

Reaction heat potential utilization in mullite and spinel based ceramics synthesis and sintering

Możliwości wykorzystania ciepła reakcji podczas syntezy i spiekania materiałów ceramicznych na bazie mullitu i spinelu

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Present work studies the potential of the utilization of the heat released from exothermic reactions in ceramic synthesis and sintering. For example the initialization of the endothermic reaction of the mullite formation is studied with heat releasing co-reactions. Exothermically reactive raw material (aluminium powder) is examined for external energy saving ceramic synthesis.

KEYWORDS: exothermic reactions, mullite synthesis

Przeanalizowano możliwości wykorzystania ciepła pochodzącego z reakcji egzotermicznej podczas syntezy i spiekania materiałów ceramicznych. Przykładowo zainicjowanie reakcji endotermicznej podczas formowania się mullitu analizowano wraz z ciepłem uwalnianym w reakcjach towarzyszących. Surowy materiał reaktywny egzotermicznie (proszek aluminiowy) poddano badaniom w celu obniżenia energii zewnętrznej niezbędnej podczas syntezy ceramiki.

SŁOWA KLUCZOWE: reakcje egzotermiczne, synteza mullitu

Porous ceramic materials for high-temperature applications are of great interest today (insulators, catalyst supports, filters etc.). Typically the synthesis of the technical ceramics, such as mullite and spinel based, requires high temperature and long sintering time. Traditional production routes consume a lot of energy and have long processing times, which increases the cost of products and consequently have high environmental burden. Therefore lower external energy requiring processing routes are sought for. Self-propagating High-temperature Synthesis (SHS) is offering one, energy efficient and rapid route for making advanced composites and intermetallic compounds and due to the low external energy consumption, SHS is feasible processing method even for environmental protection [1–2]. The SHS process is traditionally limited only to highly exothermic reactions where the released combustion energy is exploited. However, exothermic assisted synthesis of pure alumino-silicates and magnesium-aluminates based ceramics has very few publications. The utilization of the aluminium powder as the raw material for the mullite synthesis is presented in the studies of H. Balmori-Ramirez et al. [3] and A. Esharghawi et al. [4]. In the present study of A. Esharghawi et al. [5] porous mullite-based bodies were produced by SHS starting from the kaolinitic clay, Al and Mg powder mixtures. Pure mullite has not been obtained but Si and Al in metallic phases, quartz, α -alumina and $MgAl_2O_4$ spinel

were present in addition to the mullite phase. In the study of G. Xanthopoulou and G. Vekinis [6], $MgO/MgAl_2O_4$ refractories were produced by SHS resulting the spinel content up to 100%. The starting materials included Al and Mg powders mixed with various oxides and salts.

Experimental procedure

In this study, the endothermic reaction of the synthesis combined with the in-situ exothermic reactions are examined and compared to the traditional sintering. Kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), aluminium oxide hydroxide ($AlO(OH)$) and aluminium (Al) powders were selected as raw materials for the stoichiometric 3:2 mullite ($3Al_2O_3 \cdot 2SiO_2$) synthesis. Magnesium hydroxide ($Mg(OH)_2$), aluminium oxide (Al_2O_3) and Al powders were used as raw materials for the magnesium aluminate spinel ($MgAl_2O_4$) synthesis. Meta-kaolin was produced from kaolin by heat-treatment at 850 °C for 30 minutes. Five mixtures were prepared from the selected raw materials; details are presented in the table.

TABLE. Test matrix for mullite and spinel synthesis experiments

Test sample	Raw material	Raw material	Raw material	Recipe
1	Kaolin	$AlO(OH)$	-	REF: $3Al_2O_3 \cdot 2SiO_2$
2	Kaolin	Al	-	$3Al_2O_3 \cdot 2SiO_2$
3	Meta-kaolin	Al	-	$3Al_2O_3 \cdot 2SiO_2$
4	$Mg(OH)_2$	-	Al_2O_3	REF: $MgAl_2O_4$
5	$Mg(OH)_2$	Al	Al_2O_3	$MgAl_2O_4$

Raw materials were attrition milled for 10 minutes in argon atmosphere. Samples 1÷3 were cold pressed and sintered in air at 1600 °C for 1 h and samples 4÷5 at 1200 °C for 2 h (conventional method). The SHS experiments were performed for Al containing test samples 2, 3 and 5 both in air atmosphere at 1100 °C by an electric furnace and in so called self-ignition mode. Temperature of the sample during synthesis experiment was recorded with s-type thermoelement. Thermogravimetry (TGA) giving simultaneous Differential Scanning Calorimetry (DCS) signal was used for examination of thermal behaviour of raw materials and reacted materials. Directly to TGA device coupled mass spectrometer (QMS) was used for evolved gas analysis. X-ray diffractometry (XRD) was used for the phase structure analysis.

Results and discussion

■ **Thermal evolution studies.** Fig. 1 shows the TGA/DSC/QMS-curve of the raw material kaolin, measured

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from Dv50 value 6.8 μm powder. At 510 $^{\circ}\text{C}$ can be seen endothermic peak relating to the dehydration of the kaolin into the meta-kaolin phase including water 'release'. At 996 $^{\circ}\text{C}$ can be seen exothermic peak related to the reorganization of the meta-kaolin into the spinel phase. At 1211 $^{\circ}\text{C}$ mullite crystallization is occurring. For test sample 1 the thermal behaviour is similar to kaolin, differing only with first endothermic at 496 $^{\circ}\text{C}$ peak relating to the dehydration of the kaolin and also the dehydration of the $\text{AlO}(\text{OH})$.

Fig. 2 shows the TGA/DSC-curve of the raw material Al, measured from, Dv50 value 26.8 μm powder. Solid state Al oxidation can be seen at 619 $^{\circ}\text{C}$, followed by Al melting at 663 $^{\circ}\text{C}$ and liquid state aluminium oxidation at 996 $^{\circ}\text{C}$.

Fig. 3 shows the TGA/DSC/QMS-curve of the test sample 2. It can be seen kaolin dehydration to meta-kaolin releasing water at 504 $^{\circ}\text{C}$, Al oxidation at 626 $^{\circ}\text{C}$ and aluminium melting at 660 $^{\circ}\text{C}$. At 954 $^{\circ}\text{C}$ detected exothermic peak can be related both to the liquid state aluminium oxidation and the reorganization of the meta-kaolin into the spinel phase. Exothermic peak can be seen also at 1203 $^{\circ}\text{C}$ related with mass increase. For test sample 3 the thermal behaviour is similar to the test sample 2 without kaolin dehydration at 504 $^{\circ}\text{C}$.

Similar results of the thermal behavior for kaolin and aluminium were presented also by A. Esharghawi [4–5]. Test sample 4 showed only one endothermic peak at 393 $^{\circ}\text{C}$ relating to $\text{Mg}(\text{OH})_2$ dehydration. For sample 5 also Al solid state oxidation, Al melting and Al liquid state oxidation at 1042 $^{\circ}\text{C}$ can be observed.

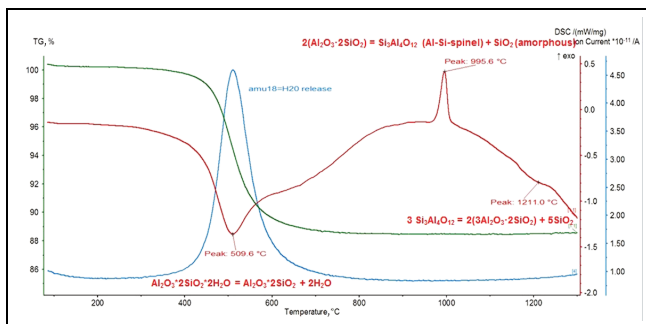


Fig. 1. The TGA (green curve)/DSC (red curve)/QMS (blue curve) – curves of the kaolin

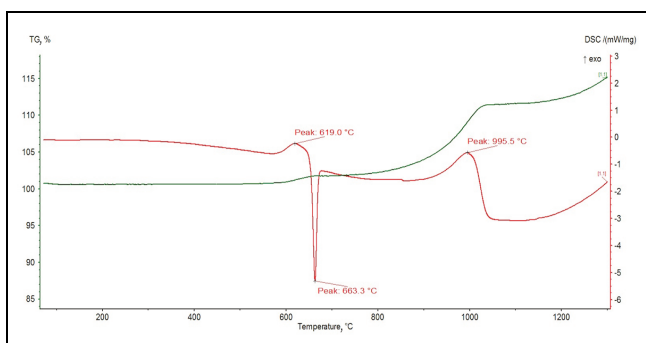


Fig. 2. The TGA/DSC-curves of the aluminium

■ **Phase structure analysis: sintering in the air.** After conventional sintering for test samples 1÷3 show stoichiometric mullite and minor aluminium oxide phases are detected. For test samples 4÷5 the magnesium aluminate spinel phase is detected as main crystalline phase with minor aluminium oxide and magnesium oxide phases present.

■ **Phase structure analysis: SHS experiments in the air.** The highest measured temperature from the sample core during process for test samples 2 and 3 was 1675 $^{\circ}\text{C}$. After SHS the aluminium oxide and the metallic Si were the

main crystalline phases, minor amount of Al were also detected (Fig. 4). For test sample 5 the process was not self-propagating in the experiments.

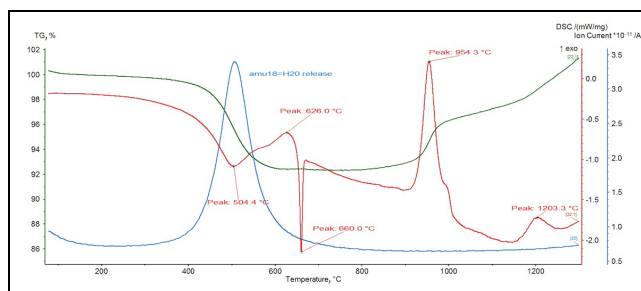


Fig. 3. The TGA/DSC/QMS-curves of the test sample 2

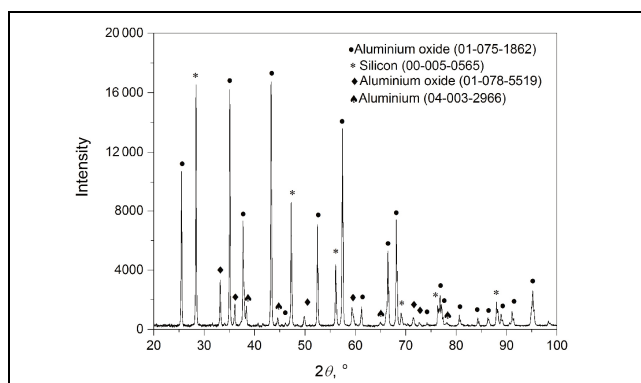


Fig. 4. The XRD patterns of the test sample 3

Summary

In this study the effect of the exothermically reactive raw material, aluminium is examined for decreasing external energy requirement in ceramic synthesis. In order to examine decreased external energy requiring synthesis, SHS experiments were performed in the air. It was found out that the aluminium oxidation at 900 $^{\circ}\text{C}$ initiates the SHS for kaolin and aluminium mixtures resulting in the Al_2O_3 - Si phase structure formation. After post heat treatment at 1600 $^{\circ}\text{C}$ for 1 hour the mullite was observed as main phase. These preliminary studies prove the potential of the utilization of SHS using kaolin and aluminium as raw materials for the ceramic synthesis. However, future research is needed for its exploitation in the mullite and magnesium aluminate spinel synthesis e.g. to provide raw materials in order to provide enough oxygen for the completing reactions.

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