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Investigation of high-temperature reactions within the $ZrSiO_4$–Al_2O_3 system

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Abstract

Solid state reactions between $ZrSiO_4$ and αAl_2O_3 in powders of stoichiometric composition $3Al_2O_3{\cdot}2SiO_2$ were studied by X-ray diffraction and electron scanning microscopy with energy dispersive X-ray analysis (SEM + EDX). Data were obtained at temperature ranging from 1400 °C to 1600 °C for a period of time ranging from 30 min to 60 h. The results indicate that $ZrSiO_4$ and αAl_2O_3 react and form crystalline ZrO_2, crystalline mullite (almost $3Al_2O_3{\cdot}2SiO_2$ composition) and non-crystalline silicon–alumina phase (pre-mullite). At the temperature of 1600 °C the fastest stage of reaction is dissociation of $ZrSiO_4$. Obtained results show that dissociation of zircon is a first-order reaction. The dissolution of Al_2O_3 particles and diffusion of Al into non-crystalline phase seem to be the slowest step of the reaction.

Keywords: A. Powders: solide state reaction; A. Sintering; D. Al_2O_3–$ZrSiO_4$; E. Refractories

1. Introduction

Mullite–zirconium refractory materials are characterized by high refractoriness under load, high resistance to action of aggressive liquids and gasses, low thermal expansion coefficient and good mechanical properties. Thus, they are commonly used in automobile industry as well as in the industry of refractory materials [1–5], most thermally loaded engine components [6], as catalyst carriers in chemical industry, as heat exchangers, filters, and also as light construction refractory materials [7]. There are several methods of production of mullite–zirconium composites. These are, among others, sintering of mullite with zirconium oxide, sol–gel methods, and reactive sintering of aluminum oxide with zircon sand [1–11]. The last method seems to be the best one for industrial production. However, mechanism of high-temperature reactions proceeding in the mentioned system has not been determined, so far. This fact results from complexity of its phase composition during the reaction, there are four crystalline phases (zirconium, aluminum oxide, mullite and zirconium oxide), siliceous amorphous phase and pores. The results obtained so far indicate that the reaction proceeds in several stages: first $ZrSiO_4$ decomposes in the surrounding of Al_2O_3 with a formation of ZrO_2 and amorphous silicon. The amorphous silicon dissolves Al_2O_3 and then reacts with it giving mullite in its most stable form (3:2). The authors [1,2,4,5] point out the presence of a transitory amorphous phase $n SiO_2{\cdot}m Al_2O_3$, known as non-crystalline mullite.

The results of the investigation of time evolution of the phase composition during the reaction between zircon sand and corundum are presented in this paper. The influence of the temperature in the process is also considered.

2. Preparation of samples and reaction course

The raw materials used in the reaction were Australian zircon of more than 99 wt% purity, grain-size under 0.08 mm and ALCOA Reactive Alumina for High Performance Refractories CTC 30 of more than 99.8 wt% purity. The detailed analysis showed the presence of the following impurities—Al_2O_3: 0.27 wt%, TiO_2: 0.14 wt%, Fe_2O_3: 0.05 wt%, CaO: 0.02 wt%, MgO: 0.01 wt%, HfO_2: 1.35 wt%, K_2O: 0.01 wt% in the zircon, and CaO: 0.02 wt%, MgO: 0.06 wt%, Na_2O: 0.11 wt%, K_2O: 0.01 wt% in the alumina.

A composition of the mixture was selected according to the stoichiometry of the reaction $3Al_2O_3 + 2ZrSiO_4 \rightarrow Al_6Si_2O_{13} + ZrO_2$. It contained 45.54% by weight of Al_2O_3 and 54.35% by weight of $ZrSiO_4$. Homogenization of the mixture proceeded for 5 h in the presence of acetone. Cylinder-shaped samples having diameter of 1 cm and height of 3 cm were uni-axially compressed

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under the pressure of 10 MPa. The samples were roasted in an electrical furnace type Nabertherm RHT08/16 at various temperatures ranging from 1300 °C to 1600 °C, with furnace heating rate of 10 °C/min. Roasting time at given temperature ranged from 0.5 to 60 h.

Microstructure and chemical composition of the samples were tested with the use of scanning electron microscope Nova Nano SEM200 with EDAX Genesis.

Quantitative measurements of the phase composition were performed using Philips X-ray apparatus (Rietveld's method of the analysis).

3. Results and discussion

A selected SEM image of the sample after 20 h of the reaction in $ZrSiO_4$–Al_2O_3 system at 1500 °C, is shown in Fig. 1. The product of the reaction is visible in the form of elongated ZrO_2 crystals surrounding $ZrSiO_4$ grain. Thickness of the product layer ranges from 1 to 3 μm. Non-altered grains of Al_2O_3 are still present in the matrix. Rising of the temperature up to 1600 °C results in a considerable acceleration of the reaction within the system (Fig. 2a). After 1 h of the sample firing the thickness of the altered layer ZrO_2 amounts for 20 μm. Chemical composition of the phase surrounding the formed ZrO_2 crystals varies with distance from the reaction front. Elemental composition determined at the points marked in Fig. 2a, is shown in Fig. 2b.

In general, aluminum concentration increases with increasing distance from the $ZrSiO_4$. Silicon concentration within area, in which decomposition of $ZrSiO_4$ takes place, remains on more or less constant level (points 2–4 in Fig. 2a), whereas outside this area the concentration of silicon decreases (points 6 and 7). The presence of aluminum inside the zone, which directly surrounds the formed grains of ZrO_2, as well as the presence of silicon behind the zone of $ZrSiO_4$, proves a bi-directional diffusion of ions of both these elements (Fig. 2b). After 60 h of the reaction, the $ZrSiO_4$ grains have been no longer observed in SEM images, they are replaced with ZrO_2 – crystal agglomerates – Fig. 3. Dark areas, observed in SEM images, represent places from where the ZrO_2 grains were pulled out during grinding operation. In spite of the long time of the reaction course, the grains of Al_2O_3 are still visible. One can also observe bright areas located near ZrO_2 grains. Enlarged images show, growing crystals of mullite within these areas (Fig. 4). Examination of the phase composition using XRD technique and their quantitative interpretation by Rietveld's method indicate that, visible effects of the reaction are observed only for the reaction at 1500 °C. When lower temperatures have been applied, the reflexes related to crystalline products of ZrO_2 and mullite (3:2), are not observed. The data also indicate that at the temperature of 1500 °C the reaction rate is rather very low.

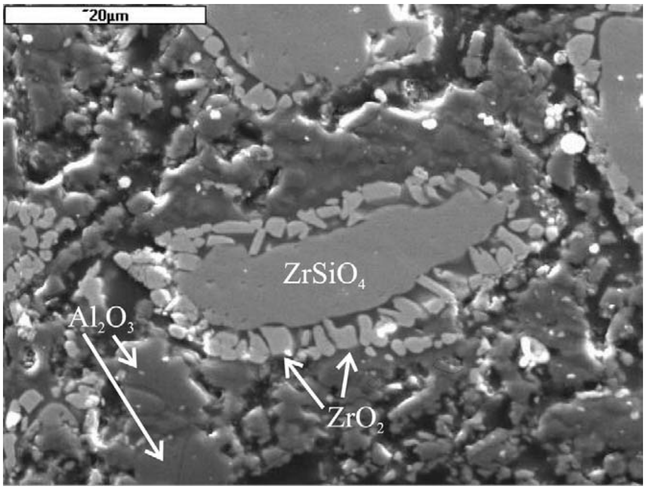

Fig. 1. Surface SEM image of sample roasted in temperature 1500 °C during 20 h.

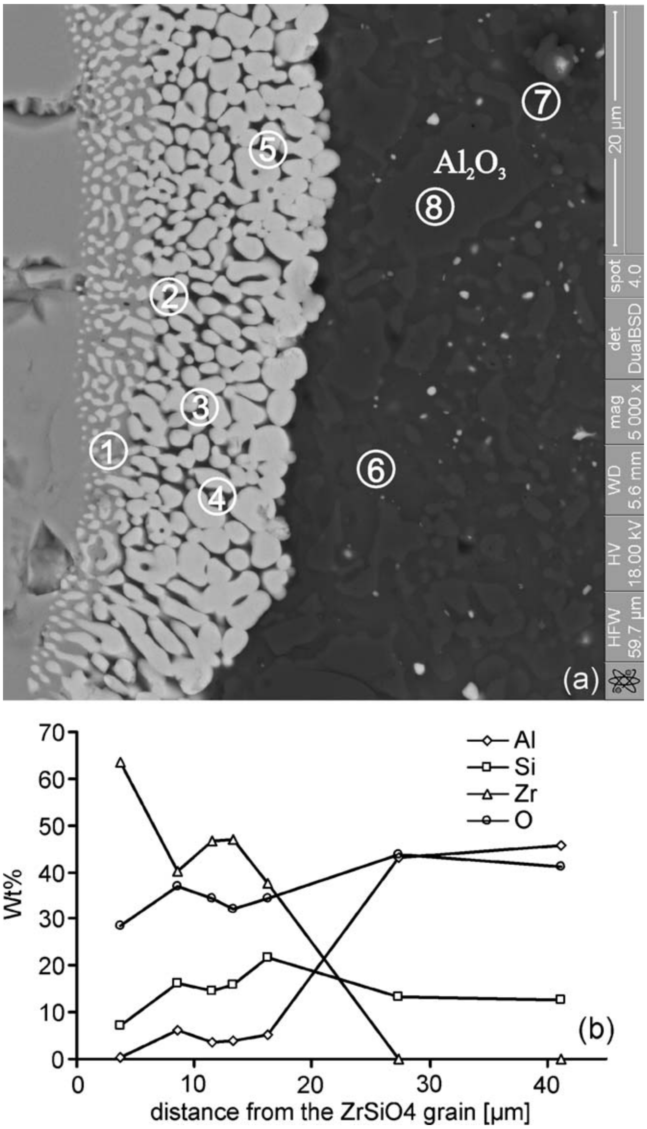

Fig. 2. (a) Surface SEM image of sample roasted in temperature 1600 °C during 1 h, with marked points of chemical composition measurement. Dark areas seen on SEM images represent places from where the grains were pulled out during grinding operation. (b) Chemical composition of samples measured in points which are marked in (a).

Changes of the mole-fraction of the substrates and the reaction products measured at various stages of the reaction occussed at the temperature of 1500 °C, are shown in Fig. 5.

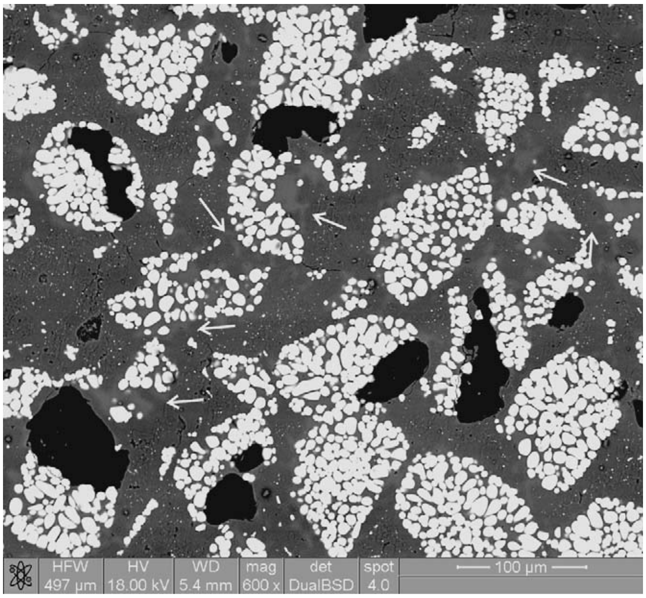

Fig. 3. SEM image of sample roasted in temperature of 1600 °C during period of 60 h. Visible areas of mullite crystallization are marked with arrows. Dark areas seen on SEM images represent places from where the grains were pulled out during grinding operation.

After 60 h of the reaction, the fraction of ZrO_2 amounts for only 9.8 wt% and the fraction of mullite amounts for 23.8 wt%. Analysis of the changes of the phase composition shown in Fig. 5, is not sufficient to draw reliable conclusions related to the mechanism of the reaction in question. The results obtained for the initial reaction stage fall within measurement errors.

The rise of the temperature up to 1600 °C causes considerable acceleration of the reaction, and after 60 h, the mullite amounts for 59.8 wt%. As seen in Fig. 6, in this temperature, the main changes of the phase composition occur within the period of 20 h. During this period practically the whole $ZrSiO_4$ is decomposed (in the surroundings of Al_2O_3) onto crystalline ZrO_2 and amorphous (not detected by XRD) silica. The amount of other crystalline phases, mullite and Al_2O_3, changes rather slowly. Thus we can conclude that at this temperature, the process of dissolution of crystalline aluminum oxide and diffusion of Al^{3+} ions within amorphous silica formed at the decomposition of zirconium silicate, is very slow. Silicon ions Si^{4+} also diffuse from the formed silica phase. The process is proved by the presence of Si between Al_2O_3 grains

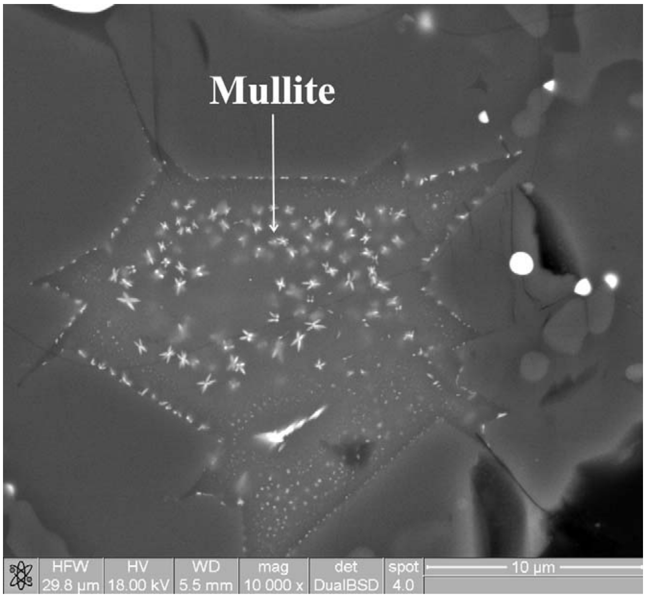

Fig. 4. Area occupied by mullite crystals on SEM image in sample roasted in temperature of 1600 °C during time period of 30 h. The image seen on a non-etched surface.

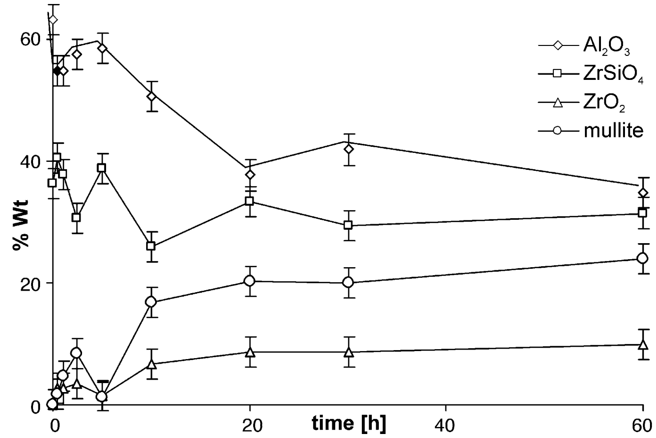

Fig. 5. Changes of phase composition-reaction hold in temperature of 1500 °C.

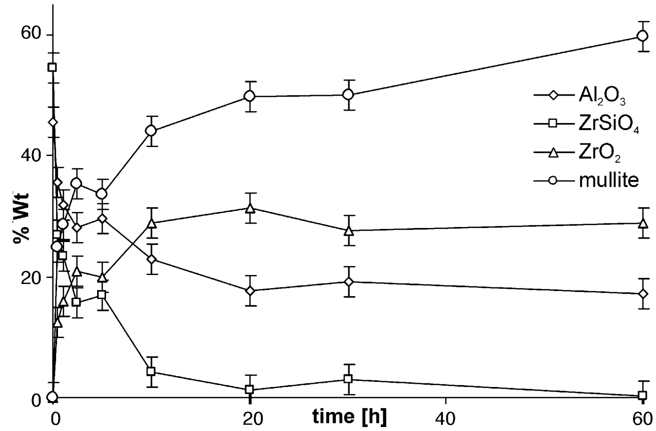

Fig. 6. Phase composition changes during reaction held in temperature of 1600 °C.

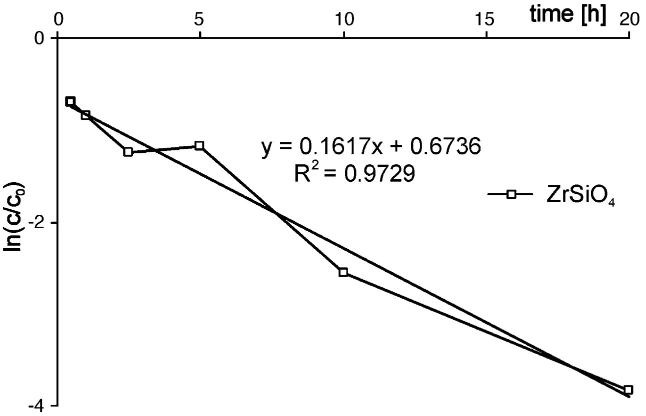

Fig. 7. Zirconium silicate diagram ln c/c_0–t.

(Fig. 2a in points 6 and 7). Experimental points (related to the time evolution of zirconium silicate phase composition), are placed in a straight line (Fig. 7), according to the dependence of $\ln c/c_0$ versus t, where c: molar concentration after time t, c_0: initial molar concentration. Therefore, we conclude that the process is a first-order reaction and its rate depends only on initial concentration of the substrate.

4. Summary

High-temperature reactions between alumina and zircon lead to the formation of mullite and zirconia. Rate of this reactions depend, as expected, on the process temperature. In case of pure components of the grain-size as used in the present study, the effect of the reaction is meaningful only in the temperature range around 1600 °C. There is no doubt that at this temperature, the first-order reaction of $ZrSiO_4$ decomposition into the oxide components proceeds. Diffusion of Al^{3+} into formed siliceous phase seems to be the slowest mechanism limiting the formation of mullite crystals and the decay of crystalline Al_2O_3.

Acknowledgements

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