Preparation of porcelain building tiles using “K$_2$O–Na$_2$O” feldspar flux as a modifier agent of low-temperature firing

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In this paper, to save energy and reduce consumption in building ceramic process, the low temperature porcelain building tiles were prepared by fast firing process using two kinds of “K$_2$O–Na$_2$O” feldspar with different amounts of alkaline and alkaline earth oxides fluxing agents, Si/Al ratio and melting point. The sintering properties of the samples were evaluated by linear shrinkage, water absorption and bulk density. The crystalline phase and microstructure of the samples were characterized by X-ray diffraction and scanning electron microscope. The results showed that the optimum linear shrinkage of 7.55%, water absorption of 0.03% and bending strength of 78.3–85.8MPa can be achieved for the sample fired at 1170–1190°C, which is attributed to the effect of the combined “K$_2$O–Na$_2$O” feldspar flux system.

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Key-words : Porcelain building tile, Sintering properties, Firing Temperature, Feldspar

1. Introduction

In recent years, porcelain building tiles, which have high technological properties, especially regarding water absorption, bending strength, corrosion resistance and stain resistance, have paid more and more attentions. Porcelain building tiles need a firing temperature of guaranteeing the main performance of the products, reducing the total melting point temperature, which leads to porcelain slab formation, and eutectic system. In the present work, to reduce the multiple composite flux system. In the present work, to reduce the firing temperature, multiple fluxes were added to the composition, and effects of the firing temperature on the properties of the samples were studied.

2. Experimental

2.1 Samples preparation

In our study, different kinds of feldspars were selected. Feldspar 1# comes from Jiangxi Province Jinning city. Chemical compositions of the raw material were shown in Table 1 by X-ray Fluorescence (PANalytical B.V., Holland). The sintering behavior of the samples must be affected by the particle size of the raw materials. Therefore, all the raw materials were crushed, grounded and passed through a 200 mesh (final raw materials powder particle size of 120–160μm) in advance for further use. Different kinds of feldspars with the mean particle size of 45μm were purchased from Pingxiang Raw Materials Factory, China. Sintering properties of raw materials are shown in Table 2.

The porcelain building ceramic tiles were prepared as shown in Table 2. Batches were prepared by milling the constituents with water (1:1) for 12min, in a fast ball milling using alumina balls with the mean diameter size of 30 mm as grinding media. The resultant slurry was oven-dried at 80°C for 3h to 3–7% water, and sieved to pass 80 meshes. The resulting powder uniaxially pressed at 10 MPa in a steel die and heating rate of 10–15°C/min, holding time of 5min at firing temperature of 1130–1210°C and oxygen atmosphere in a fast firing process. Square tiles (6g each) of 41 mm x 11 mm x 7 mm were prepared for property measurements.

2.2 Characterization

The sintering properties of the samples were evaluated by the linear shrinkage, water absorption, bulk density according to Archimedes law. The obtained experimental results were averaged for five samples keeping experimental conditions unchanged. The Linear shrinkage, $L_s$ (%), is such as Eq. (1).

\[
L_s = \frac{L_b - L_a}{L_a} \times 100\%
\]  

$L_b$ and $L_a$ are the diameter (mm) of the green and fired samples, respectively. The water absorption is measured, boiling in water for 3h and soak for an additional 24h at ambient temperature.
such as Eq. (3).

\[
\text{mined by means of the following equation:}
\]

\[
\text{sample in the water.}
\]

The crystalline phases of the samples were characterized by X-ray diffraction (XRD, PANalytical X’Pert Pro, Holland) in a 2θ range from 10 to 70° with Cu Kα radiation. The microstructure of the fired samples was observed by a scanning electron microscope (SEM, JSM-6700F, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS) system operating at an accelerating voltage of 5.0 or 15 kV (15 kV for EDS). To analysis of phase assemblages and morphology, the fresh fracture surfaces of the samples were etched for 30 min in 5HF solution. The beginning melting temperature of feldspar was characterized by a melting temperature tester (SJY-130763, China).

3. Results and discussion

3.1 XRD and SEM analysis

Figure 1 shows that the sintering properties of the samples with different mass ratio of feldspar 1# and feldspar 2# at 1190°C. With the increase of feldspar 2#, the linear shrinkage of the sample increases and reaches a maximum value of 7.55%, and thus the water absorption decreases and reaches a minimum value of 0.03%. It can be seen that water absorption decreases and then increase with the increase of feldspar 1# replacement of feldspar 2#. It can be attributed to the formation of the glassy phase, which mostly comes from the feldspar. Increasing feldspar 1# replacement of feldspar 2# causes both an increase liquid phase amount and a decrease in liquid phase viscosity due to increase of the fluxing content keeping the almost same value 0.14 of Al2O3/SiO2 ratio. The liquid phase could distribute in the open pores and thus water absorption decreases. Further increase feldspar 1# replacement of feldspar 2# content, more the fluxing contents keeping almost the same Al2O3/SiO2 ratio for the sample A6 (Table 2) cause an abrupt increase in the water absorption and decrease in the bulk density due to forced expulsion of the entrapped gases, resulting in blisters and bloating. However, although more fluxing content (e.g. the sample A5) can lower the firing temperature at 1120°C and makes the firing temperature...
range narrow which is not conducive to the commercial process. It is necessary to point out that the well sintered temperature of 1190°C for the sample A5 is higher than the start of melting temperature (1020°C) predicted from the related phase diagram of simple composition $\text{K}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$. Because the sample A5 composition has the lower amount of $\text{K}_2\text{O}$ and $\text{Na}_2\text{O}$ contents than the therothetic fluxing content. Although the therothetic fluxing content can lower the sintering temperature due to the liquid formation, more liquid formation resulting in deforming is not well controlled for the commercial process. It is obvious that suitable feldspar 1# and feldspar 2# content for improving the densification of the samples. The densification process is similar to our previous reported in the past years. Effects of the temperature on the properties of the samples are discussed using A5 prepared samples as follows.

Figure 2 shows the XRD patterns of the samples fired at different temperature. It can be seen that most of the diffraction peaks can be assigned to quartz (JCPDS files Nos. 42-0423) and a small amount of mullite phase (JCPDS files Nos. 42-0423) is observed. With the increase of temperature (>1190°C), the peak intensities of the quartz increases.

Figure 3 shows SEM surface images of the fired samples after firing in the 1130–1210°C interval. It can be seen that the surface of the samples become smooth and dense with the increase of temperature [Figs. 3(a)–3(c)]. However, when the temperature is 1210°C, some bubbles appear on the surface of samples [Fig. 3(d)]. Further characterization of the samples at different firing temperature is shown Fig. 4. It is obvious that some crystals are obtained and glassy phases also exist in the samples. When the temperature is 1130°C, some crystals are obtained [Figs. 4(a) and 4(b)]. When the firing temperature is 1170°C, a dense matrix is observed and some aggregated whiskers with size of about 0.14 μm in length and 0.03 μm in width are obtained [Figs. 4(c) and 4(d)]. Increasing the temperature to 1190°C, a dense matrix is also observed and developed whiskers with size of about 0.31 μm in length and 0.04 μm in width are obtained [Figs. 4(e) and 4(f)]. Figure S1 shows the corresponding EDS spectrum of the whiskers structure. It can be seen that the whiskers structure consists of $\text{Al}$ and $\text{Si}$ elements, and the molar ratio of $\text{Al}/\text{Si}$ is about 3:1, which is close to the stoichiometry of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) phase. Further increasing to 1210°C, some large pores appear and small particles are obtained [Figs. 4(g) and 4(h)].

Melting point is the temperature of something turning to liquid from solid phase, it is the main method to measure the fusing characteristics of fluxing agent. Figure 5 shows the beginning of melting temperature of feldspar 1# and feldspar 2# fluxing agents. At 1130°C, the corner of the two samples changes a little [Fig. 5(a) and 5(c)]. When the temperature increases to 1175 and 1185°C, the samples turn a rounded corner, respectively [Figs. 5(b) and 5(d)], indicating that the beginning melting temperature of feldspar 1# and feldspar 2# is 1175°C and at 1185°C, respectively. It is well known that different Si/Al molar ratio, fluxing contents and purity have different melting point. When
higher than 1130°C, feldspar di-
clay area, and react with to form mullite crystals,2) the formation of closed pore. When the temperature play a key important role in the formation of the mullite needle-shape mullite crystals were formed from feldspar-diatexing agents.14) Increasing the temperature of 1210°C, the closed liquid phase amount and a decrease in liquid phase viscosity. The liquid phase tends to draw the particles and thus open porosity decreases, and closed porosity increases.25) However, further increasing temperature above 1190°C, the so-called body bloating tends to expand the pores due to the pressure of the gas inside the closed pores and thus the open pores increase.26) Therefore, the water absorption decreases in the first step, reaching a maximum value at 1190°C and then increasing. In another, the linear shrinkage and bulk density increase in the first step, reaching a maximum value at 1190°C and then increasing. Bending strength of the samples initially increases with the increase of temperature. The sample reaches a maximum value of 85.8 MPa at 1190°C, and then decreases with the increase of temperature.

### 3.2 Effects of firing temperature on the sintering properties of the fired samples

Figure 6 shows linear shrinkage, water absorption and bulk density as function of firing temperature at the 1130–1210°C range. It can be seen that linear shrinkage initially increases and then decreases with the increase of temperature. The bulk density has a similar behavior with the linear shrinkage for the sample. The water absorption rate firstly decreases and then increases with the increase of temperature. When the firing temperature is 1190°C, the linear shrinkage and bulk density of the sample reach a maximum value of 7.55% and 2.42 g/cm³, respectively, and the water absorption rate reaches a minimum value of 0.03%, which are close to the properties (e. g. bending strength of 45 MPa, water adsorption of 0.06% and linear shrinkage of 7.58%) of the commercial porcelain building tiles.20) It is obvious that water absorption decreases, and the linear shrinkage and bulk density increase with the increase of firing temperature due to the formation of some glassy, which is originated from the feldspar. Further increasing the firing temperature can result in the increase of liquid phase amount and a decrease in liquid phase viscosity. The liquid phase tends to draw the particles and thus open porosity decreases, and closed porosity increases.25) However, further increasing temperature above 1190°C, the so-called body bloating tends to expand the pores due to the pressure of the gas inside the closed pores and thus the open pores increase.26) Therefore, the water absorption decreases in the first step, reaching a maximum value at 1190°C and then increasing. In another, the linear shrinkage and bulk density increase in the first step, reaching a maximum value at 1190°C and then increasing. This behavior is similar to that reported by some literature about porcelain bodies.15,18)

![Graph of linear shrinkage, water absorption, and bulk density vs. firing temperature](image)

**Fig. 6.** Curves of the sample at different firing temperature: (a) linear shrinkage, (b) water absorption (Wₜ) and bulk density (ρₕ).

### 3.3 Effects of the firing temperature on the bending strength of the samples

Figure 7 shows the bending strength of the samples at different temperatures. Bending strength of the samples initially increases with the increase of the temperature. The sample reaches a maximum value of 85.8 MPa at 1190°C, and then decreases with the increase of temperature.

Above all the experimental results, the dense, well-developed mullite needlelike crystals and dense glassy phase are achieved (Figs. 2 and 4), when the water absorption reaches a minimum value of nearly zero and simultaneously the shrinkage is the maximum value of 7.55% at 1190°C, resulting in the increase of the bending strength of the sample (Figs. 6 and 7). Further increasing to 1210°C, the sample appears a lot of liquid phase due to the similar melting points of feldspar 1# and feldspar 2# (Fig. 5), and thus liquid phase increases rapidly, which leads to slab deformation of the sample. And the corresponding mullite whisker was partially melted (Figs. 2 and 4), therefore, the bending strength of the sample declines.

### 4. Conclusions

In conclusion, a porcelain building ceramic composition was prepared by mixing 33.8% sodium feldspar, 27.2% Zhuji pore-

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**Table 1:**

| Component | Content |
|-----------|---------|
| Al₂O₃     | 19%     |
| SiO₂      | 79%     |
| CaO       | 1%      |
| Na₂O      | 0.5%    |

**Fig. 5:** XRD patterns of the samples at different firing temperatures.

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**Fig. 7:** Bending strength of the samples at different firing temperatures.
The combined "K₂O–Na₂O" feldspar flux at 1170°C shows that the samples are composed of quartz, mullite and glassy phase. The firing temperature plays a significant role on the properties of the samples. The samples are sintered at 1170–1190°C using two kinds of "K₂O–Na₂O" feldspar with different amounts of alkaline and alkaline earth oxides fluxing agents, Si/Al ratio and melting point, and endowed with 0–0.03% of the water absorption and 78.3–85.8 MPa of the bending strength. XRD and SEM results show that the samples are composed of quartz, mullite and glassy phase, and a dense matrix was held by well-developed mullite crystals and glassy phase at 1170–1190°C due to the effect of the combined "K₂O–Na₂O" feldspar flux system. The bending strength of the sample falls drastically when the temperature is higher than 1190°C. It is that the similar melting point of two feldspar generated simultaneously liquid phase rapidly, resulting in the slab deformation and fall of the bending strength of the sample.

Acknowledgement The present work was supported by the National Natural Science Foundation (Grant No. 51562013).

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