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Effect of Illite Clay Additive on Sintering, Phase Composition and Properties of Mullite-ZrO_2 Ceramics

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***Abstract* — This study focuses on the influence of illite clay on changes of ZrO_2 modifications after sintering and consolidation of mullite-ZrO_2 ceramics with or without Y_2O_3 additive.**

It was found that mullite-ZrO_2 ceramics both with 4.5 % Y_2O_3 additive or without it in presence of illite clay tend to have increased densification and compression strength after sintering. Presence of illite clay also promotes change of ZrO_2 monoclinic phase to tetragonal phase and the presence of Y_2O_3 promotes change to ZrO_2 cubic phase.

***Keywords* — Ceramics, illite clay, mullite-ZrO_2.**

I. Introduction

Nowadays, due to increasingly high requirements for materials that are used in extreme conditions, like high and rapidly changing temperature, materials that possess excellent physical, chemical, mechanical and thermal properties are required.

It is known [1]−[2] that mullite [$Al(Al_{1-2x}Si_{1-2x})O_{5-x}$] is one of the most important phases in both traditional and advanced ceramics to improve their strength. In its turn mullite-ZrO_2 ceramics appear as an attractive candidate to replace single phase Al_2O_3, ZrO_2 and also mullite ceramics in a number of applications. Attraction of mullite-ZrO_2 ceramics mainly involves elevated mechanical properties that can be achieved at relatively low temperatures, if compared to single phase ceramics. Mullite-ZrO_2 ceramics can be produced by reaction sintering starting with $ZrSiO_4$ (or ZrO_2 and SiO_2) and Al_2O_3, using the following reaction (1):

$$2ZrSiO_4 + 3Al_2O3 \xrightarrow{1400^{\circ}C} 2ZrO_2 + 3Al_2O_3 \cdot SiO_2 \qquad (1)$$

This reaction is followed by densification in a single process. ZrO_2 is dispersed in mullite matrix and provides a mechanism for „toughening" of mullite. However, mullite already starts to form at 1100 °C and the densification process remarkably runs behind [3]. To promote this process, methods or additives that stimulate the formation of small amount of liquid phase are mainly used [3]−[5].

This study follows first experiments of authors [3] on use of illite clay nanoparticles to promote sintering process and consolidation of mullite-ZrO_2 ceramics with or without of Y_2O_3 additive. The impact of illite additive on phase stability, pressure strength, as well as density. Densification and shrinkage behaviour was investigated.

II. Experimental Procedure

Two different types of starting mixtures were used. The first type was a mixture of chemical grade γ-Al_2O_3, SiO_2, ZrO_2 (monoclinic) reagents and quartz sand without illite additive (sample I-0) and the next three with illite clay additive (wt % illite additive): 5 wt % (sample I-1), 10 wt % (sample I-2) and 15 wt % (sample I-3). The second type had the same components as first one, but with added 4.50 wt % Y_2O_3 (IY-series). Quartz sand (SiO_2 98.6 wt %) was used as SiO_2 and illite clay was obtained from Laza quarry, Latvia, depth 2.5-3 m. The chemical composition of illite clay was: 8.25 wt % SiO_2, 24.00 wt % Al_2O_3, 4.85/1.05 wt % Fe_2O_3/TiO_2, 2.10/3.95 wt % CaO/MgO, 5.60/0.20 wt % K_2O/Na_2O. Starting components Al_2O_3 and SiO_2 were choosen so that they would form mullite together with ZrO_2 additive (up to 5 wt %).

The starting mixtures of powders were produced by ball-milling for 10 h in a planetary laboratory mill *Retsch PM-100* with corundum balls, in water medium.

Morphology and size of powder particles was characterized using SEM (*Hitachi-TM3000*), but powder sintering process was analysed using differential thermal analysis (DTA equipment *Setaram, Setsys Evolution 1750*) in temperature range from room temperature to 1450 °C, heating rate was 10 °/min.

Samples for conventional sintering were prepared in form of disks with 25 mm diameter and as cylinders with 30 mm height and 25 mm diameter and subjected to different firing schedules in air at maximum temperatures 1400 °C or 1500 °C (heating rate was 5.6 °/min, holding time at maximum temperature was 1 h).

The degree of sintering after firing was characterized by the relative density or densification grade, as well as by the change of linear shrinkage. The density of sintered samples was measured using Archimedes method with accuracy of ± 0.5 % using distilled water as medium.

Microstructure and phase composition of sintered samples was analysed using SEM (model *NovaNano SEM 650*, Netherlands) and XRD apparatus (model *D8 Advance Bruker*, with CuK_α radiation at scanning interval 2θ 10-60° and speed 4 °/min), respectively.

The compressive strength was determined using *Toni-Technic (Baustoffprüfung)* model *2020*.

III. Results and Discussion

A. Characterization and Thermal Treatment of Starting Powder

SEM images of powders milled for 10 h (Fig. 1) demonstrate agglomerates of particles with the mean size within ~ 3−10 μm range. In sample without illite additive particles (agglomerates) seemed mainly angular, but for powder with added 15 wt % illite clay and 4.50 wt % Y_2O_3, agglomerates appeared to be rounded and a little bit nebulous (Fig. 1, a and b). Particles in large scale nanometre range also could be found.

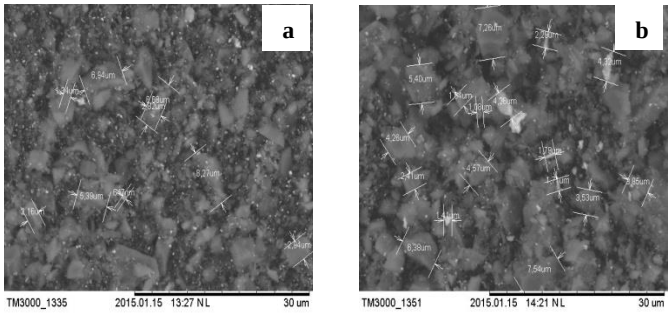

Fig. 1. SEM image of starting powder of mullite-ZrO_2, composition I-0 milled for 10 h without illite additive (a) and the same with 15 wt % illite and 4.50 wt % Y_2O_3 additive, composition IY-3 (b).

The processes occurring within powders without or with illite additive when heated in temperature range from room temperature to 1400 °C are demonstrated in DTA curve for two samples I-0 (without illite) and I-3 (with 15 wt % illite additive), Fig. 2. The main process at temperatures above 600 °C for sample I-0 is related to growing curves characterized by not pronounced, exo'-effect, which could be related to a gradual development of mullite. Three small single effects at 739 °C, 1010 °C and a little larger effect at 1215 °C indicate a small structural change. The last effect obviously points to a relatively intensive mullite formation, but the preliminary two at 739 °C and 1010 °C obviously indicate the formation of premullite source. These results correlate with phase composition shown using XRD (Fig. 5, see section B) of ceramic samples sintered at 1400 °C.

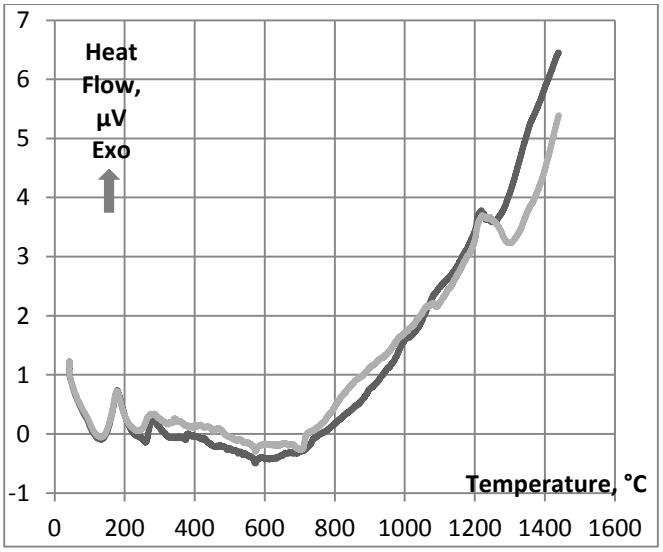

Fig. 2. DTA curves for sample I-0 without illite and I-3 with 15 wt % illite additive (labels at Fig. 3).

In turn TGA curves for demonstrate total gradual 1.60 w% losses up to 500 °C temperature for sample I-0 and 2.09 wt % up to 700 °C temperature for sample I-3. The first endo-effect at 130−132 °C for both is connected to separation of hygroscopic water from surface of particles, but all others in the temperature range from 200 °C to 700 °C obviously are connected to decomposition of admixtures. As it is shown in DTA curves at temperature higher than 600 °C a small amount of liquid phase starts to form; this is better pronounced at temperature ~ 704 °C for sample I-3 with illite additive 15 wt %. For sample I-0 without illite additive this effect is smaller and is weakly pronounced at ~ 740 °C. At higher temperatures premullite source and mullite phase starts to form. ZrO_2 modification change (from $ZrO_{2\ mon.}$ to $ZrO_{2\ tetr.}$) cannot be observed neither on DTA nor TGA curves, Fig. 2 and Fig. 3.

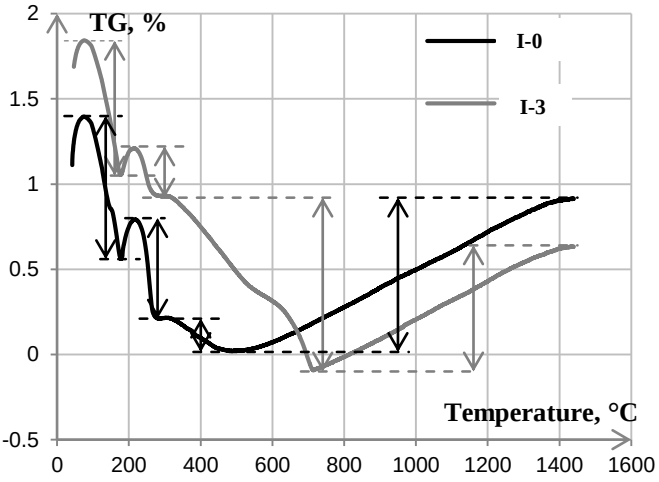

Fig. 3. TGA curves for samples without illite additive (I-0) and with illite additive 15 wt % (I-3).

The effect of 4.50 wt %.Y_2O_3 additive on DTA and TGA curve shapes is small and curves seem similar, but all effects are more pronounced.

B. Densification and Phases Composition of Sintered Samples

As it is shown in DTA curves (Fig. 2) densification process starts at temperatures 600−700 °C when a small amount of liquid phase forms. This process is accompanied by the main reaction, i. e., gradual formation of mullite, remarkable shrinkage and increase of density (Fig. 4 a and b), both by growing illite and especially by combined 4.50 wt. % Y_2O_3 and illite additive, as well as with the increase of sintering temperature.

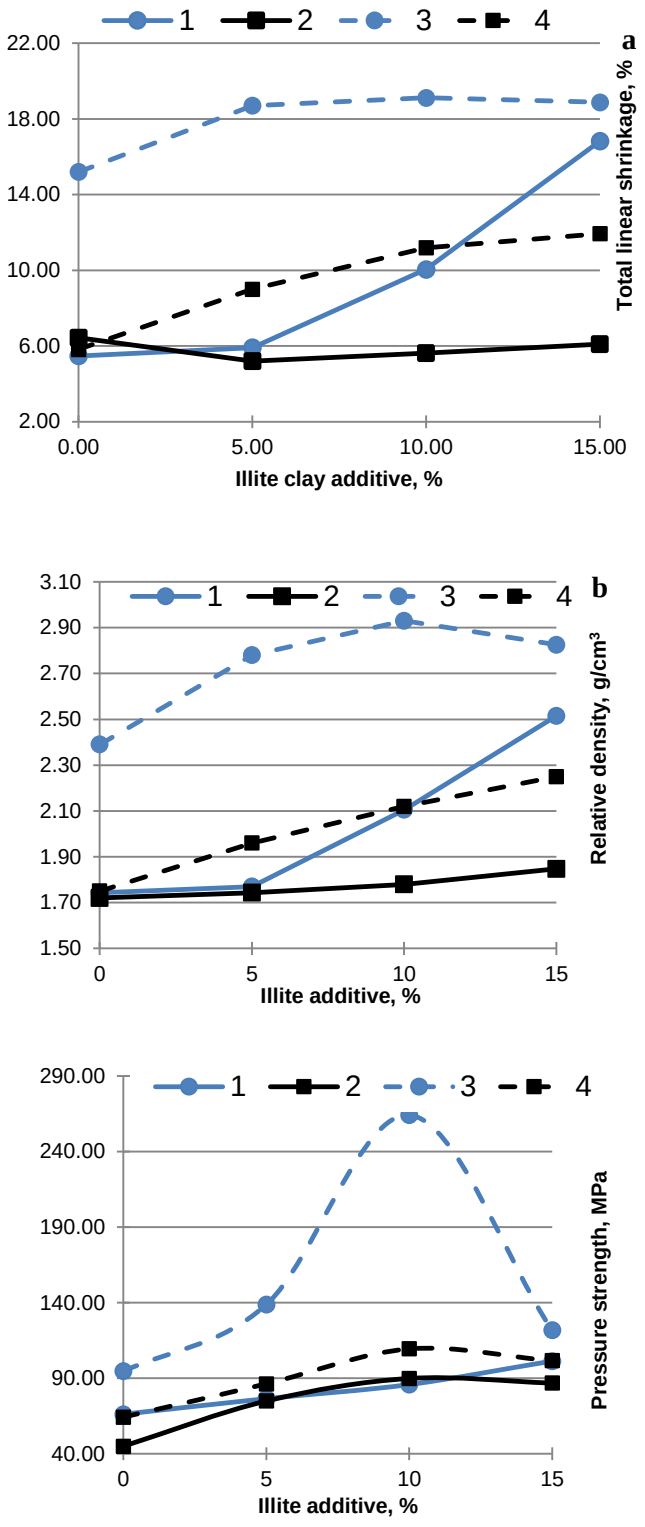

Fig. 4. Dependence of densification kinetics (a, b) and pressure strength (c) of samples with or without Y_2O_3 on the amount of illite additive: 1, 3 — IY series without and with 4.5 % Y_2O_3, at 1500 ºC; 2, 4 — the same at 1400 °C.

The following XRD (Fig. 5 and Fig. 6) show that the impact of illite additive on phase composition for both compositions (with or without Y_2O_3 additive) is varied and involves with ZrO_2 modification changes. The main phases — mullite, ZrO_2 (tetragonal) with small admixtures of ZrO_2 (monoclinic) form in all compositions without Y_2O_3. Y_2O_3 additive transforms all ZrO_2 to the cubic modification.

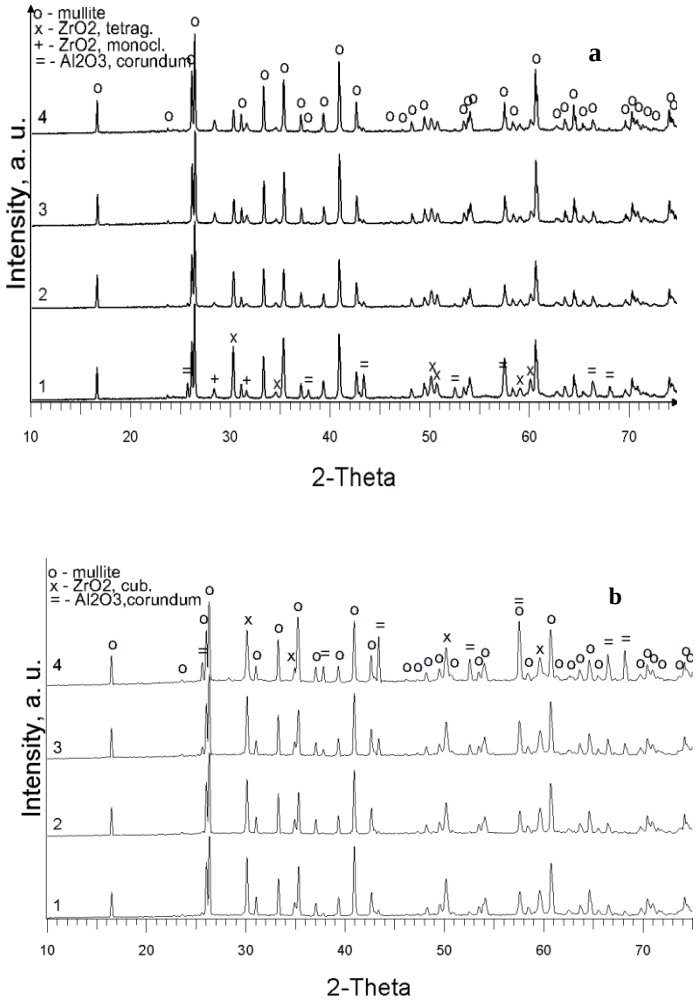

Fig. 5. XRD patterns of ceramic samples sintered at 1500 ºC — series I (a) and series IY (b).

IV. Conclusion

The impact of illite additive on densification and pressure strength behavior, as well as phase development during sintering of mullite-ZrO_2 ceramics with or without Y_2O_3 additive was investigated.

Mullite-ZrO_2 ceramics both with 4.5 wt % Y_2O_3 additive or without of it in presence of illite clay tend to have increase ddensification, are characterized by linear shrinkage and relative density and, sequentially, pressure strength.

To a certain extent it is shown that illite promotes change of ZrO_2 from monoclinic modification to tetragonal modification and in presence of Y_2O_3 to cubic modification.

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Gaida Sedmale, Inga Raubiška, Aija Krūmiņa, Aleksejs Hmeļovs. Illītu mālu piedevas ietekme uz mullīta-ZrO_2 keramikas saķepšanu, fāžu sastāvu un īpašībām.
Mullīts ir viena no svarīgākajām augsttemperatūras kristāliskajām fāzēm. Mullīta veidošanās keramikā, tajā skaitā arī keramikā, kas satur ZrO_2, nodrošina tai augstas mehāniskās, ķīmiskās un termiskās īpašības, arī pie paaugstinātām temperatūrām. Lai gan mullīta fāze sāk veidoties jau ~ 1000 °C temperatūrā, blīvu mullīta keramikas materiālu parasti iegūst viena cikla saķepināšanas procesā pie paaugstinātas temperatūras (≥ 1400 °C). Lai veicinātu šīs keramikas saķepšanu un saķepšanas temperatūras pazemināšanu, pielieto piedevas vai arī aktīvus pulverus, piemēram, γ-Al_2O_3 nanopulveri, kvarca smiltis, u.c.
Dotajā darbā ir pētīta illīta nanopulvera ietekme uz mullīta-ZrO_2 keramikas (ar Y_2O_3 piedevu un bez tās) sablīvēšanos saķepšanas procesā, iegūtā keramikas materiāla kristālisko fāžu sastāvu un īpašībām.
Darbā ir pielietoti divu veidu pulveru maisījumi, kas sastāv no γ-Al_2O_3, SiO_2,, ZrO_2 (monoklīns), ar Y_2O_3 piedevu vai bez tās. Katrai maisījumu grupai pievienots illīts 5 %, 10 % vai 15 % (masas daļas). Izejas pulveru morfoloģijas izpētei pielietots elektronmikroskops Hitachi-TM3000 un diferenciāli termiskai analīzes iekārta Setaram, Setsys Evolution 1750. Paraugi formēti disku un cilindru veidā. Saķepināšana veikta divās maksimālajās temperatūrās — 1400 °C vai 1500 °C. Keramikas fāžu sastāvs noteikts pielietojot Rentgena staru difraktometriju (D8 Advance Bruker). Raksturīgās keramikas īpašības (relatīvais blīvums, sarukums) noteiktas izmantojot EN, spiedes izturība noteikta pielietojot iekārtu *Toni-Technic*.
Ir iegūti rezultāti, kas parāda, ka saķepināto keramikas paraugu sablīvēšanās (relatīvais blīvums un sarukums) pakāpe pieaug ar illīta mālu piedevu līdz 10%. Pie lielākas piedevas (15 %) ir vērojama iekšējo poru veidošanās tendece. Savukārt Y_2O_3 piedeva, it sevišķi illītu mālu klātienē veicina sablīvēšanos saķepināšanas procesā, it seviķi pie 1500 ºC. Ir jāatzīmē arī, ka mālu klātiene veicina ZrO_2 monoklīnās modifikācijas transformāciju tetragonālā, bet vienlaicīga mālu un Y_2O_3 piedevu klātiene savukārt ZrO_2 monoklīno modifikāciju tranformē kubiskā modifikācijā.