

DETERMINATION OF THE FIRING SCHEDULE FOR A SELF GLAZING PORCELAIN

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ABSTRACT

In this study the aim was the production of a self glazing porcelain which depended upon the formation of the anorthite phase ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), by single firing. A frit was prepared by mixing 24.5 % K_2CO_3 , 31.7 % SiO_2 and 43.8 % H_3PO_4 at 1050 °C in order to satisfy the molar ratio of $\text{K}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2 = 1 : 2 : 3$ known as the Seger formula. A batch having a composition of 50 % kaolin, 35 % wollastonite and 15 % frit was prepared. The differential thermal analysis (DTA) and linear dilatometry (LD) curves of this batch were determined. The firing schedule (FS) curve which shows the variation of temperature as a function of time was derived from the LD and DTA curves. The batch was fired for 210 min. including cooling, such that the maximum temperature was 1050 °C according to the FS and a self glazing porcelain was obtained. From the X-ray diffraction patterns it was determined that anorthite phase was formed in the porcelain. It was concluded that a great amount of energy would be saved by the production of a single firing porcelain which depends on the formation of the anorthite phase instead of the production of a double-stepped firing porcelain which depends on the formation of the mullite phase ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

1. INTRODUCTION

The first step in traditional porcelain manufacture is the preparation of a workable body by mixing 50 % kaolin, 25 % feldspar and 25% quartz with water. The body is then moulded and dried and is partially sintered by a first firing at around 1000 °C at a rate of 40-50 °C hour⁻¹. After cooling the body and submerging it in a glaze suspension, a completely sintered and glazed porcelain is obtained by a second firing of the body at around 1300 °C at a rate of 100-120 °C hour⁻¹. The successive non glazing and glazing firing processes in porcelain manufacture require a lot of energy consumption¹⁻³. The spent energy effects primarily the cost of porcelain manufacture. Detailed scientific and technological research is required in order to decrease the cost of porcelain and to economise energy^{4,5}. There are attempts to decrease the firing temperature and rate by changing the chemical and mineralogical composition of the raw porcelain batch^{6,7}. There are also studies

concerning the change in the design and structure materials of the firing kilns which would result in energy economy^{10,11}. In recent years, a single firing process which depends on the formation of the anorthite phase ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) instead of a double-stepped firing process which depends on the formation of the mullite phase ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) has been designed for the manufacture of porcelain in order to economise energy¹². Mixtures of kaolin whose major clay mineral is kaolinite ($\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$), wollastonite ($\text{CaO} \cdot \text{SiO}_2$) and frit are used for the production of porcelain which depends on the formation of the anorthite phase¹³. Studies aiming at decreasing the firing temperature and period to minimum are realised by changing the chemical composition of frit and its mass ratio in the batch for porcelain¹⁴. The aim of this study was to determine the theoretical firing schedule (FS) curve¹⁵ of a specially chosen kaolin, wollastonite and frit mixture and to produce a self glazing porcelain which depends on the formation of the anorthite phase by a single firing procedure realised according to this curve.

2. MATERIALS AND METHOD

Sındırgı (Balıkesir, Turkey) kaolin was supplied by Turkish Mining and Exploration Institute. Bayramiç (Çanakkale, Turkey) wollastonite was supplied by Çanakkale Ceramic Industries. Potassium feldspar (KAlSi_3O_8) and quartz (SiO_2) were supplied by Eczacıbaşı Esan Doğa Mining Company. Boric acid (H_3BO_3) was supplied by Etibank Bandırma Borax Company. Commercially pure K_2CO_3 was used. The chemical analysis of kaolin, wollastonite and quartz were determined.

In the preparation of frit, 24.5 % K_2CO_3 , 31.7 % SiO_2 and 43.8 % H_3BO_3 were mixed in order to satisfy the molar ratio of $\text{K}_2\text{O} : \text{B}_2\text{O}_3 : \text{SiO}_2 = 1 : 2 : 3$ known as the Seger formula¹⁵. The mixture was homogenised in dry condition in a ball mill. This mixture whose density was determined was then melted in a platinum crucible at 1050 °C and was poured into distilled water right away. These frit particles were first dried and then ground in a mill (Fritsch Planetary Mill Pulverisette-5) such that they would all pass through 0.125 mm (115 mesh) screen. The density and the softening temperature of the prepared frit were determined.

50 % kaolin, 35 % wollastonite and 15 % frit were mixed and then homogenised in a ball mill. The differential thermal analysis (DTA) curve of the batch was determined by a thermal analysis instrument [Netzsch Simultaneous Thermal Analysis Instrument Model 429 (STA 429)] at a rate of 10 K min⁻¹. Cylindrical pellets were prepared by applying a pressure of 10⁴ atm cm⁻² on the samples taken from the batch. The linear dilatometry curve of a cylindrical specimen cut from one of the pellets was determined by a STA 429 instrument. FS curve was plotted by using the LD and DTA curves and the pellets were fired according to the FS curve. The maximum firing temperature during the firing process which includes also the cooling was 1050 °C and the firing period was 210 minutes. The X-ray diffraction (XRD) pattern of the porcelain thus produced was determined by a

diffractometer (Philips PW 1730) using CuK_α rays whose wavelength is 0.15418 nm and a Ni filter.

3. RESULTS AND DISCUSSION

The densities of the raw frit mixture and the frit were determined respectively as 2.89 g cm^{-3} and 3.78 g cm^{-3} . The increase in the density during the formation of the frit was due to the CO_2 evolution and shrinkage during liquid sintering. It was observed that the frit mixture softened between $800\text{-}820^\circ\text{C}$.

The chemical analyses of the materials that were used in the experiments are given in Table 1 where LOI represents the loss on ignition.

Table 1. The chemical analyses of the materials given as mass percents.

	SiO_2	B_2O_3	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI
Quartz	99.10	-	0.20	-	0.10	0.20	0.10	0.10	0.20	-	-
Frit	43.50	33.80	-	-	-	-	-	-	22.70	-	-
Kaolen	52.50	-	34.20	0.20	0.80	0.30	0.10	0.30	0.10	0.30	11.20
Wollastonite	52.00	-	0.50	0.01	0.30	45.00	0.80	-	-	-	-

The mineralogies of the raw materials were determined by using their XRD and DTA data as well as their ideal chemical formulas¹³. Kaolin contained 83 % kaolinite, 11.76 % quartz, 2.53 % albite ($\text{NaAlSi}_3\text{O}_8$), 1.98 % anorthite, and 0.59 % orthoclase (KAlSi_3O_8) (represented in mass percents). Natural wollastonite contained 93.20 % wollastonite mineral, 3.80 % quartz, 1.74 % calcite (CaCO_3), and 1.26 % kaolinite (represented in mass percents).

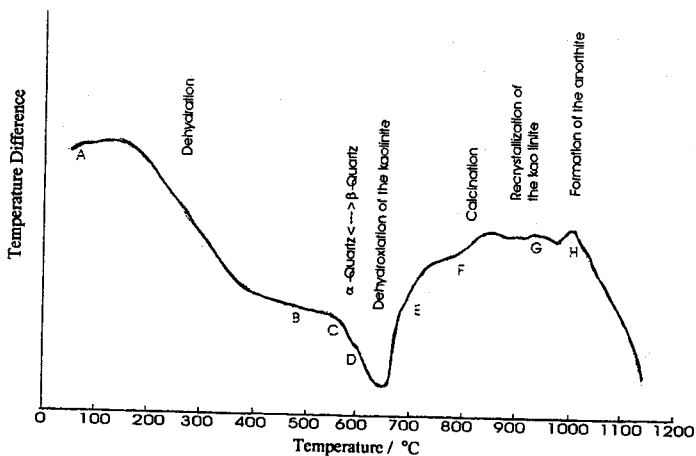


Figure 1. The DTA curve of the raw porcelain batch which was prepared by kaolin wollastonite and boron added frit.

The DTA curve of the batch for porcelain is given in Figure 1. In the DTA curve, the exothermic peak observed between 1000-1050 °C shows the formation of the anorthite phase. The formation of the anorthite phase which provides mechanical strength to the structure was completed at 1050 °C and this temperature was taken as the maximum firing temperature.

The LD curve of the batch for porcelain which was put into cylindrical form by pressing is given in Figure 2. The LD curve shows the relation between the negative and positive height change percentages of the cylinder and the temperature. The height change percentage of the cylinder can be represented as follows:

$$\varepsilon = 100 (L-L_0) / L_0 = 100 L / L_0 \quad (1)$$

where L_0 and L represent the height of the cylinder respectively at ambient temperature and at any temperature. According to this relation, the linear deformations L and ε are marked positive as the cylinder becomes taller and negative as it becomes shorter. The absolute values of the positive and negative linear deformations were added hence the cumulative linear deformation was obtained as follows:

$$\varepsilon' = \sum |\varepsilon| \quad (2)$$

$T - \varepsilon'$ curve (Figure 3) was obtained by plotting the variation of the cumulative linear deformation as a function of temperature. Shape deformations, fissures and cracks on the body as a result of the deformations during the firing process are not desired. Therefore, it is necessary that the heating rate (dT / dt) should be changed in the opposite direction of the linear deformation rate ($d\varepsilon / dT$). By considering the $T - \varepsilon'$ curve (Figure 3) and the fact that the maximum firing temperature has to be 1050 °C, the most probable FS ($T-t$) curve which was determined between the firing time (210 minutes including cooling) and the firing temperature is given in Figure 4. The discussion concerning the events between the points marked by letters on the DTA ($T-T$), LD ($T - \varepsilon'$) and FS ($T-t$) curves is summarised as follows.

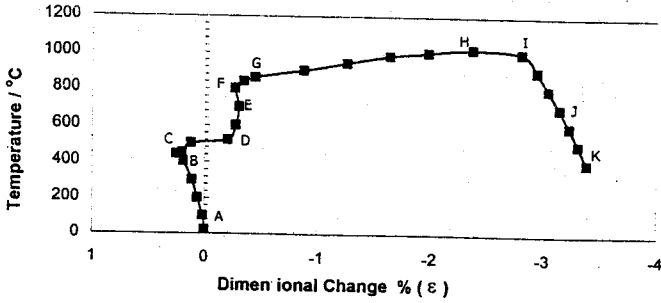


Figure 2. The TD curve which gives the firing temperature of the raw porcelain batch as a function of the absolute value of the dimensional change percentage.

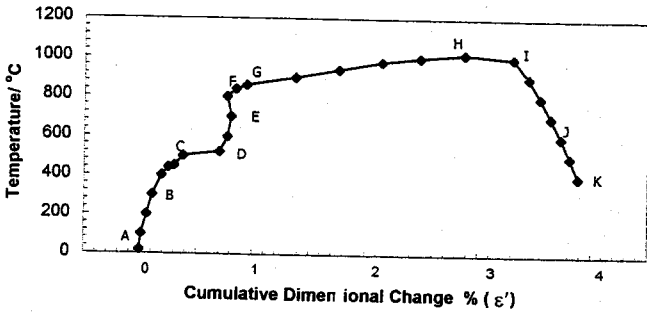


Figure 3. The TD curve which gives the firing temperature of the raw porcelain batch as a function of the cumulative dimensional change percentage.

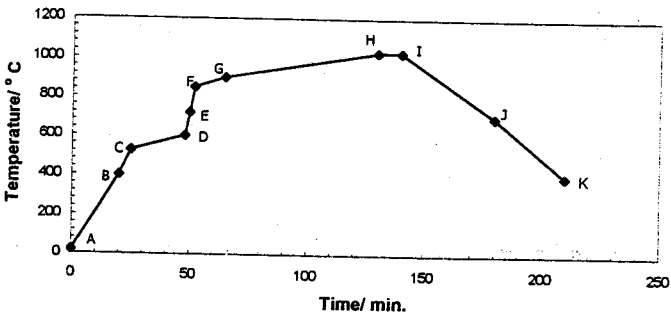


Figure 4. The FS curve which was derived by using the DTA and TD curves and which gives the firing temperature as a function of the firing period.

ABC: As the temperature rised up to 450 °C the moisture, zeolitic water and adsorbed water which were left in the body were eliminated respectively in the AB interval. The heating rate was considerably high in this interval where expansion deformation was not much. Since an important deformation was not observed in the temperature interval between 450-500 °C, the heating rate was not changed.

CD: As the temperature rised up to 573 °C along CD, the quartz which existed as an impurity in the mixture underwent $\alpha \rightarrow \beta$ phase transformation. In the meantime a sudden increase in volume took place. Since the quantity of quartz was small it was not expected that this increase would lead to a deformation on the body. On the other hand, kaolinite whose ideal formula is $Al_4 Si_4 O_{10} (OH)_8$ began to undergo dehydroxylation at 550 °C. At the same time, the shrinkage which began right from the beginning cancelled on one hand the effect of expansion and on the other hand caused a considerable decrease in volume. Therefore, the heating rate was decreased in the CD interval.

DEF: An important shrinkage was not observed as a result of the progressing dehydroxylation after 600 °C. Therefore the heating rate was increased to maximum along DE. Around 800 °C the calcite which existed as an impurity in the mixture underwent calcination but it did not cause an important deformation. Therefore, the heating rate was not changed.

FGHI: As the temperature continued to increase above 800 °C, the frit melted and filled the empty spaces between the particles and as a result a considerable shrinkage took place along FGH. Therefore the heating rate was decreased considerably and the maximum firing temperature of 1050 °C was reached at this rate. Heating was continued for a certain period at this constant heating rate along HI.

IJK: Since the shrinkage deformation which began right from the beginning slowed down considerably the cooling rate was kept considerably high. Because of the sudden shrinkage as a result of $\beta \rightarrow \alpha$ phase transformation at 573 °C the heating rate was reduced after 600 °C. There was no need to control the cooling rate for cooling to lower temperatures.

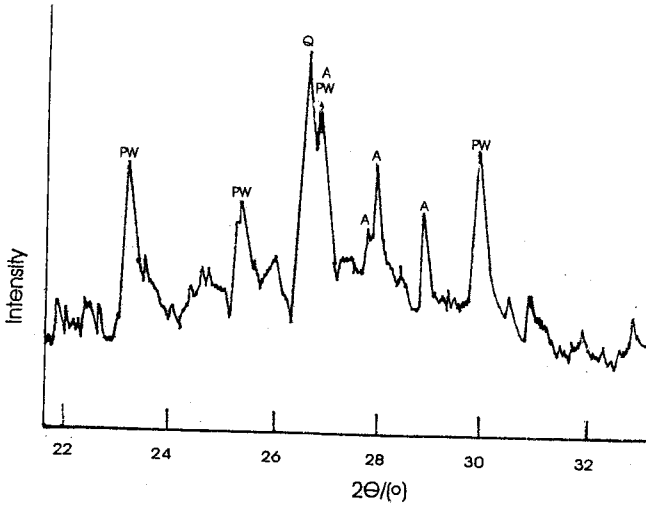


Figure 5. The XRD pattern of the porcelain produced by the firing according to the FS curve of a batch prepared from kaolin, wollastonite and boron added frit.

The fact that there weren't any cracks, fractures or shape deformations during the firing process showed that the FS curve which was determined as explained previously was suitable for use. The XRD pattern of the porcelain which was thus produced is given in Figure 5. The examination of this pattern showed that the anorthite phase which provides the mechanical strength to porcelain was formed. It was also observed that, some quartz was left free in the mixture and pseudowollastonite was formed.

4. CONCLUSION

It was understood that the production of a self glazing porcelain based on the production of the anorthite phase by single firing around 1050 °C would provide a lot of energy economy when compared to the production of a non glazed porcelain or glazed porcelain which are based on the formation of the mullite phase and require double firing during longer periods at 1000 °C and 1300 °C respectively.

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