



# Physical and Chemical Processes During Firing of $ZrSiO_4$ - $Al_2O_3$ Powders

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## Abstract

Mullite-zirconia materials are of great interest for their application in filters, catalytic carriers, heat exchangers, as well as coatings in combustion engines and classical refractories. They possess high fire and heat shock resistance as well as good mechanical and chemical resistance at high temperatures. The microstructure of the material is formed as a result of complex physical and chemical processes taking place at high temperatures. Their course depends on temperature, purity and grain size of the substrates.

In this work, the microstructure evolution was studied in the samples composed of  $ZrSiO_4$  and  $\alpha$ - $Al_2O_3$ . The samples were prepared from commercially available powders showing various grain size distributions. The oxide composition was specified according to stoichiometry of the reaction:  $Al_2O_3 + 2ZrSiO_4 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + ZrO_2$ . The final firing was carried out at temperatures ranging from 1300°C to 1600°C for the time varying from half an hour up to 60 hours. The change of chemical and phase compositions were examined with the application of XRD (Rietveld technique), FTIR and EDS analytical methods. The microstructure evolution was traced with SEM for the model samples prepared from  $ZrSiO_4$  (of grain size below 150  $\mu m$ ) and  $Al_2O_3$  (of grain size distribution D90 below 10  $\mu m$ ).

The obtained results have been used as a basis for the description of dominant mechanisms responsible for formation of the mullite-zirconia material microstructure. It has been found that the decomposition of  $ZrSiO_4$  into oxide components takes place at the first stage of firing of the  $ZrSiO_4$  and  $\alpha$ - $Al_2O_3$  powder. Then a two way diffusion of  $Si^{4+}$  and  $Al^{3+}$  ions goes on, followed by nucleation and growth of a crystalline mullite.

**Keywords:** Mullite, Zirconia, Microstructure – final, Zircon decomposition

## PROCESY FIZYCZNE I CHEMICZNE ZACHODZĄCE PODCZAS WYPALANIA PROSZKÓW $ZrSiO_4$ - $Al_2O_3$

Materiały mullitowo-cyrkoniowe znajdują się w kręgu nieustannie rosnącego zainteresowania w związku z ich zastosowaniem w filtrach, nośnikach katalizatorów, wymiennikach ciepła, a także jako powłoki w silnikach spalinowych i jako klasyczne materiały ogniotrwałe. Mają one wysoką ogniotrwałość i odporność na wstrząs cieplny oraz dobrą mechaniczną i chemiczną odporność w wysokich temperaturach. Mikrostruktura materiału kształtuje się jako wynik złożonych zjawisk fizycznych i chemicznych, zachodzących w wysokich temperaturach. Przebieg tych procesów zależy od temperatury, czystości i rozmiaru ziarna substratów.

W pracy zbadano ewolucję mikrostruktury próbek  $ZrSiO_4$  i  $\alpha$ - $Al_2O_3$ . Próbki przygotowano z proszków handlowych o różnych rozkładach wielkości cząstek. Skład tlenkowy określono zgodnie ze stochiometrią reakcji:  $Al_2O_3 + 2ZrSiO_4 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + ZrO_2$ . Wypalanie próbek przeprowadzono w temperaturach z przedziału 1300-1600°C przez czas zmieniający się od 30 min do 60. godzin. Zmianę składu fazowego i chemicznego określono stosując metody XRD (metoda Rietvelda), FTIR i EDS. Ewolucję mikrostruktury śledzono za pomocą SEM dla modelowych próbek przygotowanych z proszków  $ZrSiO_4$  o rozmiarze ziarna poniżej 150  $\mu m$  i proszków  $Al_2O_3$  o rozmiarze ziarna D90 poniżej 10  $\mu m$ .

Otrzymane wyniki wykorzystano jako podstawę opisu dominujących mechanizmów powstawania mikrostruktury materiału mullitowo-cyrkoniowego. Stwierdzono, że w pierwszym etapie wypalania proszku  $ZrSiO_4$  i  $\alpha$ - $Al_2O_3$  ma miejsce rozkład  $ZrSiO_4$  na składowe tlenki. Następnie zachodzą dwa sposoby dyfuzji jonów  $Si^{4+}$  i  $Al^{3+}$ , po których następuje zarodkowanie i wzrost krystalicznego mullitu.

**Słowa kluczowe:** mullit,  $ZrO_2$ , mikrostruktura finalna, rozkład cyrkonu

## 1. Introduction

There has been considerable interest in mullite and mullite-matrix composites in recent years due to their desirable properties. As the material used for high temperature applications, mullite has long been recognized due to its excellent resistance to creep and thermal shock in refractories [1, 2]. Mullite, however, has low fracture toughness and relatively low strength at room temperature as compared with other engineering ceramics. An addition of zirconia particles to a mullite-matrix can help overcome those issues.

Mullite-zirconia composites are widely used in technological applications due to their good properties, such as toughness, chemical stability, and resistance to creep and spalling. Mullite-zirconia refractories can be used in the forehead feeders and glass melting furnaces, as glass contact materials, such as plungers, spouts, tubes, orifice rings, etc. [3, 4]. The widespread use of this class of materials is due to their high corrosion resistance, attributed to the microstructure and to zirconia, being slightly wetted by siliceous and metallic melts. Since the solubility potential of zirconia in silica is low, the chemical attack of the refractory is comparatively low [5].

Dispersed zirconia particles, added as the second phase to mullite materials, enhance their thermo-mechanical properties. Zirconia particles toughen the material mainly as a consequence of the tetragonal-monoclinic phase transformation [6, 7] that can occur during the fracture process or during sintering cooling. In the former case, the stress induced phase transformation toughening mechanism is activated, while in the latter, the micro cracks produced in the matrix as a result of the phase transformation that occurs during the sintering cooling are responsible for the increase of crack propagation energy [8, 9]. If mullite crystals appear in a needle shape, then an additional toughening mechanism is present (bridging). There are many ways to produce mullite-zirconia composites, e.g., conventional or chemical processing of alumina, zirconia and silica powders as well as sol-gel can be used. The easiest and the most economical way to obtain homogenous mullite-zirconia ceramics is reaction sintering, in which alumina and zircon (ZrSiO<sub>4</sub>) [10] are used as the initial powders. Without sintering aids or stabilizing oxides, the densification is achieved at 1450-1500°C and the complete mullitization occurs at temperatures near 1600°C [11]. The mechanism of high temperature reactions proceeding in the mentioned mixture, however, has not been determined so far. The results of investigation concerning the time evolution of phase composition during the reaction between zircon sand and corundum are presented in this paper. The influence of the grain size distribution on the process is also considered.

## 2. Experimental

Starting powders were constituted by commercially available alumina CTC20, CTC50 (Alcoa Inc., USA) and zircon (ZrSiO<sub>4</sub>, Australian Zircon Sand, Australia). The characteristics of the raw materials are described in Table 1. Fig. 1 shows particle size distribution of starting materials.

The mixture composition was selected according to stoichiometry of the following reaction:



It contained 45.54 % by weight of Al<sub>2</sub>O<sub>3</sub> (type 1 or 2) and 54.35 % by weight of ZrSiO<sub>4</sub> (type A or B). Homogenization of the mixture proceeded for 5 hours in acetone. Cylinder-shaped samples having diameter of 1 cm and height of 3 cm were uniaxially compressed under a pressure of 10 MPa. The samples were fired in an electrical furnace Nabertherm RHT08/16 at various temperatures ranging from 1300°C to 1600°C, with furnace heating rate of 10°C/min. Firing time at the given temperature ranged from 30 minutes to 60 hours. The samples were allowed to cool from firing temperature in the furnace. The Philips diffractometer system was used for phase identification and crystallinity analysis of the powders. The quantitative crystalline phase composition was

Table 1. Chemical composition of starting materials [wt%].

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	HfO <sub>2</sub>
Alumina type 1 (CTC20)	0.11	0.06	99.69	0.01	0.01	0.02	0.09	0.01	0.00	0.00
Alumina type 2 (CTC50)	0.10	–	99.8	0.03	–	0.02	–	0.02	–	–
Zircon type A (fine)	0.02	0.02	0.18	31.89	0.01	0.02	0.11	0.04	66.35	1.35
Zircon type B (coarse)	0.00	0.01	0.27	32.76	0.01	0.02	0.14	0.05	65.40	1.35

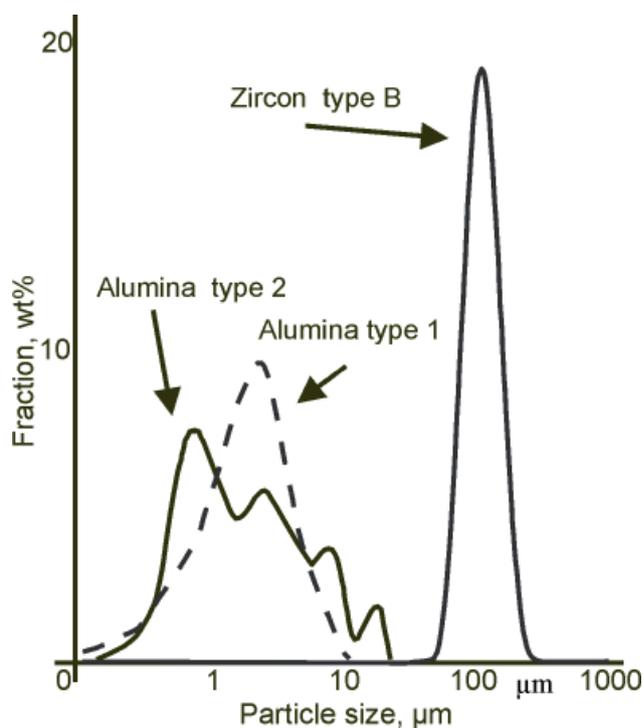


Fig. 1. Particle size distributions of starting materials. Zircon type A is not included, its D100 < 30 μm.

calculated by XRD using the Rietveld method. Final microstructures were characterized by SEM-EDAX after polishing.

## 3. Results and discussion

The sintering process of ZrSiO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> mixture involves two reactions, the first is decomposition of ZrSiO<sub>4</sub>, the second, formation of mullite. The total reaction can be expressed as the reaction above. According to the thermodynamic data from the literature [12], the free energy of the reaction in the range of 1200-1400 K can be described by this linear function of temperature, T:

$$\Delta G = 0.515 T + 72.19 \text{ [kJ/mol]}. \quad (2)$$

The calculation shows that the reaction should start when temperature T > 1400 K (about 1127°C) which is a relatively low temperature. This equation matches to the equation calculated by other authors [13].

Fig. 2 shows the results obtained in case of the samples fired for 5 h at a temperature from 1300°C to 1600°C, it is evident that the reaction starts at a much higher temperature than the temperature calculated using thermodynamic data.

The reaction products are detected after firing at 1500°C. The reaction starts at the surface of a zircon grain, as it can be seen in Fig. 3 in which there are favourable places. Then the decomposition reaction goes faster and there are places where it even does not commence. This indicates that a very

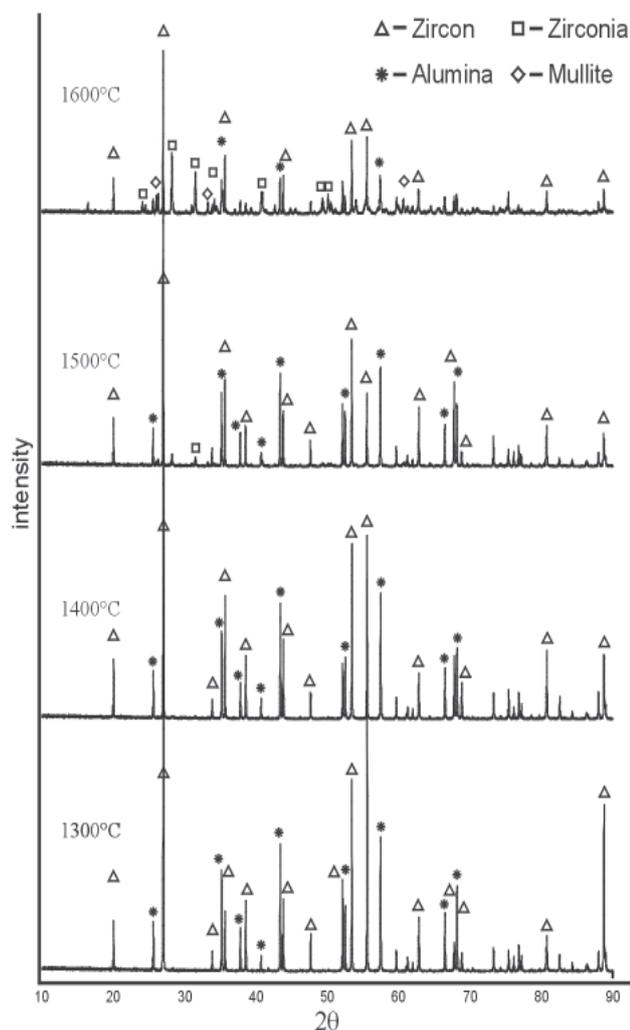


Fig. 2. X-ray diffraction patterns of samples fired for 5 h.

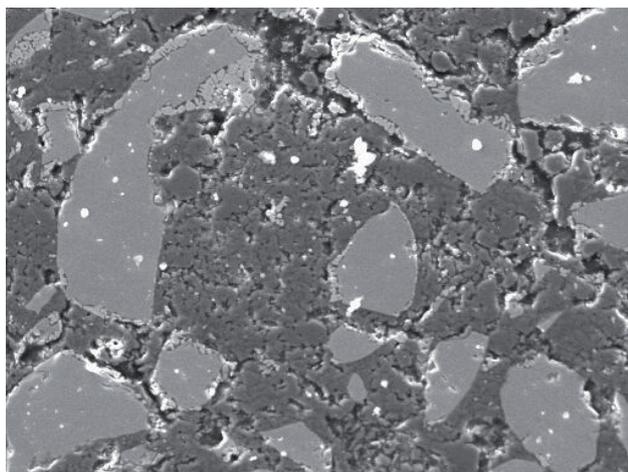


Fig. 3. SEM picture of the sample after 10 hours of firing at 1500°C; favourable places of reaction can be seen.

important role is played by surface processes at 1500°C at the reaction beginning.

Fig. 4 shows the phase composition of samples fired at 1500°C for various times. These data indicate that the reaction ceases after 20 hours; there is no decrease in the amount of zircon and increase of zirconia and mullite. It is clear that the first step necessary to develop the mullite-zirconia com-

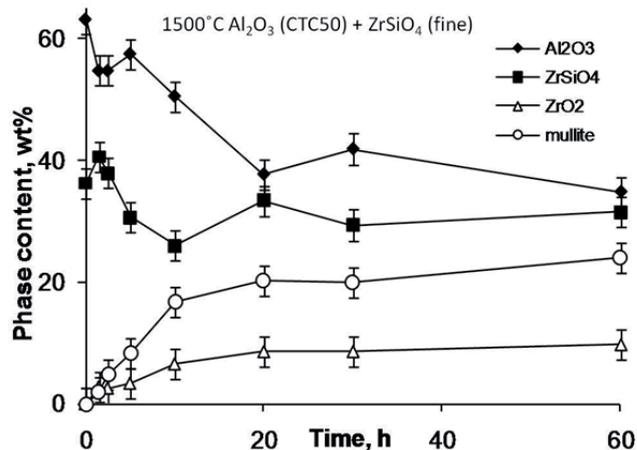


Fig. 4. Phase composition of samples fired in 1500°C.

posite is a full dissociation of zircon into crystalline zirconia and amorphous silica.

As it was shown in the literature [14-16], zircon dissociates at around 1700°C unless impurities are present in the system, then the temperature of dissolution decreases significantly. In this case alumina is the impurity, thus the dissociation stops because there is no aluminium ions right at (or very close) the surface of zircon grains. The reason for this seems to be the low diffusion coefficients of aluminium and silicon ions.

Silicon diffusion is also important because the presence of an amorphous silica phase around alumina grains leads to their dissolution and reaching this amorphous phase with alumina. Aluminium ions diffuse through this phase to the surface of zircon grains. The increase of temperature up to 1600°C enhances decomposition of zircon. A comparison of the data of Figs. 5 and 6 shows that the reaction rate is 3 times higher at 1600°C than at 1500°C. So, the synthesis of the zirconia-mullite material from zircon and alumina strongly depends upon temperature.

Fig. 5a presents an SEM micrograph of the polished non etched sample surface after the 20-h reaction at 1600°C. EDS data were collected along a white line in Fig. 5a and are shown in Fig. 5b. The results indicate that the reaction area can be divided into six zones (Fig. 5). The A zone is an area of the zircon grain with a constant level of counted zirconium and silicon atoms, no aluminium atoms are detected. The B range indicates a decomposition reaction zone of zircon. A constant aluminium concentration indicates the presence of alumina. In this area, silicon has a constant concentration, and it is higher than measured in the zircon grain. Zirconium atoms are also detected within the B range; their concentration is very low and constant. The C zone is an area occupied by zirconia crystals being one of the reaction products. There are no aluminium atoms detected in C. The amount of zirconium atoms is larger than in the zircon grain (the A zone). Some silicon atoms are also detected in C; it is due to the measuring method which counts atoms not only from the surface but also in depth. The silicon concentration is very large right at the edge of the zirconia grain (line between C and D). The data indicate that silicon diffuses into alumina, and the silicon concentration gradually decreases from the C/D edge to ~1/3 of D where the silicon concentration achieves

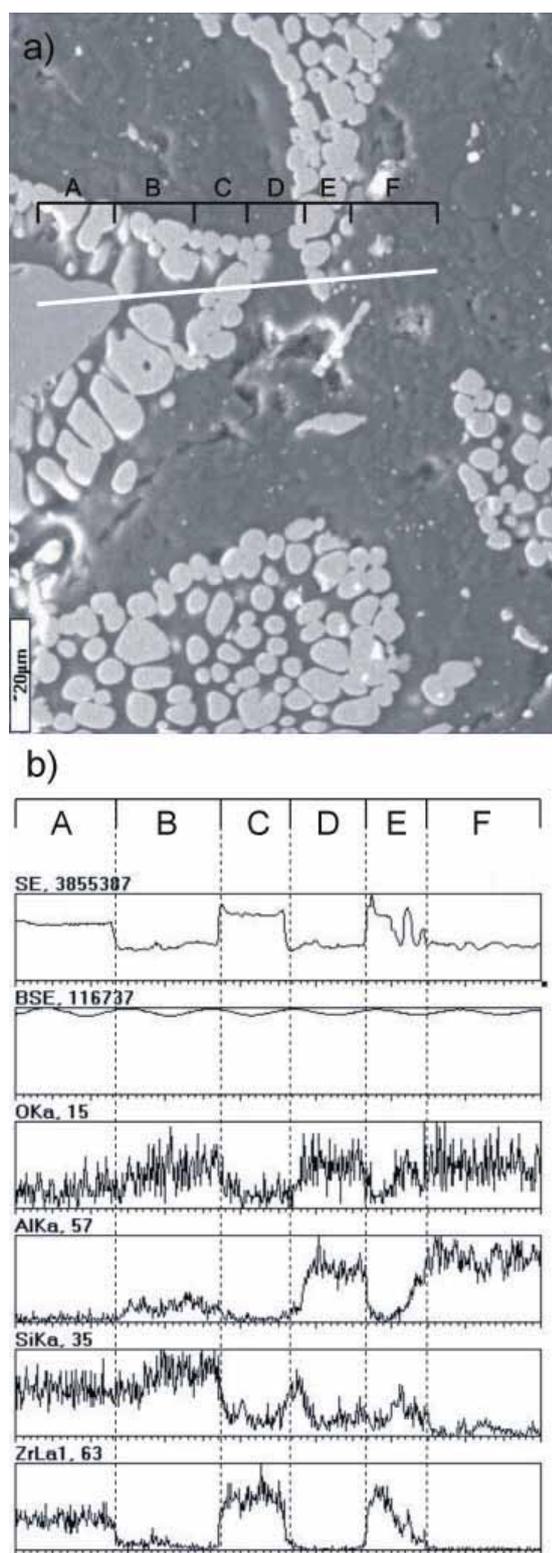


Fig. 5. SEM/EDX results: a) SEM image of sample after 20-h sintering at 1600°C, b) EDX data collected along the white line.

a plateau. Aluminium in that area behaves in the opposite way to silicon; it shows the constant large concentration from the D/E edge, which decreases in the area close to the zirconia crystal. The E zone undoubtedly contains zirconia crystals; the large silicon concentration can be seen at an outer edge of the grains. The silicon content decreases gradually as it did in the C/D range. Aluminium behaves in the opposite way to silica, increasing its content. The F zone is constituted by

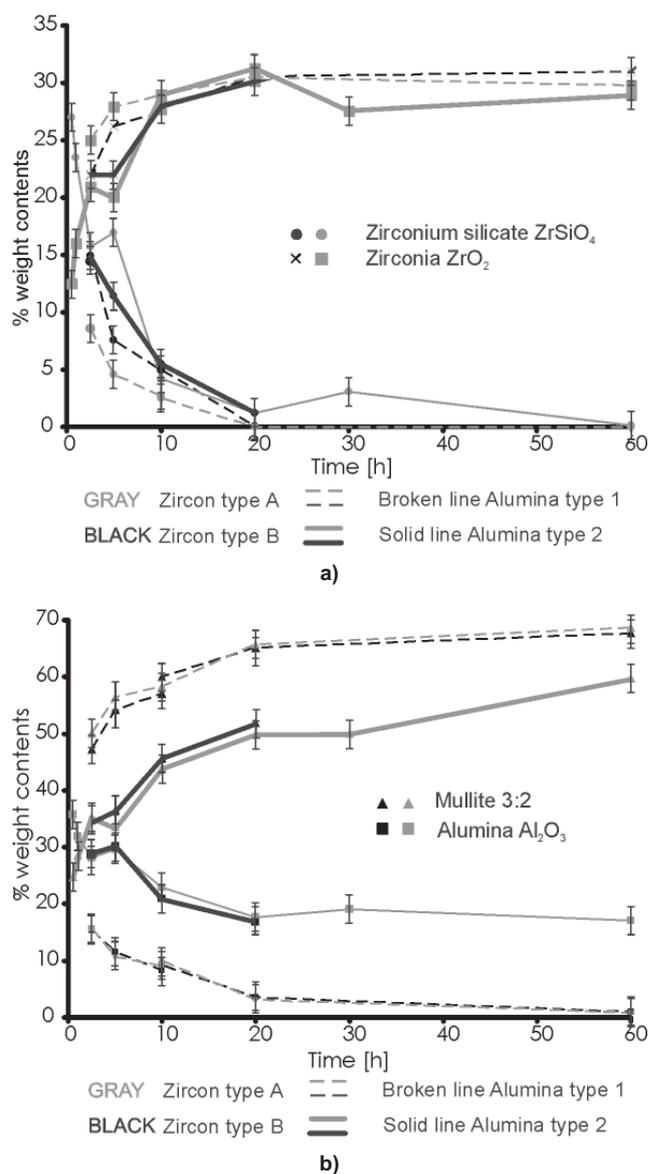


Fig. 6. Phase composition of samples prepared with different starting materials as a function of firing time at 1600°C: a) zirconium silicate and zirconia contents, b) mullite and alumina contents.

alumina grains surrounded by the alumina-silica amorphous phase. The content of alumina is high and almost constant; silicon is detectable along the F range but its content is very small. These data prove reciprocal diffusion of silicon and aluminium in the solid state.

Fig. 6a shows the amount of crystalline zircon, and zirconia after firing at 1600°C for a time ranging from 30 minutes to 60 hours. The fine (type A) and coarse (type B) zircon powders were used. In the case of alumina also the fine (type 1) and coarse (type 2) grained powders were used. The obtained data show that the reaction rate of zircon decomposition (Fig. 6a) does not depend on its grain size distribution. It suggests that the zircon decomposition is the first order reaction [17]. Fig. 6b contains the data of alumina and mullite content in the samples fired at 1600°C as a function of firing time. These data show clearly that the reaction rate of alumina dissolution is faster when finer alumina powder is used. This reaches the alumina-silica amorphous phase with alumina, thus the reaction rate of the mullite formation is faster when the fine (type 1) alumina powder is used. So,

the reaction yielding a zirconia-mullite composite depends on the alumina grain size distribution.

#### 4. Conclusions

During the solid state reaction in the  $ZrSiO_4$ - $Al_2O_3$  system, reciprocal diffusion of aluminium and silicon takes place.

At 1500°C, the reaction is controlled by two processes: diffusion of aluminium and silicon ions and surface reactions on the grains.

The processes in this system depend strongly on temperature.

The zircon grain size distribution does not have influence on its decomposition rate. The reaction rate depends on the alumina grain size distribution; the finer grains the faster reaction rate.

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