

# PHASE COMPOSITION AND PROPERTIES OF MULLITE CERAMIC IN HIGH-TEMPERATURE TESTING

Gaida Sedmale, Ingunda Sperberga, Uldis Sedmalis

Riga Technical University, Institute of Silicate Materials, Azenes str. 14/24, LV-1048, Latvia, E-mail: [gseidmale@ktf.rtu.lv](mailto:gseidmale@ktf.rtu.lv).

**Abstract:** Mullite-containing ceramics prepared from compositions - illite clay and aluminium hydroxide has been studied. High-temperature resistance of samples was studied in temperature range 1200 to 1500<sup>o</sup>C by measuring of the linear firing shrinkage, compression strength and phases composition after each temperature cycle. The changes in phase composition and structure shows that increase of content of new formations of mullite with an increasing of testing temperature takes place along with growth of dimensions of needle-like crystals of mullite. It is considered to be the factor for the preservation of mechanical strength of samples in the range of 28-32 MPa up to 1400<sup>o</sup>C.

**Keywords:** Mullite ceramic, illite clay, high-temperature testing, compression strength

## 1. Introduction

Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) is a characteristic constituent of all ceramic products made from aluminosilicates and has become a candidate as a high-temperature structural ceramic. The mullite ceramic has had and will continue to have a significant role in the development of traditional and advanced ceramics. Mullite is the only stable crystalline phase in the aluminosilicate system under normal atmospheric pressure at room through elevated temperatures [1]. Mullite exhibits high refractoriness, low thermal expansion, low thermal conductivity, good chemical and thermal stability [2-6]. The presence and the distribution of remaining glassy phases caused by impurity contents along grain boundaries or forming isolated pockets will influence the mechanical behaviour at high temperature [7].

The aim of this work was to investigate the high – temperature (1200–1500<sup>o</sup>C) behavior of mullite ceramics developed from illite clay and aluminium hydroxide.

## 2. Experimental Procedure

Mullite ceramics was obtained from four different compositions with equally changed relations between

illite clay and  $\text{Al}(\text{OH})_3$  (Table 1). It was used the clay from Devonian geological period, Liepa quarry, Latvia as the illite clay (Table 2).

**Table 1.** Investigated compositions

Sample number	Illite clay, wt.%	$\text{Al}(\text{OH})_3$ , wt.%
I	50	50
II	60	40
III	70	30
IV	80	20

**Table 2.** The characteristics of illite clay

Chemical composition, wt.%					
$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$ / $\text{TiO}_2$	$\text{CaO}/$ $\text{MgO}$	$\text{K}_2\text{O}/$ $\text{Na}_2\text{O}$	Wt. loss*
50.5	20.8	7.5/ 0.8	1.9/ 3.6	5.0 / 0.1	9.8

\* at 1000<sup>o</sup>C

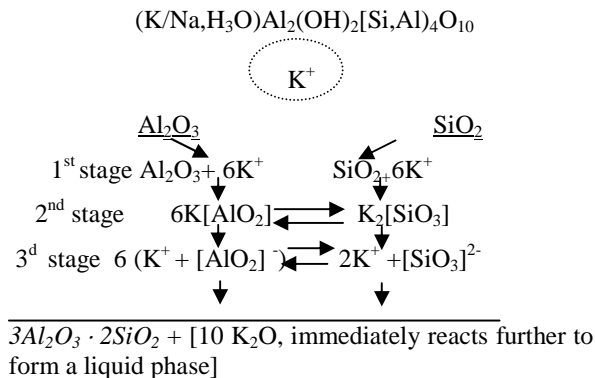
The starting compositions were prepared according to [8]. The cylindrical samples of size 35 mm (height) × 30 mm (diameter) were prepared and subjected to firing at 1100<sup>o</sup>C. High-temperature resistance of the samples subjected to the load of 0,2 N/m<sup>2</sup> of the sample was tested at four temperatures 1200, 1300, 1400, 1500<sup>o</sup>C.

In accordance with the standard DIN 51064 the rate of temperature rise up to the maximal temperature was 5 deg/min. At the maximal temperature samples were held for 1 hour. High-temperature resistance was controlled by measuring of the linear firing shrinkage and compression strength after the each temperature cycle. The samples were evaluated also visually after the each temperature cycle of testing. As the high-temperature resistance measure the temperature was accepted at which the firing shrinkage did not exceed 3 mm and after the compression test no signs of distortion of the sample uniformity or decrease of value of this parameter by more than 20 % were observed.

The changes in the phase composition after the each stage of testing were controlled by X-ray phase analysis by using the diffractometer D8 Advance (Bruker 2005), CuK $\alpha$  radiation, K $\beta$  filter 0,02 mm, spacing 0,02  $^{\circ}$  (time for the each step 0,5 sec), measurement range 2 $\theta$  from 3 to 60  $^{\circ}$  and electron scanning microscopy (SEM) model JSM-T200) from cross section of sample.

### 3. Results and discussion

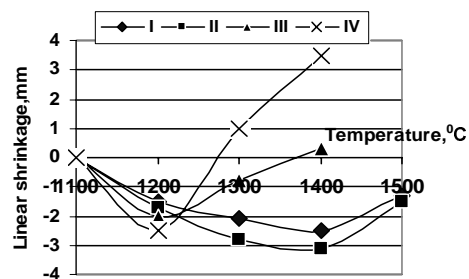
Decomposition of illite clay and presence in its chemical composition in particular K $^{+}$  (Na $^{+}$ ) ions as well as iron ions (table 2) enables the formation of the liquid phase at temperatures starting from 600-700  $^{\circ}$ C [7]. This process from only clay mineral illite schematically can be described as follows.



Along with these processes aluminium oxide (formed as a result of decomposition of Al(OH) $_3$  at temperatures  $\geq 550^{\circ}$ C), dissolve in the formed liquid phase. Simultaneously the formation of the crystallization nuclei from Fe $^{2+}$ ,  $^{3+}$ , Ti $^{4+}$  takes place. Both the liquid phase and nuclei formation promoted the crystallization of mullite and accompanying phases starting at temperatures from 1100 $^{\circ}$ C. This temperature is lower for 100-150  $^{\circ}$ C in comparison with conventional synthesized mullite from kaolinite. The

additional oxides presented in illite clays may be considered as activating agents for the crystallization of mullite. However, on the other hand, some quantities of formed multicomponent glassy aluminosilicate phase lower of the high-temperature resistance of the obtained mullite ceramics.

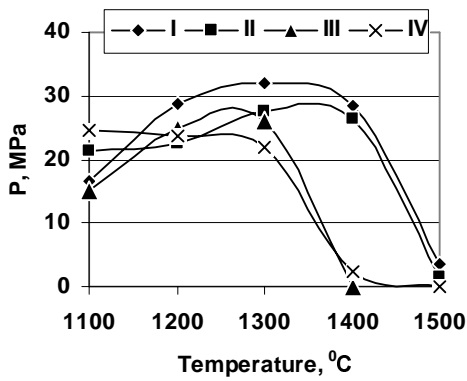
Results of measurement of the linear firing shrinkage (Fig.1) and compression strength (Fig.2) after the each temperature cycle show that at temperatures from 1200 -1300 $^{\circ}$ C the mentioned properties are noticeably changed.



**Fig. 1.** Changes in linear firing shrinkage in dependence on temperature.

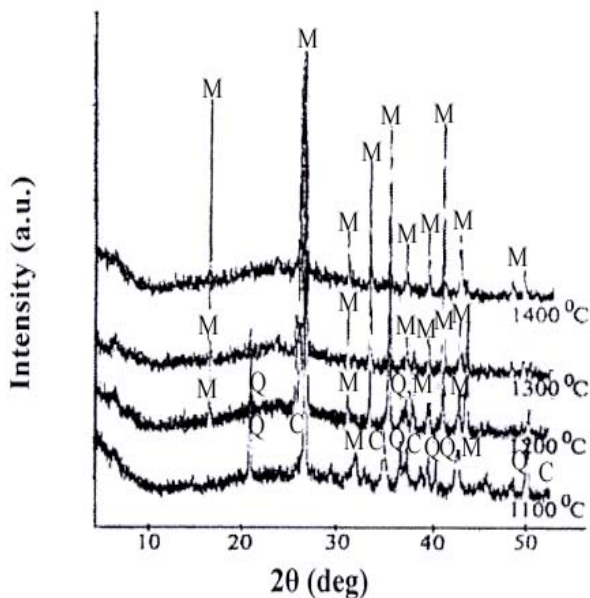
As it is shown the linear firing shrinkage is decreased at this temperature for the samples of compositions I and II. For the samples III and IV along with the increase of the illite clay content in the starting compositions, the opposite way, the increase of volume, i.e., linear dimensions become larger. This phenomenon is mainly determined by the grows of amorphous phase. Together there is reason for the formation of the additional gaseous phase (iron ions changes of the valence state) and consequently the closed pores and as a result growing of the sample volume.

The compression strength (Fig.2) values persist to be increasing up to temperature of 1300-1400  $^{\circ}$ C for samples I and II, for samples III and IV – up to 1300  $^{\circ}$ C Destruction of samples accordingly occurs at 1400 $^{\circ}$ C and 1300 $^{\circ}$ C.



**Fig. 2.** Compression strength changes with testing temperature

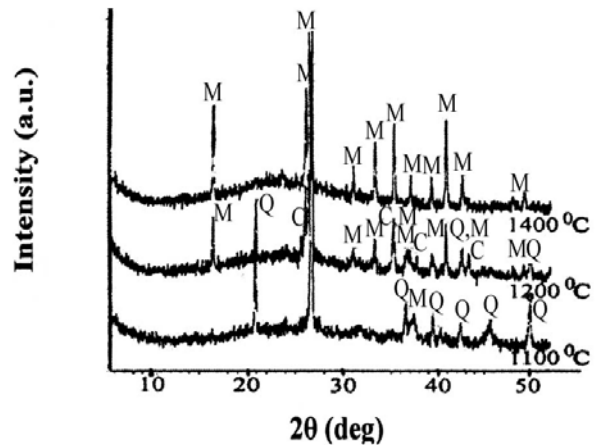
Results of X-ray phase analysis of the compositions I and III differing by the illite clay content are shown on Figures 3 and 4. It is obvious that in the starting samples fired at 1100°C along with the mullite crystalline phase forms also quartz and corundum. After the testing these samples it is shown that at temperatures starting from 1200 the mullite formation continue and at temperatures 1300, 1400°C forms as only mullite (or mullite+corundum) phases. It is the main reason that compression strength remain high value till the temperature 1400°C especially for sample I. It allows to widen the operation temperature range of up to 1400°C of such ceramics in practice.



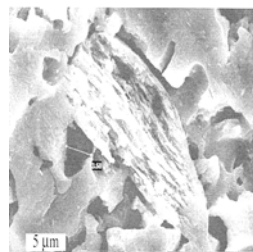
**Fig. 3.** Results of X-ray phase analysis of composition I fired at 1100 °C and after high-temperature testing at 1200, 1300, 1400 °C: M – mullite  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , Q – quartz  $\text{SiO}_2$ , C – corundum  $\alpha\text{-Al}_2\text{O}_3$ .

The relative intensity, e.g., for sample III of the diffraction maximums characteristic of mullite is noticeably increased along with the temperature increase in comparison with the corresponding diffraction maxima for the starting composition fired at 1100°C.

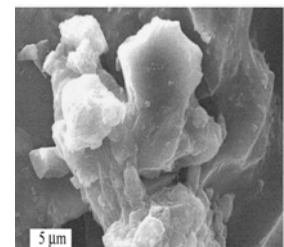
Results of analysis of samples I and III by the SEM correlate with the results of X-ray phase analysis. According to morphology the crystalline formations to verify the presence of mullite in the samples (Fig. 5).



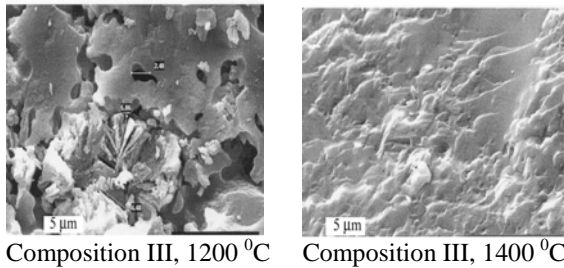
**Fig. 4.** Results of X-ray phase analysis of composition III fired at 1100 °C and after high-temperature testing at 1200, 1400 °C: M – mullite  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , Q – quartz  $\text{SiO}_2$ , C – corundum  $\alpha\text{-Al}_2\text{O}_3$ .



Composition I, 1200 °C



Composition I, 1400 °C



**Fig. 5.** Microstructure of compositions I and III fired at 1200 and 1400 °C.

If mullite crystals possess the loosened prismatic appearance in the samples of composition I at 1200 °C, at 1400 °C in the same composition the occurrence of the well-shaped mullite crystals possessing the narrow prismatic (needle-shaped) appearance is observed. These needle-shaped mullite crystals form the relatively compact structure. The mullite crystals are turned to the observer by their basal pinacoidal facet. The formation of spherulite-like crystalline aggregates of mullite and porous glassy phase is observed after the high-temperature testing of the samples of composition III at 1200 °C. At 1400 °C in the samples of this composition the formed crystals of mullite are squeezed and their characteristic habitus is not observed. In comparison with the crystalline formations of mullite in the composition I (Fig. 4), these crystals are more finely divided in the samples of composition III after the firing at 1400 °C and they form more dense crystalline aggregate due to the growing glassy phase.

Increase of formation and enlargement of the new formations of mullite, as well as the growth of needle-shaped mullite crystals in the sample of composition I at the high-temperature testing in the temperature range of 1200 to 1400 °C evidently appears to be the main factor for the preservation of mechanical strength up to 1400 °C. The obtained results correlate with the analogous results of investigations [1,9].

#### 4. Conclusions

Mullite-containing ceramics prepared at temperature 1100°C from compositions containing illite clay and aluminium hydroxide has been studied. Investigation of changes in phase composition, structure, linear shrinkage and mechanical strength of mullite ceramic samples after high-temperature testing at 1200-1500 °C have been carried out.

In the studied temperature range the increase of content of new formations of mullite takes place along with growth of dimensions of needle-like crystals of mullite that is considered to be the fundamental factor

for the preservation of mechanical strength of samples in the range of 28-32 MPa up to 1400 °C.

Along with the increase of illite clay content and corresponding decrease of total Al<sub>2</sub>O<sub>3</sub> content in the starting compositions at the high-temperature testing of samples at 1300-1400°C the content of amorphous phase is increased, the crystalline phase of mullite becomes finely dispersed and mechanical compression strength of the samples is noticeably decreased up to the destruction of the sample.

#### References

1. Aksay, I.A.; Dabbs, D.M.; Sarikaya, M. Mullite for structural, electronics and optical applications. *Journal of American Ceramic Society*, 74, 1991. p. 2343-2357.
2. Schneider, H. Thermal expansion of mullite. *Journal of American Ceramic Society*, 37, 1990. p. 2073-2076.
3. Takei, T.; Kameshima, A.; Yasumori, A.; Okada, K. Crystallisation kinetics of mullite in alumina-silica glass fibers. *Journal of American Ceramic Society*, 82, 1999. p. 2876-2880.
4. Ma, T.I.; Mazdiyasi, K.S. Mechanical properties of mullite. *Journal of American Ceramic Society*, 6, 1983. p. 699-703.
5. Viswabaskaran, V.; Gnanam, F.D.; Balasubramanian, M. Mullitisation behaviour of south Indian clays. *Ceramics International*, 28, 2002. p. 557-564.
6. Ribeiro, M.J.; Tulyagavov, U.; Ferreira, M.; Labrincha, J.A. High temperature mullite dissolution in ceramic bodies derived from Al-rich sludge. *Journal of European Ceramic Society*, 25, 2005. p. 703-710.
7. Osendi, M.I.; Baudin, C. Mechanical properties of mullite materials. *Journal of European Ceramic Society*, 16, 1996. p. 217-224.
8. Sedmale, G. P.; Sperberga I. E.; Sedmalis U.J. High – temperature ceramics on the basis of modified illite clay. *High- temperature and Technical Ceramics*, 4, 2004. p. 9-12 (in Russian).
9. Schneider, H.; Okada, K.; Pask, J.A. Mullite and mullite ceramics. John Wiley&Sons, 1994. 266 p.