

## PRODUCTION AND QUANTIFICATION OF HIGH-PURITY MULLITE AT 1600°C FROM KAOLINITIC CLAY AND CALCINED ALUMINA

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A study is performed to determine the reaction time which is required at 1600°C to obtain mullite from clay with a high content of kaolinite (clay from the La Rioja Province of Argentina) and from a stoichiometric mixture of the clay and calcined alumina of grade Almatis-A2G. The chemical composition of the raw materials was determined and they were studied by x-ray diffraction (XRD) and examined on a scanning electron microscope (SEM). The materials were then mixed in the stoichiometric proportions  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and pressed at 100 MPa. The pressed specimens were fired at 1600°C in electric furnaces for different lengths of time: 0.25, 0.5, 1, 2, 3, and 5 h. Their density and porosity were determined after they were fired. In the studies performed on the scanning electron microscope and by x-ray diffraction; the crystalline phases were identified by the Rietveld method and the amorphous phases were determined by means of the Le Bail model. The objective was to determine the amounts of primary and secondary mullite that were present and the total mullite content.

**Keywords:** synthetic mullite, sintered mullite, quantification, primary and amorphous mullite, total amount of mullite.

### INTRODUCTION

Mullite  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  is widely used to make high-alumina refractories [1, 2]. There are few published studies of the methods that are used to obtain high-purity synthetic sintered and electrofused mullite, since that is proprietary information of the companies which make these materials. However, this very obstacle has served as a stimulus to perform scientific studies with the use of regional raw-material resources. Nearly 10% of high-purity synthetic sintered mullite is composed of the glassy phase.

Most silicate-alumina refractories contain mullite. The mullite is not added to these refractories but is instead formed in the raw materials during their heating or subsequent use. Thus, the system  $\text{SiO}_2\text{--Al}_2\text{O}_3$  has been carefully studied [3, 4] in refractory clays and other silicate-alumina materials.

We performed studies to obtain high-purity mullite from kaolinitic clay and calcined alumina. The clay and alumina

were mixed in the stoichiometric proportions  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and were then pressed and fired at 1600°C for different lengths of time — from 0.25 to 5 h. Clay and a mixture of clay with alumina were studied as the raw materials and their density and porosity were determined. The study was performed on a scanning electron microscope (SEM) and an x-ray diffractometer (XRD). The crystalline phases were determined by the Rietveld method, while the amorphous phases were determined using the Le Bail Model.

### EXPERIMENTAL PROCEDURE

The study was conducted with the use of kaolinitic clay from the La Rioja deposit in Argentina (this material is referred to as Arioja) and calcined alumina of the Acal grade. Both materials were studied by XRD to determine their chemical composition and identify the crystalline phases. The chemical composition of Arioja clay, wt. %:  $\text{SiO}_2$  45.90;  $\text{Al}_2\text{O}_3$  37.00;  $\text{Na}_2\text{O}$  0.06;  $\text{K}_2\text{O}$  0.40;  $\text{CaO}$  0.08;  $\text{Fe}_2\text{O}_3$  0.77;  $\text{MgO}$  0.12;  $\text{TiO}_2$  0.99; other components 1.38; loss on calcination 13.30.

The chemical composition was determined with the use of inductively coupled plasma atomic-emission spectroscopy (ICP-AES). The silica and alumina contents in this clay were

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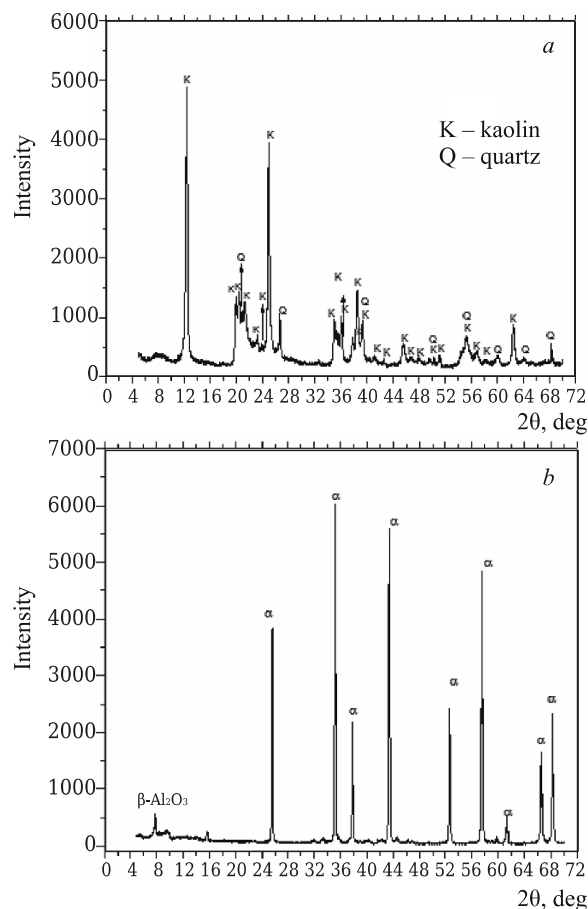


Fig. 1. Diffraction patterns ( $\text{Cu K}\alpha_1$ ) of the raw material: a) Arioja clay; b) calcined alumina.

determined to be favorable for the production of mullite. The chemical composition of the calcined alumina was taken from the specifications provided by the supplier. The specifications stated that the material had an  $\text{Al}_2\text{O}_3$  content of 99.5% and that the average grain size was 5  $\mu\text{m}$ . Figure 1 presents diffraction patterns of the Arioja clay and the calcined alumina.

The diffraction patterns of the Arioja clay (see Fig. 1a) indicate that the kaolinitic-clay raw material contains two characteristic minerals: quartz and kaolinite [5]. The kaolinite has the highest-intensity peak and the quartz has the peak of the lowest intensity. It is apparent from the diffraction pattern of the calcined alumina that the largest part of the crystalline phases consists of  $\alpha\text{-Al}_2\text{O}_3$ , while  $\beta\text{-Al}_2\text{O}_3$  ( $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ ) is present in trace amounts. Alumina  $\beta\text{-Al}_2\text{O}_3$  is obtained in the Bayer process, which uses  $\text{NaOH}$  to extract aluminum from bauxite [6].

When the loss during calcination at 200–800°C was taken into account, the clay material was determined to have a kaolinite content of 96.7% (this result was obtained by thermogravimetry (TG) on the basis of the stoichiometric composition of kaolinite).

The raw materials were mixed in stoichiometric proportions with allowance for the physical and chemical data obtained from studying the raw materials. The final composition of the mullite was  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  [7, 8]. The prepared mixture was pressed into prismatic briquettes at a pressure of 100 MPa, the dimensions of the briquettes being  $5.0 \times 0.8 \times 0.8 \text{ cm}^3$ . The same procedure was used with the Arioja clay to obtain specimens of the same shape and dimensions at the same pressure.

The specimens were then subjected to heat treatment (firing) to complete the conversion to mullite. The firing operation was performed in a tubular furnace at 1600°C for different periods of time: 0.25, 0.5, 1, 2, 3, and 5 h. The specimens were left in the furnace for a certain amount of time before being removed from it.

To prevent cracking of the specimens when they were placed in a furnace that had already been heated to 1600°C, they were preheated to 800°C for 1 h. The preheating allowed the water vapor that was formed during the decomposition of the clay to be freely released from the material.

The fired specimens were then subjected to examination: porosity and density were determined by Archimedes' method (IRAM 12510); the amount of mullite formed at the given temperatures over different lengths of time was determined by scanning electron microscopy (SEM), x-ray diffraction (XRD), and the Rietveld method (the latter was used to determine the number of crystalline phases). The mullite obtained from the clay was primary mullite; secondary mullite was formed from the clay-alumina mixture during the reaction between the calcined alumina and silica that was produced by the thermal decomposition of the clay. The combined amounts of primary and secondary mullite comprise the total amount of mullite (primary + secondary).

The percentage content of secondary mullite was calculated by taking the total amount of mullite and subtracting the amount of primary mullite after it was multiplied by the appropriate dilution factor (0.5187) [2, 9].

## RESULTS AND DISCUSSION

Density and porosity were determined only for specimens of the clay-alumina mixture so as to obtain representative values for the final properties of the mullite that was produced by sintering at 1600°C. The results are shown in Table 1.

It is evident from Table 1 that, except for the first several minutes, there is a tendency for density to increase and porosity to decrease as the heating operation continues.

The behavior that was observed can be explained as follows:

a) two processes take place simultaneously at the firing temperature during the first several minutes: the formation of mullite from the clay; the formation of mullite during secondary mullitization that occurs in the course of the reaction between the calcined alumina and silica which is produced

when the clay undergoes thermal decomposition. The first process takes place at a higher rate than the second process, since in that case there are no diffusional barriers to prevent the formation of primary mullite;

b) over a period of nearly 0.5 h (30 min), density decreases and porosity increases (the decrease and increase are relative to the results obtained over 0.25 h (15 min)). This finding confirms the completion of the secondary mullitization process — which is accompanied by expansion of the material's volume — and completion of sintering of the existing material and the newly formed material (secondary mullite). Since secondary mullite is dominant in this case, there is a decrease in density and a corresponding increase in porosity;

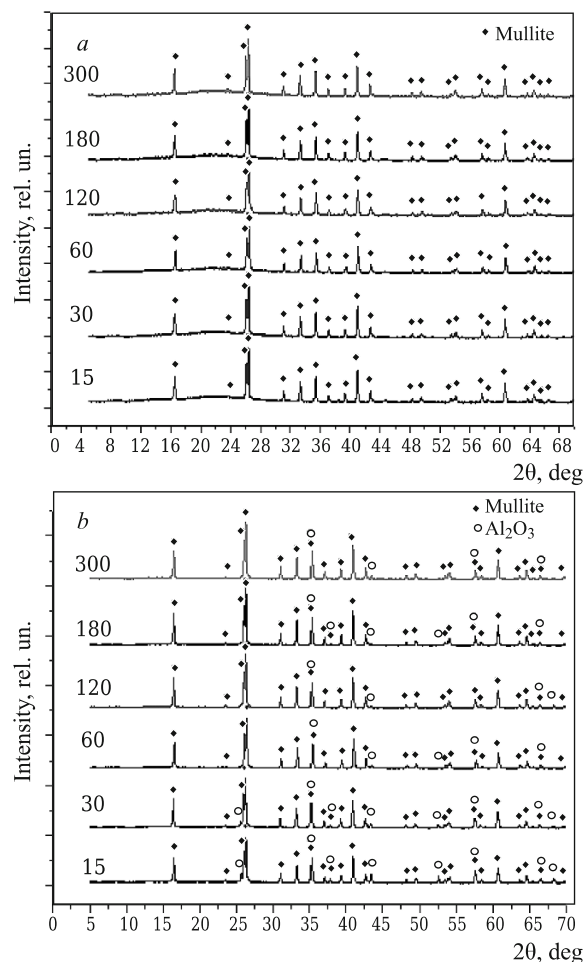
c) with heating for more than 0.5 h (30 min), secondary mullitization ends while being accompanied by complex dissolution-crystallization processes (we refer back to the discussion of the results obtained on the x-ray diffractometer), and sintering rather than mullite formation becomes the dominant process. In other words, porosity tends to decrease and density tends to increase with an increase in heating time.

The high porosity indices obtained with heating for 5 h (300 min) at 1600°C can be attributed to the fact that the specimens were quickly charged into the furnace. That was done in order to be able to further study the kinetics of the process with the use of different temperatures and heating times. As a result, the formation and sintering of mullite inside the mixture took place more slowly than in the case of the sintering of an amorphous phase having a high concentration of silica formed during decomposition of the clay prior to the reaction with alumina (the melting point of silica is approximately 1720°C, i.e. it is close to the heating temperature used in our investigation) [2, 10]. This created a low-density, high-porosity system even when heating was continued at high temperatures for an extended period of time. Such a result suggests that a significant number of closed pores was formed during rapid heating.

#### X-RAY DIFFRACTION OF THE CLAY WITH A STOICHIOMETRIC MIXTURE OF CLAY AND ALUMINA CALCINED AT 1600°C

Figure 2 shows juxtaposed diffraction patterns graphs obtained on the x-ray diffractometer. The clay was heated at 1600°C for different periods of time, and the stoichiometric mixture of clay and calcined alumina was exposed to conditions under which mullite could form. The heating of the mixture was done under the same conditions used to heat the clay.

It is apparent from Fig. 2a that only one crystalline phase — the mullite phase (primary mullite) — is present regardless of the duration of the reaction. Thanks to the properties of the chosen clay — which was composed almost entirely of kaolinite — the residual product of the reaction was



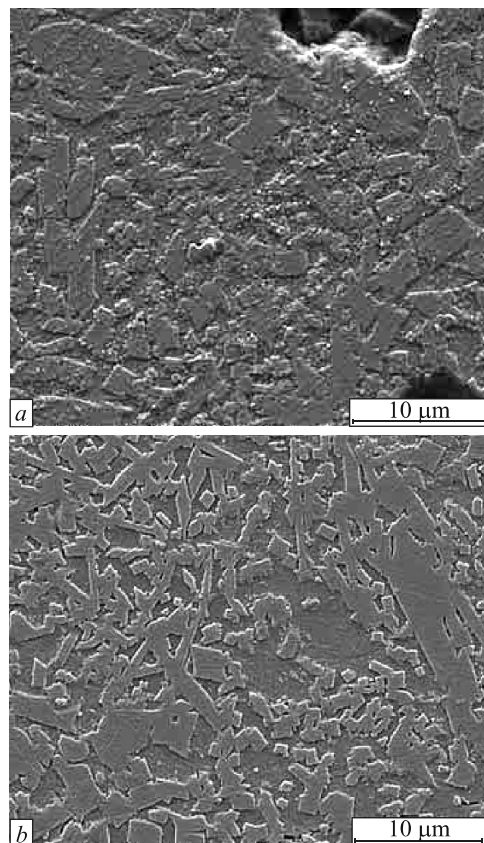
**Fig. 2.** Diffraction patterns obtained on the x-ray diffractometer ( $\text{Cu K}\alpha_1$ ) at 1600°C for periods of different lengths (indicated in minutes) during the firing operation (0.25, 0.5, 1–3, and 5 h): a) clay; b) mixture of clay and calcined alumina).

amorphous quartz. This is visible on the graph in the form of the high background and the distinct middle band at 21.80° 2θ (the highest-intensity peak of silica is seen at this position in the form of cristobalite).

Examination of this series of diffraction patterns shows mullite in the form of a crystalline phase that is present in the same amounts. The glassy or amorphous phase is seen in the form of the wide band centered at 21.80° 2θ.

**TABLE 1.** Density and Porosity of Specimens of a Mixture of Clay and Alumina Fired at 1600°C for Different Lengths of Time

| Indices                    | Firing time, h |       |       |       |       |       |
|----------------------------|----------------|-------|-------|-------|-------|-------|
|                            | 0.25           | 0.5   | 1     | 2     | 3     | 5     |
| Density, g/cm <sup>3</sup> | 2.24           | 2.19  | 2.21  | 2.28  | 2.31  | 2.34  |
| Porosity, %                | 25.29          | 26.26 | 24.84 | 20.59 | 19.62 | 17.86 |



**Fig. 3.** Micrographs of clay obtained on the scanning electron microscope; the clay was pressed at 100 MPa and fired at 1600°C for 5 h ( $\times 8000$ ): *a*) polishing was done without chemical etching; *b*) with chemical etching by 5% HF.

The graphs obtained from a mixture of clay and alumina and shown in Fig. 2*b* also indicated the presence of mullite in the form of the main crystalline phase.

In Fig. 2*b*, which shows graphs obtained from a mixture of clay and alumina, mullite is again present in the form of the main crystalline phase. The amorphous phase seen previously in the form of a wide band centered at  $21.80^\circ 2\theta$  is not visible in this case. The specimen contained a very small amount of crystalline alumina  $\alpha\text{-Al}_2\text{O}_3$ . The reaction was nearly complete after 1 h thanks to the nearly complete absence of the  $\alpha$ -alumina phase. The fact that there were small amounts of alumina present with the use of heating periods of different durations means that when we used a stoichiometric mixture to form mullite we obtained a certain amount of a glassy phase that was amorphously enriched with silica. The glassy phase did not enter into reaction with the available alumina, so the system did not undergo complete transformation.

### MICROSCOPIC STRUCTURE OF THE CLAY WITH A STOICHIOMETRIC MIXTURE OF CLAY AND ALUMINA CALCINED AT 1600°C

We pressed specimens at 100 MPa to be able to determine and differentiate between the microstructure of mullite formed from the clay and the microstructure of mullite formed from the reaction of the stoichiometric mixture of clay and calcined alumina. The specimens were fired at 1600°C over 5 h and then examined under a scanning electron microscope (SEM).

To remove the glassy and amorphous phases formed during calcination (these phases are visible when the specimens are studied by XRD on an x-ray diffractometer), we chemically etched the specimens with 5% hydrofluoric acid HF for 10 min. Figures 3 and 4 show the above-mentioned micrographs.

Figure 3*a* shows the micrograph of clay that did not undergo chemical etching. The surface of the mullite that was formed (primary mullite) and the amorphous phase are both visible. The low relief was due to the fact that the glassy amorphous phase eroded more rapidly than the mullite during polishing. The micrograph of the etched specimen (Fig. 3*b*) shows the presence of a distinct relief on the mullite (primary). Thus, the amorphous phase with the high silica content was removed by the hydrofluoric acid.

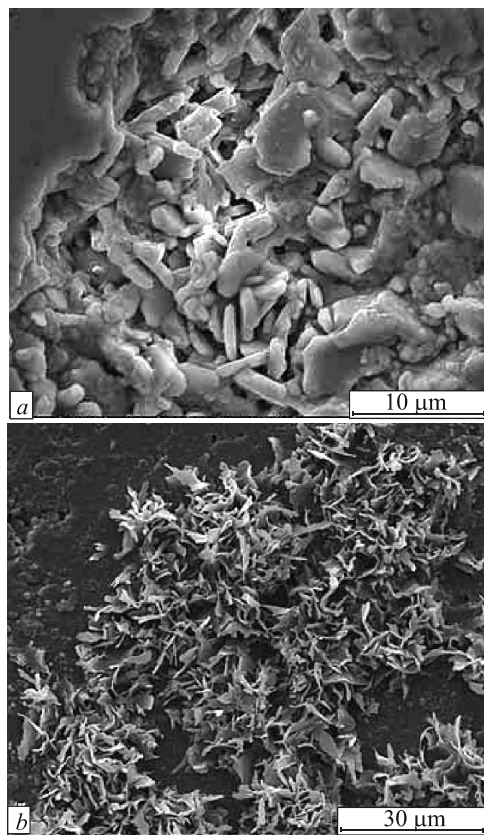
Figure 4*a* shows a micrograph of the mixture of clay and alumina without chemical etching. It can be seen that mullite is present in the form of sticks with rounded tips. These are sintering zones of different sizes that are not positioned in any particular order [11]. The micrograph in Fig. 4*b* is of a specimen that was chemically etched with 5% HF for 10 min. It can be seen from the micrograph that the laminar memory of the mixture is left uncovered by chemical etching of the glassy phase. This means that the mullite plates are positioned in the form of a raised relief (the micrographs were obtained on the pressed surface).

### QUANTIFICATION OF THE PHASES PRESENT IN THE CLAY AND THE STOICHIOMETRIC MIXTURE OF CLAY AND ALUMINA

We used the Rietveld method to determine the quantities of the crystalline phases that were present by means of XRD and we used the Le Bail model to determine the amorphous phase that was formed in the system. Here, the silica glassy phase was entered into the computer program with excess defects in the dimensions of the crystallites (volatile amorphous silica) [13].

Only the structure factor improved when the glassy phase was determined with the use of the Le Bail model. For the other phases, there were improvements in not only the structure factor but also the cell parameters and the parameters that describe the model. To improve the background the intensity was kept at a constant level within the range from 5





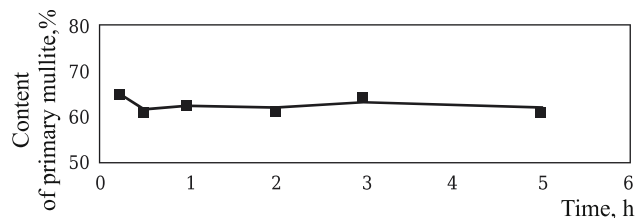
**Fig. 4.** Micrographs of the clay-alumina mixture obtained on the scanning electron microscope; the mixture was pressed at 100 MPa and fired at 1600°C over 5 h ( $\times 8000$ ): *a*) polishing was done without chemical etching; *b*) with chemical etching by 5% HF.  $\times 3000$ .

to 45°, where the amorphous band is located. The intensity of the background was improved in the remaining part of the diffraction pattern.

#### Quantification of the crystalline phases and amorphous clay

The amounts of the crystalline phases that were present (mullite, quartz, and cristobalite) were determined by the Rietveld method, while the contents of the amorphous phases were determined using the Le Bail model (Table 2).

Table 2 shows the composition of the (primary) mullite phase, quartz phase, and amorphous phase. The results indicate the absence of cristobalite as a crystalline phase. Also, all of the mullite indices of the clay (59.40%) are greater than the maximum amount that could theoretically be formed in accordance with the chemical composition of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . However, the indices are within the limits of the error associated with the use of the quantification method. The error is also dependent on the amount of the amorphous phase formed in the system. The quantification error is smaller in systems with 10% amorphous phase.



**Fig. 5.** Time dependence of the content of primary mullite in clay fired at 1600°C.

#### Results of quantification of primary mullite at 1600°C

Figure 5 shows the change in the content of primary mullite in the clay over time. The glassy phase formed at 1600°C is more fluid than the compositions which contain alumina (it has a lower viscosity), which facilitates and intensifies diffusion during the dissolution-crystallization process. This supports the view that mullite content undergoes broad fluctuations over time [11, 14].

Primary mullite is formed over a period of time averaging 2 h. However, the solubility of mullite in the glassy phase increases at higher temperatures, as is the case in most systems in which dissolution-crystallization takes place.

It is apparent from the silica-alumina phase diagram [15] that an increase in the content of alumina compared to the content of silica is accompanied by a decrease in the system's melting point and an increase in the amount of liquid in the amorphous matrix compared to amount of solid material that is present. These findings validate the proposition that the system undergoes dilution.

#### Quantification of the amorphous and crystalline phases in the stoichiometric mixture of clay and alumina

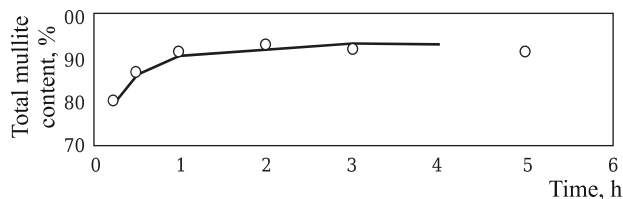
Table 3 shows the results obtained from quantification by the Rietveld method with the use of the Le Bail model of the clay-alumina mixture.

After firing at 1600°C for 2 h, total mullite content reaches roughly 92%, the amounts of the amorphous phase and alumina remain roughly the same, and a small amount of

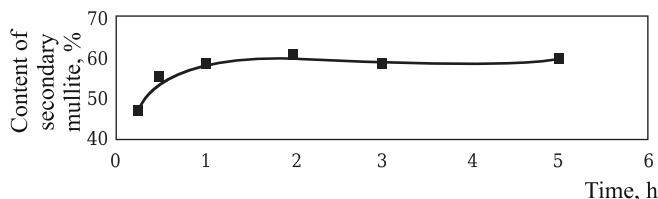
**TABLE 2.** Contents of the Phases in Clay Fired at 1600°C for Different Lengths of Time

| Time, h | Content*, %       |        |                 |
|---------|-------------------|--------|-----------------|
|         | mullite (primary) | quartz | amorphous phase |
| 0.25    | 64.98             | 1.03   | 33.99           |
| 0.50    | 61.28             | —      | 38.72           |
| 1       | 62.78             | 0.81   | 36.41           |
| 2       | 61.58             | 1.81   | 36.61           |
| 3       | 64.40             | —      | 35.60           |
| 5       | 61.62             | —      | 38.38           |

\* No cristobalite was observed



**Fig. 6.** Total mullite content of the clay-alumina mixture in relation to firing time at 1600°C.



**Fig. 7.** Secondary-mullite content of the clay-alumina mixture at different times during the mixture at 1600°C (the content of secondary mullite was determined based on the total mullite content minus the content of primary mullite).

quartz is present. No significant changes in total mullite content are seen in this case, compared to the case of clay (primary mullite). This result is due to consumption of the glassy phase. Thus, the rate of the mullite dissolution-crystallization process in the glass decreased. The viscosity of the glassy phase increased compared to the clay's glassy phase because it contained more alumina. As a result, the refractoriness of the system also increased.

#### Quantification of the total amount of mullite at 1600°C

The total content of mullite that was formed was taken from Table 3. We then used this data to construct the time-dependence curve of the transformation process (Fig. 6).

Figure 6 shows the total amount of mullite (the sum of primary mullite and secondary mullite);

**TABLE 3.** Contents of the Phases in the Stoichiometric Mixture of Clay and Alumina after Its Firing at 1600°C for Different Lengths of Time

| Time, h | Content*, %     |                   |        |                |
|---------|-----------------|-------------------|--------|----------------|
|         | mullite (total) | $\alpha$ -alumina | quartz | amorphous zone |
| 0.25    | 80.85           | 14.89             | 0.41   | 3.85           |
| 0.50    | 86.75           | 7.91              | 0.05   | 5.29           |
| 1       | 91.33           | 3.49              | 0.15   | 5.03           |
| 2       | 92.82           | 2.77              | 0.50   | 3.90           |
| 3       | 91.86           | 4.12              | 0.16   | 3.86           |
| 5       | 91.49           | 3.83              | 1.26   | 3.43           |

\* No cristobalite was observed.

- primary mullitization: mullite formed from clay;
- secondary mullitization: mullite formed from the reaction of alumina and the amorphous phase of silica in the clay.

It was observed that at 1600°C the mullitization process is completed in 1 h. The amount of mullite formed reaches 92% and remains at that level. The amorphous phase and small quantities of different substances dispersed throughout the material account for the remaining 8%. The final indices of the system are nearly the same as the indices for the high-purity (91% mullite) synthetic mullite available in the European market.

#### FORMATION OF SECONDARY MULLITE

The content of secondary mullite was calculated based on the quantitative composition of the clay (primary mullite) and the stoichiometric mixture of clay and calcined alumina (the total amount of mullite) that was fired at 1600°C for different lengths of time. The results in Table 4 were obtained by taking the total amount of mullite and subtracting the content of primary mullite (the content of primary mullite was determined by multiplying the amount of clay by the dilution factor of the mixture (0.5187)).

Table 4 shows the effect of firing time on the fractional content of primary mullite (clay) in a system diluted with calcined alumina  $\text{Al}_2\text{O}_3$ . The mullite underwent dissolution and precipitation in the system, as occurred in high-silica clay in the amorphous phase [8, 16, 17].

Figure 7 shows the content of secondary mullite formed in the clay-alumina mixture when it was fired at 1600°C for different periods of time.

Figure 7 shows that there were small fluctuations in the content of secondary mullite at the point corresponding to longest firing time. However, these variations are within the limits of the error that is allowed when the quantification method is used. There was a small amount of amorphous phase, as there was in the clay.

**TABLE 4.** Total Mullite Content, Content of Mullite Dissolved in the Primary System with  $\text{Al}_2\text{O}_3$ , and Content of Secondary Mullite after Firing at 1600°C for Different Lengths of Time

| Firing time, h | Content, %               |   |  |
|----------------|--------------------------|---|--|
|                | total content of mullite | content of primary mullite (system diluted by $\text{Al}_2\text{O}_3$ ) | content of secondary mullite (minus the primary mullite) |
| 0.25           | 80.85                    | 33.71   | 47.14  |
| 0.50           | 86.75                    | 31.79   | 54.96  |
| 1              | 91.33                    | 32.56   | 58.77  |
| 2              | 92.82                    | 31.94   | 60.88  |
| 3              | 91.86                    | 33.40   | 58.46  |
| 5              | 91.49                    | 31.96   | 59.53  |

## CONCLUSION

The Rietveld – Le Bail methods of quantitative analysis were used to analyze the phases in systems such as mullite (primary) in kaolinitic clay and in a mixture of clay and alumina that was fired at 1600°C for different lengths of time.

When subjected to intense firing at 1600°C, the clay (96.7% kaolinite) forms a large amount of the glassy phase and contains large amounts of silica and primary mullite. The dissolution-crystallization (glass – mullite) process continues as long as the system remains at that temperature, so large fluctuations in the amount of mullite which is formed are seen over time. Such fluctuations decreased to a minimum in the firing of the mixture of clay and alumina, since the mobility of the glassy matrix is reduced by presence of a large amount of alumina and its greater refractoriness.

Secondary mullite is formed during the reaction between the alumina in the mixture and the silica which is formed by the thermal decomposition of the clay. The content of secondary mullite was calculated for heating periods of different lengths by taking the total amount of mullite formed from the clay-alumina mixture and subtracting the amount of primary mullite formed from the clay.

Study of the system showed that at 1600°C (with heating for different lengths of time) primary mullitization takes place almost instantaneously, while the secondary-mullite transformation reaches its maximum in 2 h.

Quantitative analysis of the system showed that when the transformation proceeds to completion, the amount of mullite in the crystalline phase is consistent with the indices that characterize mullite of similar quality (roughly 92% mullite and 8% crystalline phase) which is for same on the market.

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