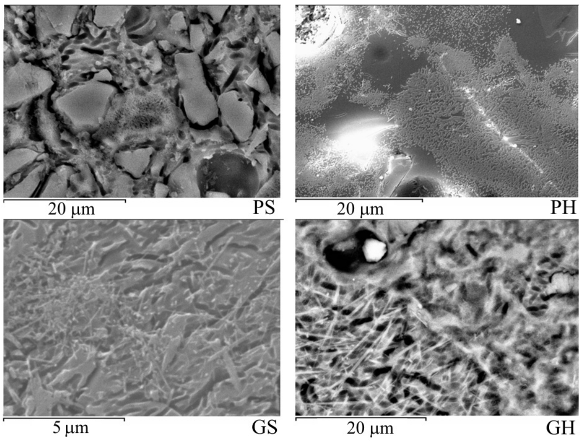

Fig. 3a Micrographs of etched specimens of porcelains with 3 h soaking time

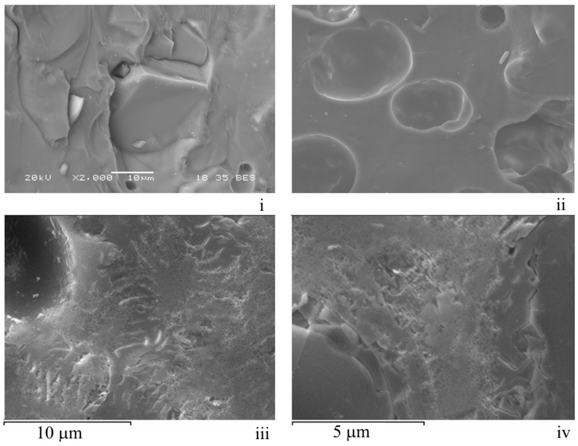

Fig. 3b Micrographs of porcelains compositions showing i, ii – the influence of 4 h soaking time in soft porcelain compositions and iii, iv – microstructure behavior of hard porcelain compositions after dilatometry analysis

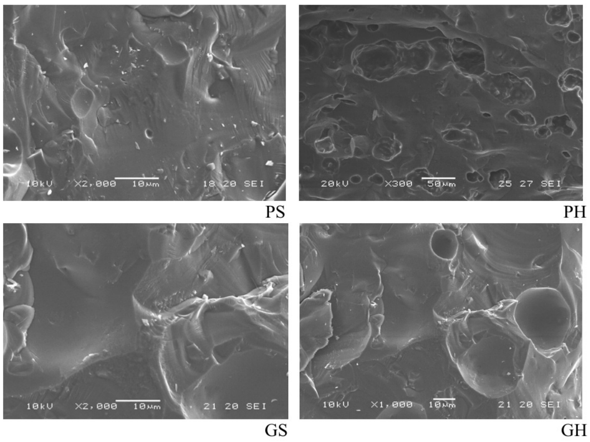

Fig. 3c Micrographs of fresh fracture of porcelain compositions with 3 h soaking time

bedded in the matrix of soft porcelain compositions, become numerous when glassy-matrix is used as replacement of feldspar (Fig. 3). The microstructure of glassy porcelain compositions showed more secondary mullite concentration that should results on the difference in thermo-chemical reactions mechanism of mixture containing alkali-glassy matrixes with those with feldspar. This also results in difference in amorphous phase content that directly influence the thermal expansion of porcelain. Such properties (thermal expansion as well as microstructure) are influenced by the soaking time (Fig. 2). On the contrary, the other properties of porcelain compositions investigated in this work are improved by the reduction of the glass content as substitution for feldspar. Authors [2] reported that glass which close in chemical composition to glass phase of porcelain, as replacement of feldspar and quartz undergoes mullite as primary crystalline phase with sharp changes in the structure of porcelain materials. The amount of secondary mullite present significantly increased. The presence of short, well separated and interlocking mullite needles surrounded by cordierite crystals, rutile and quartz modified considerably the microstructure of porcelain compositions and results on the decrease in discontinuity observed in dilatometry curves. The decrease in discontinuity was ascribed to the improve in crystallization that reduced the amount of free quartz in the matrix [2]. It comes that using the chemical approach to design compositions and understanding the influence of the source of alkali-ions (that influence the global mechanism of diffusion during sintering) are on great importance for the determination suitable porcelain product for specific application. Non-contact dilatometry analysis with its advantage of optical follow up of the specimens with the hot stage microscope coupled as function of time and temperature gives possibility to predict with more confidence the behaviour of the final product.

Conclusions

The thermal expansion of porcelain compositions have been studied with non-contact dilatometer, DTA and hot-stage microscope. From the results,

- Soft porcelain with relative higher alkali content and low alumina exhibited thermal expansion in the range of 7.42 to $8.85\cdot10^{-6}$ K^{-1} being influenced by the soaking time which were found to govern quartz dissolution and amount of liquid phase in the matrix.
- Hard porcelain with high alumina were found to less expanded (5.79 to 6.21×10^{-6} K^{-1}). The more extensive mullitization and the low quartz content in the final product result on the less importance in discontinuity in the thermal expansion curves compared to soft compositions.
- Alkali-silicate glassy matrixes as replacement of feldspar result in the development of microstructure more different from that of products containing feldspar and as consequence the thermal expansion were different.
- It has been possible to make correlation between the expansion behaviour and the microstructure as function of composition and thermal cycle.
- Thermal characterisation of porcelain bodies enable to master the suitable thermal cycle for the better characteristics of final products.
- Non contact dilatometry appears more suitable for the design of porcelain compositions and their thermal cycle and the prediction of their behaviour in service.

References

1 R. A. Dugdale, R. C. McVickers and S. D. Ford, J. Nucl. Mater., 12 (1964) 1.
2 K. N. Maiti and S. Kumar, Br. Ceram. Trans J., 91 (1992).
3 S. S. Khajotia, J. R. Mackert Jr., S. W. Twiggs, C. M. Russel and A. L. Williams, Elimination, Dent. Mater., 15 (1999) 390.
4 K. J. Anusavice, P. H. Dettoff, S. W. Twiggs and P. C. Lockwood, J. Dent. Res., 62 (1983) 1082.
5 J. R. Mackert Jr., Perspectives in dental ceramics, J. D. Preston, Ed., Proceedings of the Fourth International Symposium on Ceramics, Chicago: Quintessence 1988, pp. 53–64.
6 W. D. Kingery, H. K. Bowen and D. R. Uhlmann, Introduction to Ceramics, 2nd Ed., Wiley, New York 1976.
7 G. Isgro, C. J. Kleverlaan, H. Wang and A. J. Feilzer, Biomaterials, 25 (2004) 1447.
8 C. W. Fairhurst, D. T. Hashinger and S. W. Twiggs, J. Dent. Res., 68 (1989) 1313.
9 C. W. Fairhurst, K. J. Anusavice, D. T. Hashinger, R. D. Ringle and S. W. Twiggs, J. Biomed. Mater. Res., 14 (1980) 435.
10 E. Kamseu, C. Leonelli, D. N. Boccaccini, P. Veronesi, P. Miselli, G. Pellacani and U. Chinje Melo, Characterisation of Porcelain Compositions using two China Clays from Cameroon, Ceramic International, in press (science direct).

11 E. Kamseu, C. Leonelli, D. N. Beccaccini, P. Veronesi, V. M. Sglavo, U. C. Melo and D. Njopwouo, Alkali-silica Glassy Matrixes (AGM) as Replacement for Feldspar in Conventional Porcelain Compositions, Communication 3rd African MRS Conference. 7–10 Dec. 2005, Marrakech, Morocco.

12 Y. S. Iqbal and W. Edward, J. Am. Ceram. Soc., 83 (2000) 3121.

13 O. Isik Ece and Zenbe-e Nakagawa, Ceram. Int., 28 (2002) 131.

14 S. B. Vazquez, J. C. M. Velazquez and J. R. Gasga, Am. Ceram. Soc. Bull., 77 (1998) 81.

15 S. I. Warshaw and R. J. Seider, R. M. Fulrath and J. A. Pask, Eds, Wiley, New York 1996.

16 H. Anmin, L. Ming and M. Dali, J. Therm. Anal. Cal., 84 (2006) 497.

17 M. Goswami, A. Sarkar, B. I. Sharma, V. K. Shrinkhande and G. P. Kothiyal, J. Therm. Anal. Cal., 78 (2004) 699.

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