A study on the effect of different minerals on the pyroplastic deformation of ceramic samples was carried out in a muffle furnace. For fair comparison, samples with same chemical composition were used. The mixtures with different minerals were pressed into rectangular bar and placed on alumina supports in the furnace. The green bodies were heated up to their desired temperature and stabilized for 2 h. The solid phases in the sample which were introduced by different raw materials were found to be responsible to the pyroplastic deformation. The influence of andalusite and fly ash powders on the pyroplastic deformation was strong but slight deformation was observed if kaolin clay and calcinated kaolin clay were employed separately. It suggests that the distribution of solid particles in glassy phase plays an important role in the extent of pyroplastic deformation of porcelain sample.

1. Introduction

To resolve the scarcity of natural resources, it is desirable for all the porcelains to be light weight, especially for a hefty ceramic, sanitary ware. However, the low strength and large deformation are the biggest obstacles to the weight reduction of porcelain products. It was reported[6,7] that the extent of deformation is inversely proportional to the square of decreasing amount of wall thickness and the strength of the body is directly proportional to wall thickness. Thus, to reduce the quantity of deformation and enhance the strength of porcelain, a thick wall is required, which lead to the increased weight of porcelain.

Lots of efforts[2-4] were made on the improvement of ceramic strength. For instance, small-sized quartz and uniform distribution of small pores were found to be beneficial to the mechanical strength of porcelains. On the other hand, the pyroplastic on the porcelains has also been studied by a number of researchers,[9-13] First, the pyroplastic deformation was found to be related to the system viscosity. Lee[9] reported the grain growth and the relative density increasing made the value of system viscosity higher. Second, the study[10,11] of pyroplasticity in porcelains showed that the pyroplastic deformation was strongly affected by the feldspar, albite and kaolin clay. Tunçel and Özel[12] proposed that the ratios of Na$_2$O/K$_2$O and SiO$_2$/Al$_2$O$_3$ affected the system viscosity as well as the pyroplastic deformation of sanitary ware porcelain bodies. Furthermore, the quantity of deformation reduced significantly, if the ratios of Na$_2$O/K$_2$O and SiO$_2$/Al$_2$O$_3$ were 4 and 5, respectively.

Many researches showed that the main reasons for pyroplastic deformation of porcelains were the content of minerals and chemical composition of sample. Most studies mainly focused on ternary systems: clay-feldspar-quartz. Glassy phase, mullite and quartz are found to be the main phases in the porcelain sample. However, in the same system, different chemical composition only affected the viscosity of melts but the morphology of solid phases and microstructure of samples are the same if clay, feldspar and quartz are the main components of the porcelain sample. On the other hand, the morphology and the content of different solid particles in the melts were relevant to the liquid viscosity.[10,13] Thus, if the morphology of solid particles is the same, the content of solid phases would play an important role in the pyroplastic deformation. The content of mullite phases in the system was already reported as the main parameter on the system viscosity.[12] But, whether the morphology of solid phases affects the pyroplastic deformation is unclear.

The study presented in this report considers the effect of different solid phases on the pyroplastic deformation of porcelain samples. Because in the clay-feldspar-quartz system, mullite phases were found to be responsible for the pyroplastic deformation, thus, for fair comparison, different minerals were used in this study to introduce different solid phases (other than mullite phase) and understand the influence of those solid phases on the pyroplastic deformation. The morphology and distribution of the different solid particles in the sample are the main focus.

2. Experimental procedure

2.1 Sample preparation

Six materials from different suppliers were prepared, with respect to kaolin clay, calcinated kaolin clay, clay-ash powders, andalusite, quartz and feldspar. All the materials were analyzed by X-ray Fluorescence (XRF) analyzer (Axios-Advanced, PANalytical B.V., Netherlands) before experiment in order to determine the chemical composition of starting materials. Four types of samples were prepared, namely F1 to F4. Each sample consists of three starting materials. Quartz and feldspar were used in all types of samples and one of the other minerals (kaolin clay, calcinated kaolin clay, fly-ash powders and andalusite) is used to understand the influence of different minerals on the pyroplastic deformation of porcelain sample. Meanwhile, the batch formulas are calculated according to the chemical composition of each sample. The chemical compositions of different starting materials used in the sample preparation and different samples are listed in
Summary of specimens were measured by EDS which is attached to the SEM. The chemical compositions of different phases in the scanning electron microscope (JSM-5610LV, Japan) was employed. The chemical compositions of different phases in the specimens were measured by EDS which is attached to the SEM.

Cooling, the sample was taken out for analysis. After other impact on the pyroplastic deformation of the sample. After cooling, the quantity of maximum deformation (mm), b is the bar thickness (mm) and l is the distance between two supports (mm). Figure 1 shows the schematic drawing of experiment system, in which, s is calculated by \( h_0 - h \), where \( h_0 \) is the height of the supports and \( h \) is the distance between the bottom of specimen and the bottom of the support. Figure 2 shows the pyroplastic index as a function of firing temperature. The figure evidently shows that the deformation of samples F1 and F2 differs substantially from samples F3 and F4.

The X-ray diffraction patterns obtained from the detachment of samples baked at 1573 K for 2 h are shown in Figure 3. Two main phases in sample F1 to F3 can be identified by the patterns, namely quartz and mullite. However, in sample F4, andalusite phase, instead of mullite phase is found along with quartz phase.

| Table 1. The chemical composition (wt%) of raw materials |
|--------------------------------------------------------|
| Raw materials          | SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | MgO | K₂O | Na₂O | L.O.I |
|------------------------|------|-------|-------|------|-----|-----|-----|------|------|
| Kaolin clay            | 49.42| 35.19 | 2.12  | 0.15 | 0.06| 0.08| 0.07| 0.07  | 12.39|
| Calcinated kaolin clay | 55.56| 40.53 | 0.84  | 1.20 | 0.17| 0.13| 0.18| 0.19  | 0.49 |
| Fly ash                | 46.40| 42.66 | 1.52  | 2.10 | 2.06| 0.13| 0.48| 0.09  | 3.55 |
| Andalusite             | 44.72| 47.85 | 1.97  | 0.24 | 0.31| 0.34| 1.30| 0.43  | 2.41 |
| Feldspar               | 66.18| 18.64 | 0.10  | tr.  | 0.17| tr. | 12.45| 2.01  | 0.50 |
| Quartz                 | 98.32| 1.01  | 0.08  | tr.  | 0.12| 0.09| 0.10| 0.10  | 0.10 |

Table 2. The chemical composition (wt%) of sample F1 to F4

| Sample | SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | MgO | K₂O | Na₂O |
|--------|------|-------|-------|------|-----|-----|-----|------|
| F1     | 71.35| 23.95 | 1.23  | 0.08 | 0.11| 0.07| 2.74| 0.46 |
| F2     | 71.29| 24.24 | 0.46  | 0.60 | 0.16| 0.09| 2.63| 0.53 |
| F3     | 71.32| 22.71 | 0.71  | 0.91 | 0.97| 0.09| 2.79| 0.49 |
| F4     | 71.17| 23.77 | 0.86  | 0.10 | 0.21| 0.18| 3.10| 0.62 |

Table 3. The batch formulas (wt%) of the sample

| Sample | Kaolin clay | Calcinated kaolin clay | Fly ash | Andalusite | Feldspar | Quartz |
|--------|-------------|------------------------|---------|------------|----------|--------|
| F1     | 52.0        | —                      | —       | —          | 20.0     | 28.0   |
| F2     | —           | 49.4                  | —       | —          | 20.0     | 30.6   |
| F3     | —           | —                     | 42.5    | —          | 20.0     | 37.5   |
| F4     | —           | —                     | —       | 40.4       | 20.0     | 39.6   |

Visual examination reveals great differences of pyroplastic deformations for different samples after the experiments. The influence on the pyroplastic deformation by different mineral is strong. Slight deformation was observed in samples F1 and F2 whereas strong deformation is performed in samples F3 and F4.

To describe the pyroplasticity, the pyroplastic index (PI) is defined by the following equation:

\[
PI = \frac{s b^2}{l^2}
\]

Where \( s \) is the quantity of maximum deformation (mm), \( b \) is the bar thickness (mm) and \( l \) is the distance between two supports (mm).

3. Results

After experiment, the quantity of pyroplastic deformation was measured by the Vernier Caliper. X-ray diffraction (XRD) (Rigaku Rint D/max-III, Japan) was used to identify the phases of different samples. Small parts of the samples were peeled off and crush into very fine powders for the XRD analysis. The microstructure of the specimen was analyzed by scanning electron microscopy (SEM) after Au-Pd coating. In this study, scanning electron microscope (JSM-5610LV, Japan) was employed. The chemical compositions of different phases in the specimens were measured by EDS which is attached to the SEM.

The pyroplastic index as a function of firing temperature.

Fig. 1. The schematic drawing of experiment system.

Fig. 2. The pyroplastic index as a function of firing temperature.
of pyroplastic deformation in sample F3 is actually the largest, which indicates that the micro-structure in sample plays an important role. SEM analysis is performed in order to gain the information about the morphology of the phases. Figure 4 shows the morphology of sample F1 and F2 fired at 1573 K with etching in the 5% HF solution for 60 s. The micro-structures of sample F1 and F2 are similar. The elongated club-shaped mullite and quartz are found. It should be pointed out here that the result of EDS analysis may not be accurate. There is one opinion that the mullite phases are surrounded by the glass matrix which makes the EDS analysis difficult, so the accurate stoichiometric chemical composition requirement of mullite from the sample is impossible. However, it is still believed that the primary mullite is in clay relict region and beside that region, elongated club-shaped phases are the secondary mullite.15) Those secondary mullite crystals form a network of cross-linking structure and distribute uniformly.

The microstructure of sample F3 fired at 1573 K is performed in Fig. 5. Figure 5(a) shows the micro-structure of sample F3 after etching in the 5% HF solution for 60 s. Some phases are found agglomerated on the sphere ball surface. To identify those phases, the same specimen without etching was sent to SEM analysis after polishing. Figure 5(b) is the Back-scattering electron (BSE) image of the region with higher magnification. Two phases are identified. Phase 1 is found to be the liquid phase. Phase 2 is the mullite compound. In fact, this phase is found to be accumulated by some small mullite phases. To gain an insight into the agglomeration phenomena of mullite phases in sample F3, the raw material, fly-ash powders are sent for XRD and SEM analysis. The original powders and the powders fired at 1573 K are compared. The XRD patterns in Fig. 6 show that mullite is one of the main phases in both original powders and the powders fired at 1573 K. Figure 7 shows the microstructures of the fly-ash powders before and after heating. Figure 7(a) shows the microstructure of the original fly ash powders. The floaters are found as different small balls in the picture. EDS analysis gives the composition of the floater. The result indicates that those floaters are high melting point according to the phase diagram.16) Figure 7(b) is the morphology of fly ash powders fired at 1573 K with etching.
in 5% HF solution for 60 s. The mullite crystals grow on the surface of the floaters.

Figure 8(a) shows the secondary electron microphotograph of sample F4 fired at 1573 K with etching in 5% HF solution for 60 s. The square shaped crystals are isolated according to the picture. To identify those “small islands”, the detachment of the same specimen was sent to SEM analysis without etching. Figure 8(b) is the Back-scattering electron (BSE) image of sample F4. Two phases are detected by EDS analysis. The white phases are numbered as phase 3, which contain mostly Al₂O₃ and SiO₂ and the mole fraction is approximately 1:1. Phase 3 is recognized as andalusite phase. Phase 4 is the rest part, containing K₂O, Na₂O, Al₂O₃ and SiO₂ and it is suggested that this part is liquid phase. The chemical compositions of the phase 1 to phase 4 are summarized in Table 4.

4. Discussion

4.1 The effect of kaolin clay on pyroplastic deformation

The influence on the quantity of pyroplastic deformation by kaolin clay and calcinated kaolin clay is limited. It is believed that the transformation of kaolinite into mullite can be described as three stages with the rising of temperature.¹⁷,¹⁸

Table 4. The chemical composition (wt %) of the phase 1 to phase 4

| Phase     | SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | CaO | K₂O | Na₂O |
|-----------|------|-------|-------|------|-----|-----|------|
| Phase 1   | 71.93| 21.29 | 0.49  | 0.61 | 1.26| 3.59| 0.82 |
| (glassy phase) |      |       |       |      |     |     |      |
| Phase 2   | 27.47| 68.30 | 1.47  | 0.63 | 0.50| 1.63| tr.  |
| (mullite) |      |       |       |      |     |     |      |
| Phase 3   | 42.25| 49.33 | 6.09  | 0.55 | tr. | 1.77| tr.  |
| (andalusite) |     |       |       |      |     |     |      |
| Phase 4   | 75.63| 15.21 | 0.96  | 0.42 | tr. | 5.71| 1.58 |
| (glassy phase) |      |       |       |      |     |     |      |

Fig. 6. XRD patterns of original fly ash powders and fly ash powders fired at 1573 K.

Fig. 7. The microstructures of the fly-ash powders (a) original morphology (without etching) (b) fired at 1573 K (etching in 5% HF solution for 60 s).

Fig. 8. The microstructure of sample F4 fired at 1573 K (a) secondary electron image (etching in the 5% HF solution for 60 s) (b) Back-scattering electron image (without etching).
1. The dehydroxylation takes place at approximately 873 K and the kaolinite (Al₂O₃·2SiO₂·2H₂O) becomes metakaolinite (Al₂O₃·2SiO₂).
2. At 1198 K, the meta-kaolinite starts to decompose into Al-Si-Spinel (2Al₂O₃·3SiO₂) and SiO₂.
3. However, the Al-Si-Spinel phase only stays in a narrow temperature range and above 1298 K, Al-Si-Spinel turns into mullite (3Al₂O₃·2SiO₂ and SiO₂).

In the experiment, the raw material, calcinated kaolin clay, already decomposed into mullite and quartz. Differing from kaolin clay, the calcinated kaolin clay is a non-plastic material and this is the main difference between those two materials. However, the liquid phase does not appear in the first stage, thus, this stage is not the main effect on the quantity of pyroplastic deformation. That is the reason why the samples with kaolin clay and calcinated kaolin clay deform almost the same.

The lowest melting point among those three raw materials is feldspar which is above 1273 K. Along with the generation of liquid, the sample becomes dense and soft. There are two kinds of mullite in sample F1, namely primary mullite and secondary mullite. The distribution of those two kinds of mullite is studied and it is concluded that the primary mullite is located in the clay relic region which is the decomposition of kaolinite. With the generation of liquid phase, the mullite and quartz start to dissolve. The saturation of mullite in the melt results in the precipitation and growth of mullite in the liquid phase. Those needle shaped mullite phases are recognized as secondary mullite.

Lots of researches argued that the strength of ceramic body can be enhanced by mullite whiskers. However, it is also believed that the uniform dispersion of solid particles suspension in liquid makes viscosity higher and the viscosity of melts during the heating is one of the parameters which influence the deformation of porcelain. Since the feldspar begins to melt, under the heating is one of the parameters which influence the defor-

### Table 5. The content (wt%) of different phases in sample

| Sample     | Quartz | Mullite | Andalusite |
|------------|--------|---------|------------|
| F1(1533 K) | 52.7   | 47.3    | —          |
| F1(1573 K) | 49.1   | 50.9    | —          |
| F2(1533 K) | 44.0   | 56.0    | —          |
| F2(1573 K) | 42.3   | 57.7    | —          |
| F4(1533 K) | 41.8   | —       | 58.2       |
| F4(1573 K) | 36.9   | —       | 63.1       |

in sample F1 and F2, the mullite crystals in sample F3 grow by agglomeration and this may be the main reason that the descending of sample F3 after experiment is larger than sample F1 and F2. The floaters in fly ash powders are covered by mullite crystals and mullite crystals grow on the surface of the floaters during the heating. As the mullite already in fly ash powders, the growth of mullite in sample F3 becomes easier and causes the agglomeration. It is believed that the value of viscosity decreases if the solid particles agglomerate and settle down. Therefore, the influence of agglomerated mullite particles on the viscosity of the melts in the sample is limited. The low value of liquid viscosity in sample F3 allows the large quantity of deformation of the sample.

### 4.3 The effect of andalusite on pyroplastic deformation

Little mullite is found in sample F4 fired at 1573 K according to the XRD analysis. It is found that slowly mullitization happens below 1673 K. Only about 20% andalusite grains transforms in the first two hours at 1623 K. The firing temperature of experiment here is no more than 1593 K which means the mullitization of andalusite is lower than 20%. The semi-quantitative assessment in XRD analysis by Jade 6.5 reveals that with temperature increasing, the amount of andalusite phase in sample F4 grows but the silica content reduces. But the content of different components in other samples keeps steady with the temperature rising. This semi-quantitative assessment only considers the content of the main solid phases in the XRD patterns without the liquid phase and the content of those phases are normalized. In the XRD patterns, mullite and quartz are found in sample F1 and F2, whereas andalusite and quartz are found in sample F4, so only two phases in each sample are presented. Table 5 presents the content of different phases in different samples fired at 1533 and 1573 K respectively. One hypothesis can be drawn as following: the solubility of andalusite in the melts (which is generated by the feldspar) is low even with the temperature rising, so more silica is dissolved into the melts during the heating.

The quantity of pyroplastic deformation of sample F4 indicates that the sample deforms a lot, if andalusite is involved. The illustrations are given as following:

1. Although the EDS analysis can only semi-quantify the content of the chemical composition, the high content of K₂O component in the liquid phase of sample F4 lower the viscosity value and influence the deformation value of sample as a result.
2. The SEM morphology shows that the distribution of andalusite in sample F4 is not uniform as well as the distribution of mullite in sample F3. The heterogeneity of andalusite distribution in the liquid causes the viscosity value of liquid phase low and makes the sample deforms.

It should be pointed out here that the flow of the glassy phase at high temperature plays an important role on the distortion...
of the ceramics shape.\textsuperscript{32)} Hence, the value of viscosity of those liquid phases during the heating becomes essentially important. Lots of studies\textsuperscript{33}\textsuperscript{35}) show that the distribution of solid particles makes the liquid more viscous, so the embedded phase in the glassy phase is crucial to the pyroplastic deformation. Differing from mullite whiskers precipitation and growth in the sample F1 and F2, the mullite or andalusite phases in sample F3 and F4 are introduced by fly ash powders and andalusite minerals, respectively. All the raw materials are grained and mixed together physically. Although all the materials are grained and mixed well, it is difficult to guarantee the uniformed distribution of those phases in the melts during the heating. The heterogeneous distribution leads to the solid particles agglomeration.

5. Conclusion

The influence of different minerals on the pyroplastic deformation of porcelain was studied experimentally. The mullite crystals introduced by different raw materials were with different morphologies. The un-decomposition of andalusite phase in the samples with large crystals introduced by different raw materials were with different morphologies. The un-decomposition of andalusite phase in the sample F1 after experiment was one evident. The agglomeration of solid particles was evidentially found in the samples with large deformation. The main factor on the pyroplastic deformation was found to be the distribution of solid phases in the liquid phase during the heating. The results indicated that the evenly dispersion of solid particles over the glassy phase of the sample would reduce the quantity of deformation.

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