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Effect of the Chemical Composition on The Pyroplastic Deformation of Sanitaryware Porcelain Body

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Abstract. Pyroplastic deformation is the bending of a ceramic specimen caused by gravity during heat treatment. It can be defined as the loss of shape of product during its firing. Pyroplastic deformation is related to properties of liquid phases formed during firing. Therefore, the effect of the chemical composition on the pyroplastic deformation of sanitaryware porcelain was investigated in this study. Systematical compositional arrangements were made according to different combinations of (SiO_2/Al_2O_3) and (Na_2O/K_2O) ratios by using Seger formula approach. Pyroplastic deformation behaviour of compositions within a controlled firing regime was investigated by using fleximeter. The bodies were also prepared in a special form by slip casting method at laboratory scale in order to determine the pyroplastic deformation of the samples. The experimental results showed that a definite combination at SiO_2/Al_2O_3 ratio of 5 and Na_2O/K_2O ratio of 4 give the lowest pyroplastic deformation in the porcelain body formulations. The pyroplastic deformation value of this composition was determined as 25 mm which is 44% lower than that of the standard composition (45 mm).

1. Introduction

Sanitaryware articles are porcelain products generally produced from "vitreous china" and desired to have water absorption values of less than 0.5%. Vitreous china is typically the vitrified product of mixtures of clay, quartz sand and feldspar, after heat treatment at temperatures in the range 1200°C-1300°C [1]. After firing, the major phases of vitreous china are mullite and glass; there is also a moderate proportion of unreacted silica, normally in the form of α-quartz and minor amounts of porosity [2].

Pyroplasticity is related to an excess of liquid phases formed during firing or to a reduced viscosity of these phases [3]. Because of its high amount of glassy phase, vitreous china porcelain has a high tendency to deform creating a big problem for the production of sanitaryware products having complex shapes and high wall thickness values. The amount of deformation by creep is a function of temperature, stress time and structure. However, deformation behaviour during firing is a result of

many additional factors such as chemical composition and particle size of raw materials, green density and heating rate [4].

The aim of this work is to determine the effect of chemical composition on the pyroplastic deformation of vitreous china porcelain by changing (SiO_2/Al_2O_3) and (Na_2O/K_2O) ratios. In this study, the amount of ($SiO_2+Al_2O_3$) was kept constant to be 23±0,5 whereas different combinations of (SiO_2/Al_2O_3) and (Na_2O/K_2O) ratios were designed in order to produce different body formulations.

2. Experimental

In this work, an industrial sanitaryware body was selected as standard (VC-STD). The standard body consists of clay1 (4 %), clay2 (10 %), clay3 (12 %), kaolin1 (13 %), kaolin2 (11 %), sodium feldispar (30 %) and quartz sand (20 %) by mass. Chemical compositions of these raw materials are given in Table 1. Nine different compositions designed using Seger formulation with different (SiO_2/Al_2O_3) and (Na_2O/K_2O) ratios are given at Table 2.

Table 1. Chemical composition of raw materials

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2
Clay1	65.81	27.99	1.24	0.17	0.36	0.40	2.51	1.54
Clay2	60.97	32.32	2.45	0.30	0.60	0.23	1.82	1.31
Clay3	61.87	30.96	1.93	0.46	0.55	0.16	2.59	1.49
Kaolin1	48.13	35.75	0.85	0.08	0.26	0.11	2.99	0.00
Kaolin2	49.82	35.13	0.90	0.15	0.17	0.00	0.77	0.30
Sodium feldispar	68.91	17.80	0.11	0.62	0.07	11.46	0.26	0.26
Quartz Sand	90.74	5.81	0.25	0.04	0.05	0.11	0.38	0.19

All of the slips were adjusted to have the same physical properties. The solid concentration of slips held constant at 70 % by mass. The liter weight of slips was measured by using pycnometer and was held at 1750-1770 g/lt. Fordcup viscosity of slips was 55-60 s. The particle size distribution of slips was measured by using laser particle size analyzer (Malvern, Hydro 2000G). The mean particle size of non-plastic raw materials, d(50) was 12-14 μm. The samples used for all characterization analysis were shaped by slip casting method in plaster moulds. To determine the pyroplastic deformation behavior of samples, two different kinds of samples were used. Rod shaped samples having 85x7x7 mm size were produced for calculation of pyroplastic deformation index (PI) values and fired by using optical fleximeter (Misura, ODLT Flex 1400-30) with a firing regime of 10°C/min to 650°C, 5°C/min to 1000°C, 3°C/min to 1250°C and waiting 40 min at peak firing temperature. After fleximeter analysis, the pyroplastic index values (PI) of samples were calculated according to Equation (2.1). [3].

$$PI = sb^2 / l^4 \quad (2.1)$$

where,

s: Max deformation (mm)

b: Sample thickness (mm)

l: Distance between supports (mm)

To investigate the performance of compositions in an industrial manner, specific shaped big deformation samples were used to measure amount of pyroplastic deformation of selected bodies in mm. The samples for industrial trial were selected according to their lowest pyroplastic index and water absorption values. These samples were fired at electrical kiln with a firing regime of 10°C/min to 1000°C, 5°C/min to1250°C and kept 40 min at peak firing temperature. Water absorption of all samples was done according to the test methods given at TS-605 standards. The microstructural analysis of etched samples for 10 s in aqueous 5% hydrofluoric acid solution was done by using scanning electron microscope (SEM) in combination with energy dispersive X-ray spectroscopy (EDX) (Zeiss, Supra).

3. Results and Discussion

Calculated PI and water absorption values of fired samples are given in Table 2. Although the compositions K1, K2 and K4 had very low pyroplastic index values comparing to VC-STD, they were not suitable for industrial production because of their high amounts of clay contents (up to 80%). Therefore, only the compositions K3, K5, K6 and K7 were tested in an industrial manner. The results show that the composition K6 has the lower water absorption and pyroplastic deformation. At Figure 1(a), K6 is shown comparatively with VC-STD. The pyroplastic deformation value of this composition was determined as 25 mm which is 44% lower than that of the standard composition (45 mm).

Table 2. Seger formulation of bodies and characterization results of samples after firing at 1250 °C

			Optical fleximeter samples		Industrial samples	
Compositions	SiO_2/Al_2O_3	Na_2O/K_2O	Water absorption (%wt)	P.I.*10^6 (mm^{-1})	Water absorption (%wt)	Pyroplastic deformation (mm)
VC-STD	4.7	3.9	0	2.85	0	45
K1	3	1	0	1.52	-	-
K2	3	3	0.22	1.10	-	-
K3	3	5	1.41	1.06	1.27	21
K4	4	1	1.11	1.42	-	-
K5	4	3	0.79	1.85	0.43	27
K6	4	5	1.52	1.52	0.26	25
K7	5	1	1.88	1.58	0.46	30
K8	5	3	1.47	2.51	-	-
K9	5	5	1.41	2.44	-	-

Figure 1(b) shows the evolution of pyroplastic deformation index depending on "SiO_2/Al_2O_3" and "Na_2O/K_2O" ratios. The pyroplastic index of bodies does not significantly change with the increase of ratio SiO_2/Al_2O_3 when Na_2O/K_2O is 1. However, increases in Na_2O/K_2O ratios enhance the pyroplasticity with increasing SiO_2/Al_2O_3 ratio. According to obtained results, the ratio Na_2O/K_2O is more effective on pyroplastic deformation of vitreous china porcelain than SiO_2/Al_2O_3 ratio. Inside the structure of glassy phase, the ability of alkali ions are related with the network of SiO_2 and Al_2O_3. Al_2O_3 is a glass forming oxide and it is also a modifier. According to the glass system, Al_2O_3 can form AlO^{-4} tetrahedras by going through SiO_2 network structure [5]. Since aluminium-oxygen tetrahedra with four bridging oxygens have an excess negative charge of -1, an associated cation must be present in the vicinity of each such tetrahedron to maintain local charge neutrality. Aluminum oxide provides 1.5 oxygens per aluminium-oxygen tetrahedron, the oxygen provided by the alkali oxide is needed to complete the requirement of 2.0 oxygens per tetrahedron for fully linked tetrahedra. Since the oxygen supplied by the R_2O components are consumed in the formation of aluminium-oxygen tetrahedra, they are not available for the formation of non-bridging oxygen. It follows that each added aluminium ion can be considered to remove one non-bridging oxygen from the structure [6]. From that point of view the increase of Al_2O_3 in the glassy phase can cause the decrease of non-bridging oxygen in the system. In this study the glassy phase compositions of K6 and VC-STD were investigated by SEM-EDX analysis (Figure 2). The ratio of alumina to total alkali oxides $Al_2O_3/(R_2O+RO)$ is called alumina solubility [7] and in this study the alumina solubility in the glassy phase was calculated in molar basis. The alumina solubility of K6 body (6,75) was calculated to be higher than that of VC-STD (5,58). The high alumina solubility in the glassy phase of K6 body can lower the effects of non-bridging alkali oxides and cause a more fully linked network structure. Thus, such a circumstance lowers pyroplastic deformation. According to the SEM-EDX analysis of glassy phases of bodies, it is obvious that the

glassy phase of K6 contains higher amount of SiO_2 than the glassy phase of standart body. Increases in the SiO_2 level in the glassy phase cause corresponding increases in the glassy phase viscosity; and as a result of that pyroplastic deformation decreases [7].

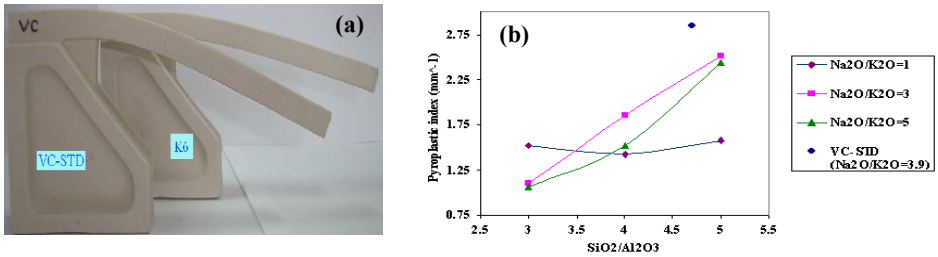
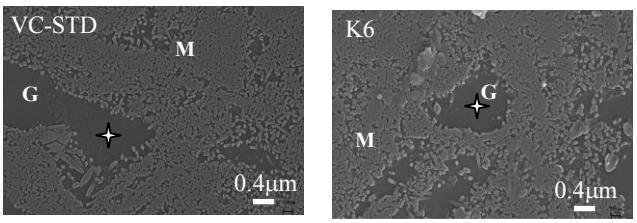


Figure 1. (a) VC-STD and K6 fired as big deformation samples **(b)** Evolution of pyroplastic deformation index depending on "SiO_2/Al_2O_3" and "Na_2O/K_2O" ratios.



Oxide(wt %)		
Oxide	VC-STD	K6
SiO_2	66.5	69.2
Al_2O_3	29.6	28
Na_2O	2.1	1.7
K_2O	1.2	1.1
CaO	0.3	-
MgO	0.3	-

Figure 2. SEM secondary electron images of bodies and glassy phase compositions detected by point EDX analysis (G: Glassy phase; M: Mullite).

4. Conclusions

The results of industrial trials showed that water absorption values are appropriate to the TS-605 standards (<0.5 wt%) and, at the same time, the deformation values are lower than that of the standard body (VC-STD). In this study, the effect of the chemical composition on pyroplastic deformation of sanitaryware porcelain was investigated. The results showed that the ratio Na_2O/K_2O has a more powerful effect on pyroplastic deformation than SiO_2/Al_2O_3 ratio. According to experimental results, a definite combination at SiO_2/Al_2O_3 ratio of 5 and Na_2O/K_2O ratio of 4 produce the lowest pyroplastic deformation in the porcelain body formulations. The results of the SEM-EDX analysis showed that, the glassy phase composition affects pyroplastic deformation. The increase in the amount of alumina solubility and the amount of SiO_2 in the glassy phase, causes reduction in pyroplastic deformation of the porcelain body.

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